DSC/TG and SEM Studies of Synthesized Potassium Sulphamate (PS) and Potassium Dinitramide (KDN) Crystals

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Abstract: *In the present paper, thermal decomposition and crystal researches of synthesized potassium sulphamate (PS) and potassium dinitramide (KDN) crystals were* <u>*studied*</u> *using differential scanning calorimetry/ thermal gravimetry (DSC/TG) and scanning electron microscope (SEM) techniques, respectively. Initially, PS crystals were synthesized using sulphamic acid and potassium hydroxide pellets. Afterwards, PS crystals were used for synthesizing potassium dinitramide (KDN) crystals by the nitration of PS in sulfuric and nitric acid mixture. One sample of PS was used for studying DSC/TG curves, while three samples of KDN crystals were used for the studying DSC/TG curves. The three samples of KDN crystals which were used in the present studies are, a) stored KDN (1 month), b) stored KDN (2 months), and c) washed KDN. All the obtained DSC/TG curves of three KDN crystals are dissimilar to each other, and the probable reasons for this dissimilarity are discussed in the manuscript. For further clarifications, TG curve of KN was compared with the TG curves of three samples of KDN used in the present study. It was observed that, while storage, KDN slowly converts into KN with some rate which gradually changes the physical and chemical properties of KDN.*

Key Words: *Potassium Sulphamate, Potassium dinitramide, Crystal structure, Thermal decomposition, Storage time effect*

1. INTRODUCTION

In the recent years space organizations and space industries witnessed tremendous increase in the frequency of rocket launches for space related activities [1]. Currently, most of the rocket/ space shuttle launch utilizes ammonium perchlorate, NH_4ClO_4 (AP) as an oxidizer entity for generating sufficient thrust from booster rockets at the time of take-off. However, combustion products of AP are not environmentally benign in nature, and can lead to disastrous effects on

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the flora and fauna near the vicinity of the launch site and also to the upper ozone layer. Hence, researches are going on worldwide to implement the use of green oxidizers and green fuels in all kind of rocket propulsion.

Some of the available green oxidizers are AN, ADN, HNF, and HAN [2]. However, production, fabrication and operating cost of a rocket launch will be a costly affair if we switch towards green propulsion. The reason is that mass production and effective utilization of green oxidizers are in their initial stage also being a costly affair. Out of four mentioned green oxidizers, AN is the only cheapest and easily available oxidizer. However, AN shows poor combustion efficiency and has some physical and chemical drawbacks due to which its utilization in rocket propulsion is still in progress [1]. Out of the four green oxidizers, only ADN has great potential to replace AP and to be utilized in both solid and liquid green rocket propulsion [3]. Hence, effective synthesize and utilization of ADN crystals is an important step towards achieving green propulsion in reality.

For the synthesis of ADN crystals, potassium sulphamate (PS) and potassium dinitramide (KDN) are the initial compounds. For maximum synthesize of ADN crystals, one must know the efficient utilization of PS and KDN crystals along with their physical and chemical properties. From the next paragraph, discussion is provided over the physical and chemical properties of PS, KDN, and ADN crystals, and how the PS and KDN crystals are used to synthesize ADN crystals.

Potassium sulphamate (PS) is a white crystalline salt of potassium and sulfamic acid having the molecular formula of KNH_2SO_3. Other names of potassium sulphamate are potassium sulphamate; sulfamic acid, potassium salt (1:1); and sulfamic acid, monopotassium salt [4]. The first detailed study over the crystal structure of PS crystals was performed by Brown and Cox in 1940 using XRD technique [5]. It was observed that the crystal of PS was ionic in structure having no hydrogen bonds. Upon crystallization, PS converts into orthorhombic structure. The lattice parameters are, a = 8.32Å, b = 8.28Å, and c = 5.90 Å, while crystal space group was *Pbma* [6]. There are several other studies in literature over the crystal structure of potassium sulphamate [7, 8] and on other sulphamate based compounds [9]. Properties like conductivity, dielectric properties, and phase transitions of PS were reported in Ref. [6, 10, 11]. Some other studies like elastic properties [9], electron spin resonance spectrum [13], and viscosity analysis [12], [14] of PS crystals were also performed till date. Crystal structure studies of sulfamic acid were mentioned in Ref. [15, 16]. Similarly, crystal structure studies of potassium dinitramide [KDN, $KN(NO_2)_2$] mentioned in Ref. [17, 18]. KDN is a dinitramide anion (DA) based compound having oxidizing properties, and can be used with ammonium nitrate (AN) to make green energetic materials (GEM's) [19]. Sulphamate based compounds like ammonium sulphamate ($NH_4NH_2SO_3$), potassium sulphamate (KNH_2SO_3), and sodium sulphamate ($NaNH_2SO_3$) are some of the conceivable candidates for the mass production of ammonium dinitramide [$NH_4N(NO_2)_2$, ADN] and potassium dinitramide (KDN) [20]. All these three sulphamate based compounds are the donor of nitramide precursor, which serve as the key intermediate in the formation of nitro functional groups by the rapid exchange of cations during the nitrification reactions [21-23]. There are several feasible routes to synthesis ADN as discussed in Ref. [24], however sulfamic acid derivatives based synthesize of ADN is the preferred one and also cost effective [25, 38]. ADN is free from chlorine, environmentally safe, and has the potential to replace ammonium pechlorate (AP, NH_4ClO_4) and hydrazine (N_2H_4) in future green space missions [26, 27]. Potassium dinitramide (KDN) is an intermediate product while synthesizing ammonium dinitramide (ADN) crystals. KDN crystals were used for synthesizing ADN crystals by treating it with ammonium sulphate, and isopropyl alcohol as discussed in Ref. [28]. Purity of KDN crystals plays an important role in

synthesizing pure ADN. Since, while storage KDN slowly degrades into potassium nitrate (KN) crystals, which changes the physical and chemical properties of KDN. Based on DSC/TG curves, the present paper discusses how storage time affects the purity of KDN.

KDN is an important dinitramide anion (DA) based compound with different application areas [29]. However, the most important application of KDN is to enhance the phase stabilization and combustion properties of ammonium nitrate (NH_4NO_3, AN) [19, 30]. In this way, mixture of AN/KDN can be utilized for making green oxidizers for future green propulsion [19, 30,31]. Apart from ADN and KDN, some other interesting green energetic materials are ammonium nitrate (AN), hydrazinium nitroformate (HNF), HNIW (*hexanitro hexaazaisowurtzitane*) or CL-20, and trinitramide [32-34]. Structural effects of PS on the synthesis of ADN [20], the effect of molar ratio, nitration time, and reaction temperature during KDN synthesis using PS crystals [21, 22], the effect of sulphamate conterion on ADN purity [35, 38], the effect of KDN purity on synthesized ADN [28], and the effect of nitric acid density during sulphamate nitration [36] have been addressed by several authors. Apart from synthesizing ADN and KDN, PS crystals were also used to synthesize heterocyclic nitramines [37]. From the above discussion, it can be stated that it is important to obtain the maximum amount of ADN crystals by using the minimum amount of PS and KDN crystals for cost effectiveness and for mass production of ADN. For this, crystal structure and thermal behavior of PS and KDN crystals is important to understand. In the present paper, effort has been done to understand the effect of storage time on KDN purity by using DSC/ TG technique. Apart from it, crystal structure of PS and KDN are also studied using scanning electron microscope (SEM) technique.

2. SYNTHESIS OF POTASSIUM SULPHAMATE (PS) AND POTASSIUM DINITRAMIDE (KDN) CRYSTALS

2.1 Chemicals and Lab equipment

Sulfamic acid (*Sigma-Aldrich, 99.3%, A.C.S Reagent*), potassium hydroxide flakes (*Sigma-Aldrich, 90%, Reagent grade*), ethanol (*Merck, analytical reagent grade*), fuming nitric acid (*Merck, 100% pure*), sulfuric acid (*Acros Organics, 95%, A.C.S. Reagent*), and acetone (*Merck, for synthesis, reagent grade)* have been utilized. Apart from above mentioned chemicals, distilled water and ice cubes were also used and was prepared in chemistry lab. Some of the lab equipment which were utilized during PS and KDN synthesis are, ultra-low immersion chiller *(Mukherjee scientific, India),* rotary evaporator (*IKA, Germany)*, microbalance (*Sartorius),* vacuum oven (*Simoco, India)*, deep freezers (*Mukherjee scientific, India)*, and hot plate magnetic stirrer. Some other synthesis chemistry lab essentials are also used during the synthesis.

### 2.2 Preparation of Potassium Sulphamate (PS)

Firstly, 125 g of sulfamic Acid (H_2NSO_3S) was suspended in a 50 ml of distilled water. In another solution, about 25 g of potassium hydroxide (KOH) was dissolved in a 50 ml of distilled water. Slowly and with continuous stirring, potassium hydroxide solution was poured onto the suspended sulfamic acid solution. Mixing of both solutions were performed till a neutral solution was obtained (*with the help of pH meter*). Afterwards, 100 ml of ethanol was taken in another beaker, and the complete *KOH + sulfamic acid* solution was poured into ethanol. Since, potassium sulphamate is insoluble in ethanol; it will get precipitated at the bottom of the mixture in the form of white crystalline salt. The salt was filtered off with the

help of a filter paper and a funnel. Filtered PS salt was again washed with 25 ml of ethanol to remove other possible impurities from the salt. Afterwards, all the PS salts were scratched from the filter paper with a spatula. Finally, the obtained PS salt was kept inside the oven at 70°C for drying. It will take nearly 20 hrs for obtaining 80 g of completely dried PS salt. When dried, the salt was grounded onto a very fine powder with the help of powder grinder. The obtained PS crystals were stored in vacuum desiccators. The chemical reaction for obtaining PS salt is shown below:
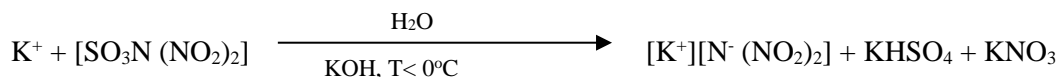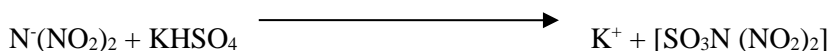
$$KOH + H_2NSO_3H \rightarrow K^+[NH_2SO_3^-] + H_2O$$
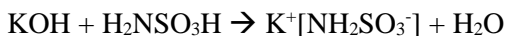
2.3 Preparation of Potassium Dinitramide (KDN)

In the first step, 50 ml of nitrating mixture was prepared by mixing 10 ml of 95% conc. sulfuric acid and 40 ml of 100% pure nitric acid (fuming) in the ratio of 1:4 in an Erlenmeyer flask. This nitrating mixture was further poured into a two necked round bottom flask prior to putting two necked round bottom flask in methanol kept at -40°C in an ultra-low immersion chiller. Afterwards, potassium sulphamate (15 g) was added in small portions of 3 g with mild agitation of the nitrating mixture with the help of a magnetic stirrer for 10 minutes. The nitrating mixture + PS crystals were left for another 30 mins for further reaction with vigorous agitation of the mixture with the help of magnetic stirrer. The reaction proceeds with the formation of dinitramide anion $[N^- (NO_2)_2]$ and potassium sulfate ($KHSO_4$). The viscosity of the solution increases as the potassium sulfate ($KHSO_4$) precipitates. The reaction mechanism between potassium sulphamate and nitrating solution is shown below:

$$K [H_2NSO_3] \xrightarrow[T = -40°C]{H_2SO_4/HNO_3} N^-(NO_2)_2 + KHSO_4$$
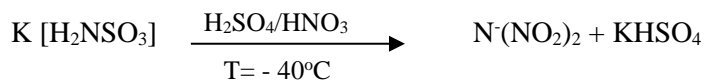
After 30 minutes, the nitrating mixture was immediately poured onto a finely crushed mixture of ice and distilled water (150 ml) maintained at -10°C. Afterwards, a cold solution of 150 ml potassium hydroxide (50%) solution was added gradually in nitrating mixture + cold water solution. The temperature was maintained in the range of -10°C to 0°C. At the neutralization point, the colour of the mixture turned to characteristics green-yellow. Continue the neutralization process till the solution turned weakly basic (*pH=8*). At this point stop, the neutralization process was stopped as white solid precipitates get formed at the bottom of the solution. This obtained waste white precipitate was referred to as *salt A*, while most of the KDN, potassium nitrate (KN), and potassium sulfate were present in the mixture in soluble state. The reaction mechanism is shown below:

$$N^-(NO_2)_2 + KHSO_4 \longrightarrow K^+ + [SO_3N (NO_2)_2]$$

$$K^+ + [SO_3N (NO_2)_2] \xrightarrow[KOH, T< 0°C]{H_2O} [K^+][N^- (NO_2)_2] + KHSO_4 + KNO_3$$

The obtained precipitate or *salt A* was filtered off with the help of funnel and filter paper, while characteristic green-yellow liquid was stored in a separate beaker. Afterwards, *salt A* was washed with distilled water and collected in a separate beaker. The characteristic green-yellow liquid solution was concentrated on a rotary evaporator to about 1/4th of the volume, till waste *salt B* gets precipitated. *Salt B* was again filtered off and washed with distilled water and collected in the same beaker as used previously. The remaining filtrate was evaporated to dryness to obtain a mixture of potassium sulfate, potassium nitrate, and potassium dinitramide (*salt C*). Finally, *salt C* was mixed with acetone in a separate Erlenmeyer flask. Manually or

with the help of magnetic stirrer *salt C + acetone mixture* was shaken vigorously for 20 mins. As the potassium dinitramide is soluble while other salts are insoluble in acetone, the potassium dinitramide slowly get dissolved in acetone. Acetone mixed KDN was collected in another beaker. Finally, acetone mixed KDN and water mixed KDN (*stored in the first two steps for salt A and salt B*) are added together. This complete solution of water and acetone contains only potassium dinitramide (KDN) in soluble state. For obtaining the dried KDN, liquid was again concentrated using a rotary evaporator. The characterization details of the obtained KDN were discussed in Ref. [19]. The obtained dried KDN crystals are stored in vacuum desiccators.

3. INSTRUMENTATION

Obtained PS and KDN crystals were studied using scanning electron microscope (SEM) [*Make: Jeol, Japan*], and simultaneous differential scanning calorimetry (DSC/TG) [*Make: Netzsch, Germany*] techniques. The resolutions used for obtaining SEM images are 100X, 200X, 350X, and 500X. For obtaining DSC/TG-DTG curves, alumina crucible with a perforated lid, heat flow rate of 5°C/min, sample mass of 2 mg, and purge gas flow rate (N_2 gas) of 60 ml/min was used during the experimentations. Apart from it, photographic images of PS and KDN crystals which were obtained through synthesis process is also presented.

4. RESULTS AND DISCUSSIONS

This section is divided into two parts i.e. structural analysis of PS and KDN crystals, and DSC/TG analysis of PS and KDN crystals for clear and enhanced understanding.

4.1 *Structural analysis of PS and KDN crystals*

4.1.1 PS Crystals

The obtained image of synthesized PS salt is shown in Figure 1, while SEM images of PS crystals at the resolutions of 100X and 500X is shown in Fig. 2.

Fig. 1: Synthesized PS crystals

Synthesized PS salt was white in colour as shown in Fig. 1. After drying, PS salt was packed in an air-tight polythene bags and stored in a vacuum desiccators. PS salt can cause skin, eye, and respiratory irritation and are also harmful to aquatic life with long lasting effects [4]. The stored PS salt was used for KDN synthesis, and it was observed that the KDN yield (*nearly 6.5 g*) and its purity remains constant after each synthesis. Hence, it can be stated that PS

crystals are stable while storage and also the purity of PS salts remains intact for long duration. SEM images of PS crystals in the resolutions of 100X and 500X are shown in Fig. 2(a), and Fig. 2(b), respectively.

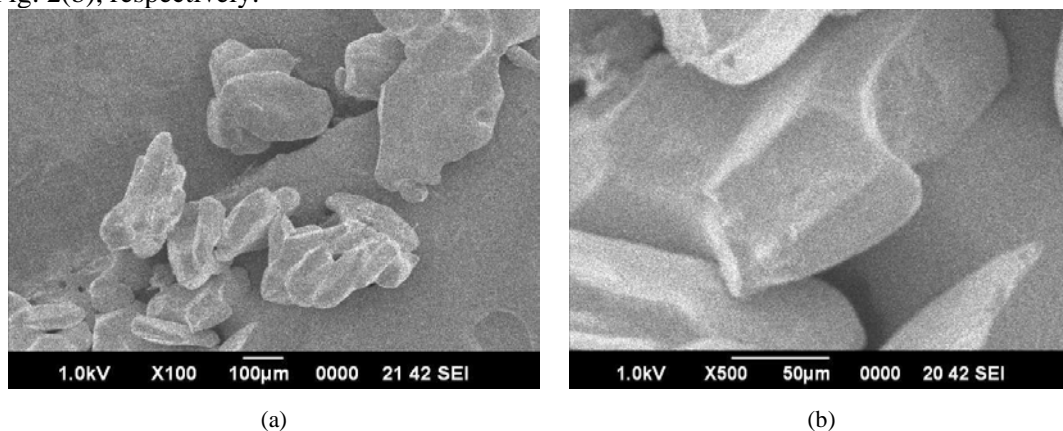(a)   (b)

Fig. 2 (a, b): SEM images of PS crystals at 100X and 500X

SEM images of PS crystals were previously reported in Ref. [20]. In Ref. [20], PS was synthesized using 5 different solvents and their effects on the synthesis of ADN were studied. In the present study, surface morphology and particle size of the synthesized PS was observed with SEM. Prepared PS salt exhibit smooth surfaces with prism like edges, but have irregular shapes as observed from Fig. 2(a). Most of the obtained PS crystals were appeared as flat flakes, with no porous surface, and with conical edges as previously observed in Ref. [6]. The length of the lab-made PS crystals is distributed in between 150 to 250μm, while breadth is in between 50 to 100 μm as observed from the SEM image provided in Fig. 2(b).

4.1.2 KDN crystals

Obtained image of synthesized KDN is shown in Figure 3, while the SEM images of KDN crystals after drying at the resolutions of 100X and 350X are shown in Fig. 4.

Fig. 3: Synthesized KDN crystals

Synthesized KDN was yellowish white in colour as shown in Fig. 3. After drying, KDN crystals were packed in an air-tight polythene bag and stored in vacuum desiccators. During storage, KDN slowly decomposes to form potassium nitrate, KNO_3 [KN]. This formed KN forms a eutectic mixture with KDN and change the physical and chemical properties of KDN [39-41]. Physical and chemical properties of KDN vary from sample to sample as it strongly depends upon the percentage of KN present in the KDN crystals [42]. Also, KDN is slightly hygroscopic in nature and can absorb moisture from the atmosphere [19].

Because of this reasons, KDN crystals are stored in vacuum desiccators. Effects of KN on the melting and decomposition temperature of KDN are discussed separately in *Section 4.2*.

SEM images of KDN crystals in the resolutions of 100X and 350X are shown in Fig. 4(a), and Fig. 4(b), respectively.

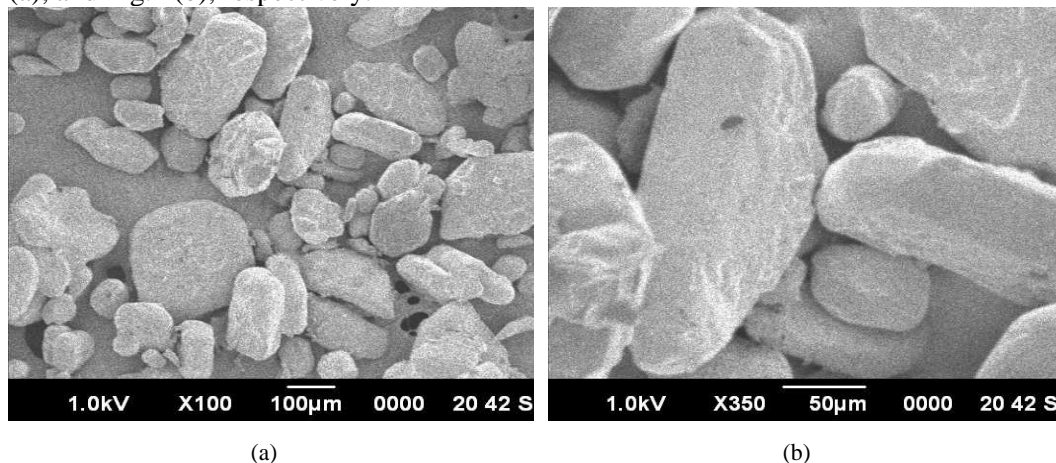(a)   (b)

Fig. 4(a, b): SEM images of KDN crystals at 100X and 350X

SEM images of KDN crystals were not reported previously. From the observed SEM images of KDN (Fig. 4), it can be observed that the prepared KDN crystals don't have smooth surfaces and also have irregular shapes (*i.e. spherical, cylindrical, cuboidal, prismatic etc.*). The length of the lab-made KDN crystals are in between 100 to 200μm, while the breadth is in between 50 to 100 μm as observed from the SEM images.

4.2 DSC/TG-DTG Analysis

4.2.1 DSC/ TG-DTG analysis of Potassium Sulphamate (PS) Crystal

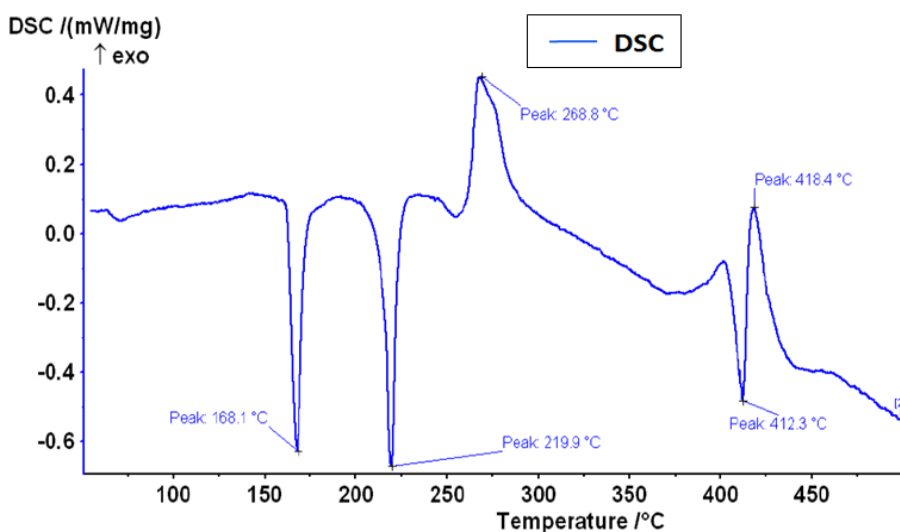DSC curve of PS crystal is shown in Fig. 5a, while TG-DTG curves of PS crystal are shown in Fig. 5b.
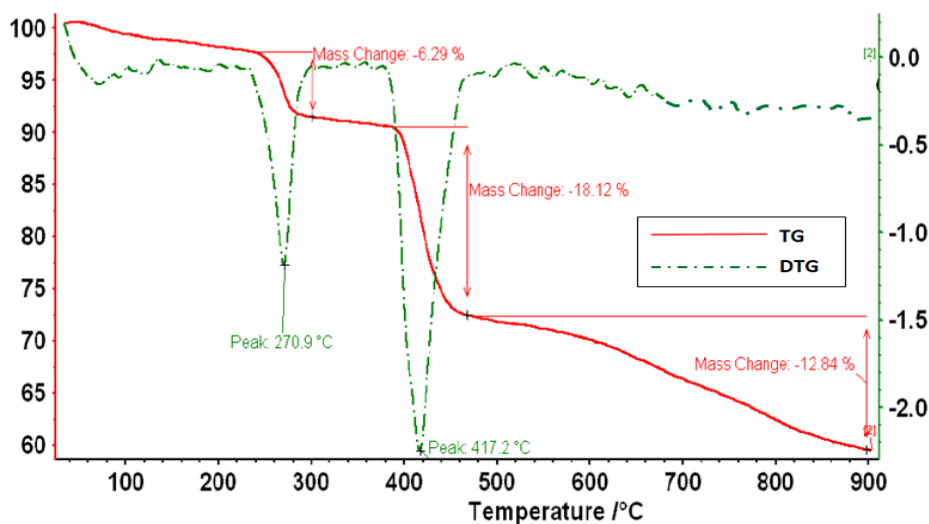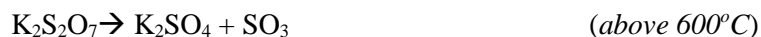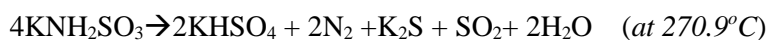

Fig 5a: DSC curve of PS

Fig. 5b: TG-DTG curves of PS

The DSC curve [Fig. 5a] depicts three endothermic peaks i.e. $168.1^{\circ}C$, $219.9^{\circ}C$ and $412.3^{\circ}C$, respectively, and two exothermic peaks at $268.8^{\circ}C$ and $418.4^{\circ}C$, respectively. The endothermic peaks at $168.1^{\circ}C$ and at $219.9^{\circ}C$ indicates the polymorphous transformation which corresponds to a change in internal structure and phase change of PS crystals by melting at increased temperature [11]. Exothermic peak at $268.8^{\circ}C$ corresponds to decomposition of PS crystals. In previously reported literatures, exothermic decomposition of PS crystals was observed at around 260 to $265^{\circ}C$ [20, 22]. During decomposition, PS crystals decomposed into potassium bisulphate ($KHSO_4$). Decomposition of potassium bisulphate takes place when heated above $300^{\circ}C$ [43] to form potassium pyrosulphate ($K_2S_2O_7$) crystals. In the present case, $KHSO_4$ crystals may get decomposed between $412.3^{\circ}C$ and $418.4^{\circ}C$, to form $K_2S_2O_7$.

The TG-DTG curves of PS crystals [Fig. 5b] depict three steps decomposition up to $900^{\circ}C$. First step DTG decomposition peak was observed at $270.9^{\circ}C$, which corresponds to the decomposition of PS crystals into $KHSO_4$ crystals. In the previous literature [36], PS crystals in the presence of HNO_3 decomposed into $KHSO_4$, N_2O, and H_2O. However in the present case, PS crystals may decompose into $KHSO_4$, N_2, K_2S, SO_2, and H_2O. Potassium sulphide (K_2S) is very stable compound having melting point of $840^{\circ}C$, and decomposition temperature of $912^{\circ}C$ [44]. Second DTG decomposition peak was observed at $417.2^{\circ}C$, which corresponds to the decomposition of $KHSO_4$ crystals into $K_2S_2O_7$ crystals. Afterwards, a very slow decomposition was observed from around $500^{\circ}C$, however and an accelerated decomposition was observed after $600^{\circ}C$. After $600^{\circ}C$, $K_2S_2O_7$ crystals slowly start to decompose into potassium sulphate (K_2SO_4) crystals. Since, K_2SO_4 is very stable compound having melting point at around $1069^{\circ}C$, and hence no such major peaks were observed after $500^{\circ}C$ in the TG-DTG curves. Decomposition steps of PS crystals can be summarized as:

$$4KNH_2SO_3 \rightarrow 2KHSO_4 + 2N_2 + K_2S + SO_2 + 2H_2O \quad \textit{(at 270.9}^{o}\textit{C)}$$

$$2KHSO_4 \rightarrow K_2S_2O_7 + H_2O \quad \textit{(at 417.2}^{o}\textit{C)}$$

$$K_2S_2O_7 \rightarrow K_2SO_4 + SO_3 \quad \textit{(above 600}^{o}\textit{C)}$$

4.2.2 DSC/ TG analysis of Potassium dinitramide (KDN) and potassium nitrate (KN) Crystals

DSC of freshly prepared KDN is discussed in Ref. [19, 42]. DSC curves of stored KDN (*1 month*), stored KDN (*2 months*), and washed KDN up to 400ºC are presented in Fig. 5a and discussed after. DSC of potassium nitrate is not provided in Fig. 6a, since the decomposition of potassium nitrate (KN) starts only after 600ºC. Due to which, net enthalpy (J/g) values of various endothermic and exothermic peaks present in DSC curves of KDN and KN are very different, and hence curves are not comparable and errors occur. Although, TG curves of washed KN has been discussed and presented along with pure KDN, stored KDN, and washed KDN up to 1000ºC in Fig. 6b.

DSC and TG analysis of stored KDN (*1 month*) was performed after one month of synthesizing the KDN crystals. Afterwards, KDN was again stored in vacuum desiccators inside an air-tight polythene bag for next one month. DSC and TG analysis of stored KDN (*2 months*) were performed after keeping it for next 30 days inside the vacuum desiccators. Washed KDN was obtained after washing the stored KDN with acetone since; the KN is insoluble in acetone while KDN is readily dissolved in acetone. Finally, KDN dissolved acetone was evaporated to obtain the little amount of washed KDN crystals. In the next day, DSC and TG analysis of washed KDN was performed when the KDN crystals get completely dried up.
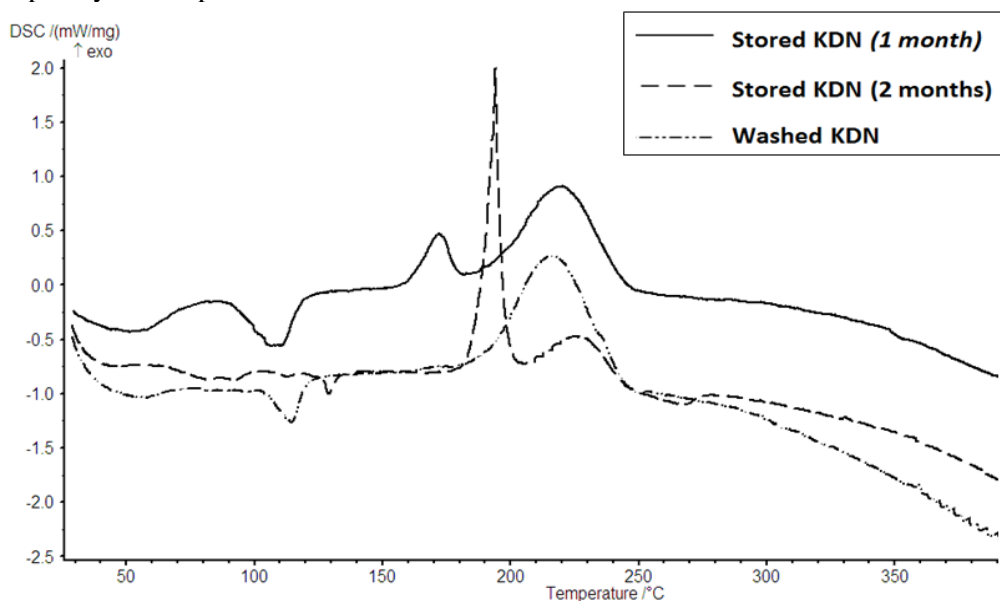

Fig. 6a: DSC curves of stored KDN *(1 month)*, stored KDN *(2 months)*, and washed KDN

From the DSC plot [Fig. 6a], it can be observed that DSC of all the three different types of KDN used in the present study shows one endothermic peak and two exothermic peaks. For stored KDN (*1 month*) and washed KDN, endothermic peak was observed at around 116ºC which corresponds the melting of KDN crystals. This result shows that, not much amount of KN is present in both types of KDN crystals. For stored KDN *(2 months),* melting was observed at around 129ºC. Apart from melting peak at 129ºC for stored KDN *(2 months)*, one minor endothermic peak is also observed at around 95ºC, which is the eutectic melting point of mixture of potassium nitrate (KN) and potassium dinitramide (KDN).

After melting peak, exothermic decomposition peaks were observed for all three types of KDN. For 1 month and 2 months old stored KDN crystals, two consecutive exothermic decomposition peaks were observed. For 1 month old KDN, decomposition peaks are observed at around 175ºC and 260ºC, while for 2 months old KDN, decomposition peaks are observed at around 195ºC and 270ºC. While for washed KDN, only one decomposition peak was observed at around 245ºC. The reasons for two consecutive decompositions peaks in stored KDN crystals are due to the presence of KN as impurity in its crystal, while in washed KDN only one decomposition peak was observed as there was no KN as impurity present in it.
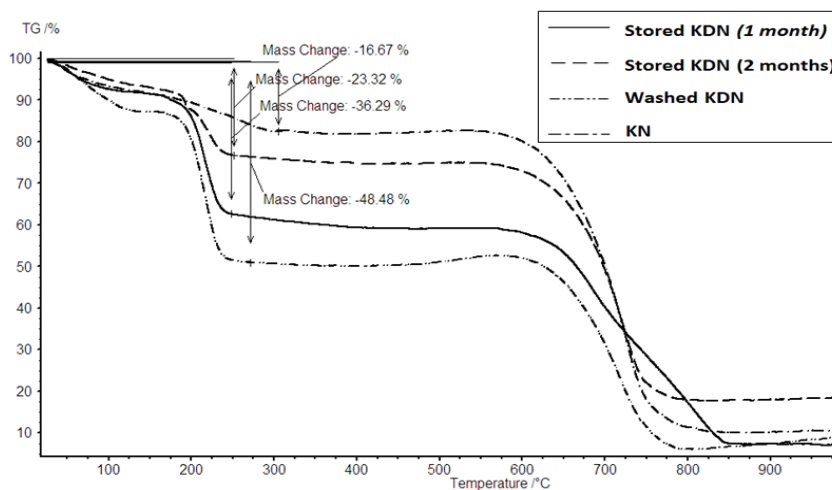

Fig. 6b: TG curves of stored KDN *(1 month)*, stored KDN *(2 months)*, and washed KDN

From the TG plot [Fig. 6b], it can be observed that the TG curves for all the three types of KDN and one sample of KN are completely different from each other's. In all the TG curves, two step decompositions are observed. The first step decomposition for all the three types of KDN are observed between 200 and 220ºC, as previously observed in DSC curves, also. The first step decomposition corresponds to the decomposition of KDN into potassium nitrate and nitrous oxide (N_2O) [19]. The loss of corresponding mass for pure KN, one month stored KDN, two months stored KDN, and washed KDN in the first step is of 16.67%, 23.32%, 36.29%, and 48.48%, respectively. In the pure condition i.e. washed KDN crystals nearly decompose up to 50% ($\approx 48.48\%$) in the first step to form KNO_3 crystals. Second step decomposition was observed between 600 and 800ºC, in which KNO_3 crystals decomposition starts to form potassium nitrite (KNO_2) and gaseous oxygen [19]. Potassium nitrate decomposition starts at about 600ºC, while KNO_2 decomposition starts at about 700ºC [45]. Percentage mass loss during second step decomposition was maximum for KN, and minimum for washed KDN.

The rate of conversion of KDN into KN while storage is summarized in Table 1.

Table 1: Rate of conversion of KDN into KN while storage

Samples	% mass loss for first step decomposition	Formulation used	%KDN converted into KN while storage
Washed KDN	48.48	(48.48 – 36.29) / 48.48	**25.14 %**
Stored KDN *(1 month)*	36.29		
Stored KDN *(1 month)*	36.29	(36.29 – 23.32) / 36.29	**35.73%**
Stored KDN *(2 months)*	23.32		

From Table 1 it can be stated that storage KDN slowly converts into KN with some rate. In the first month, 25.14% of pure KDN converts into KN; while in the second month, 35.73% of KDN converts into KN. Hence, with storage time the rate of conversion of KDN into KN increases. Although, this rate of conversion of KDN into KN should be up to some particular period of storage time, and after which no conversion will take place.

5. CONCLUSIONS

In the coming years, the uses of rockets and space shuttles will go to increase in exaggerated rate for conducting various manned interplanetary missions, space tourism, searching of life in space, and for space exploration. Currently ammonium perchlorate (AP) and hydrazine based propellants are used in booster stage and as a thruster, respectively. AP is toxic, while hydrazine is both toxic and carcinogenic in nature. Apart from health hazards, both AP and hydrazine have low storage life, and can cause corrosion of the storage media. In this way, AP is dangerous for low earth atmosphere, while hydrazine is not suitable for long duration space missions. To tackle this kind of hazardous situations, space scientific community are consistently working to develop less toxic chemicals with long storage life for rockets and space crafts for executing successful space missions.

Many space organizations around the globe are working on the development of green oxidizers/ fuels and propellants for propulsion. As previously discussed, ADN, HNF, AN, and hydroxyl ammonium nitrate (HAN) along with many others potential green oxidizers are currently in developing stage and research are going on to replace ammonium perchlorate and hydrazine based propellants with green oxidizers [31].

ADN is also a potential candidate of green oxidizers and KDN is a precursor to synthesis ADN. Hence, it's important to synthesis maximum amount of ADN from the given amount of KDN to develop an economic green propulsion system. However, purity of KDN is also highly dependent on storage method and storage time as discussed previously. Hence, KDN must be stored in the most scientifically correct way to retain its purity for long term for the production of pure grade of ADN. Some of the important conclusions which can be summarized from the present study are given below:

a. While storage purity of potassium sulphamate (PS) crystals doesn't change drastically, since the amount of KDN obtained by using stored PS crystals are nearly consistent all the times.

b. PS crystals are shiny crystals with prism like structure, while KDN crystals are irregular in shapes and sizes.

c. PS crystals undergo two steep steps decomposition up to 500°C, and afterwards continuous slow rate decomposition takes place. Decomposition at 270.9°C corresponds to the decomposition of PS crystals into $KHSO_4$ crystals. Second decomposition at 417.2°C corresponds to the decomposition of $KHSO_4$ crystals into $K_2S_2O_7$ crystals. After 600°C, $K_2S_2O_7$ crystals slowly start to decompose into potassium sulphate (K_2SO_4) crystals. K_2SO_4 is very stable compound having the melting point at around 1069°C.

d. While storage KDN slowly converts into KN crystal. With time, the rate of conversion of KDN into KN increases. In the first month, 25.14% of KDN converts into KN; while in the second month, 35.73% of KDN converts into KN.

e. In first step decomposition, KDN converts into KN; in second step decomposition, KN converts into KNO_2; and in third step decomposition KNO_2 converts into K_2O.

f. Fresh KDN also possess high heat of decomposition (J/g).

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