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The hygrothermal aging effects of titanium hydride potassium perchlorate for pyrotechnic combustion

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ABSTRACT

Titanium hydride potassium perchlorate (THPP) is a well-known pyrotechnic initiator commonly utilized in the field of aerospace propulsion. The current study experimentally elucidates the effects of hygrothermal aging on the pyrotechnic combustion of THPP and proposes two methodologies for analysis. The first technique implements a two-step isoconversional method to analyse the hygrothermally aged THPP with Differential Scanning Calorimetry (DSC), and the second method offers a novel aging prediction methodology by comparing the experimental heat of reaction values against idealized equilibrium values. As the heat of reaction plays a major role on determining propellant's performance, NASA Chemical Equilibrium with Applications (CEA) was used to predict its value. The knowledge of the combined aging effects is directly connected to the performance, lifetime, and safety of a pyrotechnic initiator that utilizes the THPP. The values of heat of reactions for different samples with different aging duration were estimated based on their composition extracted from the X-ray Photoelectron Spectroscopy (XPS) study.

1. Introduction

The performance of pyrotechnic materials is directly related to the combustion process and the chemical kinetics associated with this process. However, a deviation from the original chemical structure of the pyrotechnic composition may occur, especially along microscopic features such as surface cracks and particle interfaces, during long-term storage or transport. Such changes or degradations of the propellant over time is termed as aging and has been known to cause the energetic materials to fail [1]. One should make a note that this performance failure of the energetic materials may manifest as decreased reactivity leading to failure to ignite, failure sustained combustion, or decreased heat of reaction [2,3]. Therefore, it is extremely essential to analyse the effects of aging on the pyrotechnic compositions and predict the corresponding degradation in their performance.

Various studies aimed at understanding the aging of energetic materials utilize one-step reaction scheme wherein the chemical kinetic parameters of pre-exponential factor and activation energy are determined from the data collected by Differential Scanning Calorimetry (DSC). These characteristic parameters can yield the reaction rate representing the performance as well as the shelf life of the energetic materials. Therefore, knowing the kinetic parameters has been crucial for understanding the aging process.

The study by Wang et al. [2] has investigated the thermal stability of pyrotechnic mixtures under the combinative effect of elevated temperature and humidity by evaluating the critical temperature of thermal explosion and activation energy. Sorensen et al. [4] have investigated the thermal aging of titanium hydride and potassium perchlorate based compositions (THPP compositions) using DSC as well as high-resolution thermogravimetry (TG) to obtain the kinetic parameters by isothermal analysis. Trache et al. [5] have conducted a DSC study of the thermal decomposition of aged double-base propellants composed of nitrocellulose and nitroglycerin using Ozawa and Kissinger methods of kinetic analysis to predict the serviceable life of the propellant. Sanborn et al. [6] investigated the accelerated aging behaviour of THPP and zirconium potassium perchlorate (ZPP) compositions aged at 121 °C for 2, 9, and 12 months using the high-resolution thermogravimetry (HR-TG). The analysis for each component material including Viton-b, TiH_2, and $KClO_4$ was also conducted.

Collins [7] has proposed the ignition reaction scheme for $TiH_{0.15}$/$KClO_4$ pyrotechnics. The metal fuel particles could be passivated by air and encapsulated by oxide coating when exposed to atmosphere. Accordingly, when the $TiH_{0.15}$/$KClO_4$ powder is heated, dissolution of oxidizing coating occurs at the beginning resulting in generation of reactive titanium and the exothermic reaction with oxidizer is initiated. Erickson et al [8] amended the reaction scheme proposed by Collins by applying the Auger depth profiles to isothermally oxidized single crystals. Their results show that instead the dissolution mechanism that

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Collins proposed, the major factor for ignition process is the growth of a TiO_2 layer adjacent to the gas-solid interface.

Compositions based on titanium hydride (TiH_2) and potassium perchlorate ($KClO_4$) or THPP compositions are commonly utilized as pyrotechnic initiator [9] in the aerospace and propulsion industry wherein the pressure induced by their rapid combustion is exploited. The widespread usage of this material also entails a large-scale production and storage under a wide range of temperature and humidity conditions. However, studies elucidating the hygrothermal aging effects on THPP propellant are extremely rare.

The current study reports an experimental investigation into the hygrothermal aging of certain THPP compositions. Generally, most of investigations of pyrotechnic aging utilizes accelerated aging experiments and certain analytical techniques [10]. In the current study, additional spectroscopic data was combined with the DSC technique to predict the aging effects. Typical DSC analysis elucidates the heat flow associated with the chemical reaction occurring within a given sample. The DSC thermograms are insightful towards understanding the chemical kinetics of the given sample using only a small amount of sample mass. In addition, the current study utilizes X-ray photoelectron spectrometer (XPS) that has been the simplest and the most accurate way to obtain the elementary, qualitative and quantitative composition of the sample surface [11].

The kinetic parameters of aged and un-aged THPP propellant were obtained using the differential isoconversional Friedman method [12], which provides definite advantage [13] over simple single-step analysis as well as integral isoconversional methods [14,15]. The objective of the XPS investigation was to acquire the chemical compositions of THPP powders in terms of the molar ratio of concentration of each component. Furthermore, the experimental heat of reaction was compared against the theoretical value evaluated by combining XPS data with NASA Chemical Equilibrium with Applications (CEA) [16] program in order to reveal the effect of aging on the THPP compositions.

As the heat of reaction is one of the dominant performance for energetic materials, the aging evaluation can be proceeded by comparing these values. Therefore, to assess the aging effects and obtain the theoretical heat values, the NASA CEA program was adopted. The CEA program calculates chemical equilibrium product concentrations from any set of reactants and determines thermodynamic as well as transport properties for the product mixture. Meanwhile, the NASA CEA program does not evaluate any specific reactions. In the “hp” problem selected in the current study, Gibbs free energy was minimized by changing the system temperature and overall chemical composition. This program directly yields equilibrium product composition, equilibrium temperature, and thermodynamic properties through this process.

The data obtained in the current study can quantify the hygrothermal aging process and demonstrates a trend in heat of reaction of various aged THPP samples.

2. Experimental investigation

The THPP mixtures being studied were in a powder form and were formulated with a mass ratio of 32% TiH_2, 63% $KClO_4$ and 5% Viton-b (hexafluoropropene-vinylidenefluoride-copolymer). The titanium hydride (powder 98%) that is nearly stoichiometric, potassium perchlorate (powder, ≥99%) and Viton-b was from Rockwood Lithium, Barium & Chemical Inc., and Dupont, respectively. The aged and unaged THPP samples were stored in a flammable storage cabinet. Also, the temperature maintained a constant room temperature and by using a desiccant the humidity level was controlled to decreased state. The aging was performed in a chamber with controlled temperature and relative humidity. The powdered sample was placed in the middle of chamber with the temperature and relative humidity fixed to 71 °C and 100%. Under these conditions the THPP sample was aged for 10 and 12 weeks. This, the three samples in this study were unaged, 10 weeks aged, and 12 weeks aged THPP. Table 1 summarizes the list of pyrotechnic samples under study with the corresponding range of aging conditions. The aging temperature 71 °C followed the aerospace industrial guideline [17] while the humidity level was set at highest possible value in order to simulate the most adverse conditions similar to previous studies [1,18]. Henceforth, each sample will be referred by the serial number (#n).

Table 1
Aging conditions of THPP samples.

Sample	Aging condition
#1	Unaged
#2	Aged at 71 °C with relative humidity 100% for 10 weeks
#3	Aged at 71 °C with relative humidity 100% for 12 weeks

2.1. DSC study

The calorimetry experiments were carried out using the DSC-3+ instrument from Mettler Toledo at heating rates of 0.5, 1, 2, and 4 °C/min in the temperature range of 30 to 600 °C with a constant nitrogen purge flow of 85 ml/min. During DSC experiment, self-heating of the sample may occur during an exothermic process with larger sample masses or faster heating rates [19,20] and these factors should be proper methods [21]. On the other hand, the DSC thermograms may not provide clearly resolved peaks at very low sample mass and heating rate. As a rule of thumb, the product of sample size can be obtained by sample mass times the heating rate. However, the sample mass varies for all kinds of samples, so this factor must be obtained from empirical repetitions. In order to avoid these issues, each sample mass (m) in mg was determined based on corresponding heating rate (β) in °C/min using the relationship $m \times \beta \leq 1$. The relationship was obtained by empirical repetitions, so this relation is pertinent for only hygrothermally aged THPP samples. Despite varying sample mass, due to the absence of self-heating of the sample and uniformly resolved peaks at each heating rate, the DSC thermograms may be said to be mass-independent. The samples were sealed in 40 μm standard pierced aluminium pan and every experiment was carried more than 3 times to confirm the exact thermal behavior and ensure the repeatability of the experimental thermograms.

2.2. XPS study

The chemical composition and the quantitative value of the THPP were determined by Sigma Probe SYSTEM X-ray photoelectron spectrometer of UK VG Company, equipped with micro focused monochromatized Al Kα X-ray sources (1486.6 eV) and a spherical analyzer.

3. Results and discussion

3.1. DSC thermograms

Fig. 1 shows the DSC thermogram for sample #1 with one endothermic peak, three exothermic peaks, and a tangential baseline. The endothermic peak at 300 °C indicates the solid-state rhombic to cubic phase transition of the potassium perchlorate [4]. In case of the stoichiometric reaction between titanium hydride and potassium perchlorate [22], only one exothermic peak at 541.5 °C has been reported. Prior to peak analysis, Kai-Tai et al. [23] studied the reaction characteristics of a slow-burning tungsten-potassium perchlorate delay compositions with and without Viton additive using DSC as well as TG. The paper reported that the addition of Viton polymer to pyrotechnic mixtures was observed to result in an increase in the number of exothermic peaks in the DSC thermograms. The 1st exothermic peak was attributed to the reaction between tungsten, potassium perchlorate, and Viton while the second stage was proposed to be a reaction of mixtures

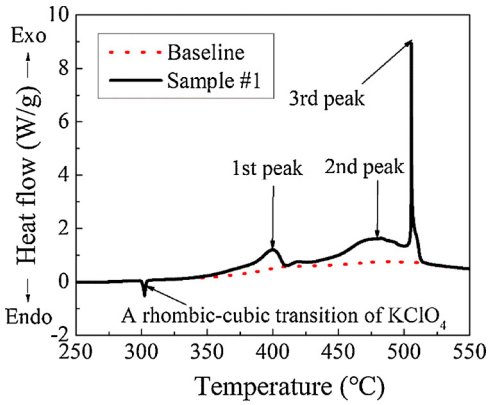

Fig. 1. The DSC thermogram for sample #1 at β = 1 °C/min.

without Viton. Therefore, it can be assumed that the 1st peak at 400 °C indicates the reaction between titanium hydride, potassium perchlorate, and Viton similar to the case reported by Kai et al. [23] The 2nd exothermic peak with a broad temperature range of 450 to 500 °C represents the reaction of titanium hydride, potassium perchlorate and a small quantity of potassium chlorate ($KClO_3$) generated from the decomposition of potassium perchlorate. During the process corresponding to the 2nd peak, TiO_2 may be formed by the reaction of TiH_2, $KClO_3$, and $KClO_4$. Subsequently, the conversion of $KClO_3$ into $KClO_4$ may occur due to the catalytic activity of metal oxides such as titanium dioxide (TiO_2) as suggested by Rudloff et al. [24]. This process retains the $KClO_4$ in the composition even after the main reaction process was completed. Consequently, the 3rd exothermic peak at 504 °C was attributed to the decomposition process of remaining $KClO_4$ similar to the results reported by Sorensen et al. [4].

Based on the various observations extracted from the thermograms, a reaction scheme for the THPP propellant combustion may be proposed. Fig. 2 represents an idealized reaction scheme for the unaged THPP sample, which was divided into five sections. Actually, the pure potassium perchlorate decomposes about at 592 °C [25]. In this paper, however, the decomposition reaction of potassium perchlorate occurred at the first step. This reduction in the temperatures has been attributed [25,26,27] to the solid-state reactions, increased inter-diffusion of reactive components beyond the Tammann temperature, and inadvertent formation of local hotspots in the sample, as well as crystal defects such as distortions, dislocations, and cracks. In addition, similar reaction schemes have been reported elsewhere [4,23,24].

Fig. 3 shows the DSC thermograms at the heating rates of 0.5, 1, 2, and 4 °C/min for all the THPP samples. Both the initiation and end of the exothermic peaks corresponding to various chemical reactions were observed to occur at higher temperature range as the heating rate was increased, while the endothermic transformation of potassium perchlorate remained at 300 °C regardless of the heating rate. As the change in location of peaks with the heating rate is observed only for kinetically driven process, the endothermic peak of phase transition of potassium perchlorate does not change.

Table 2 shows the thermal behaviour of THPP samples at various heating rates to quantify the hygrothermal aging effects on THPP propellants. The hygrothermal aging resulted in the Viton chemical reaction represented by the 1st peak to be displaced to higher temperatures. In contrast, the reaction of THPP without Viton and the decomposition process of $KClO_4$ displayed as the 2nd and the 3rd peak respectively, moved to lower temperatures under hygrothermal aging. The temperature differences between aged and unaged THPP were evident, but sample #2 and sample #3 had similar peak temperatures. However, the difference in the 10 and 12 week aging duration was evident in the onset temperatures of the sample that demonstrated an increasing tendency with the aging duration. Thus, it could be seen that hygrothermal aging slowed the initiation of reaction in the THPP pyrotechnic.

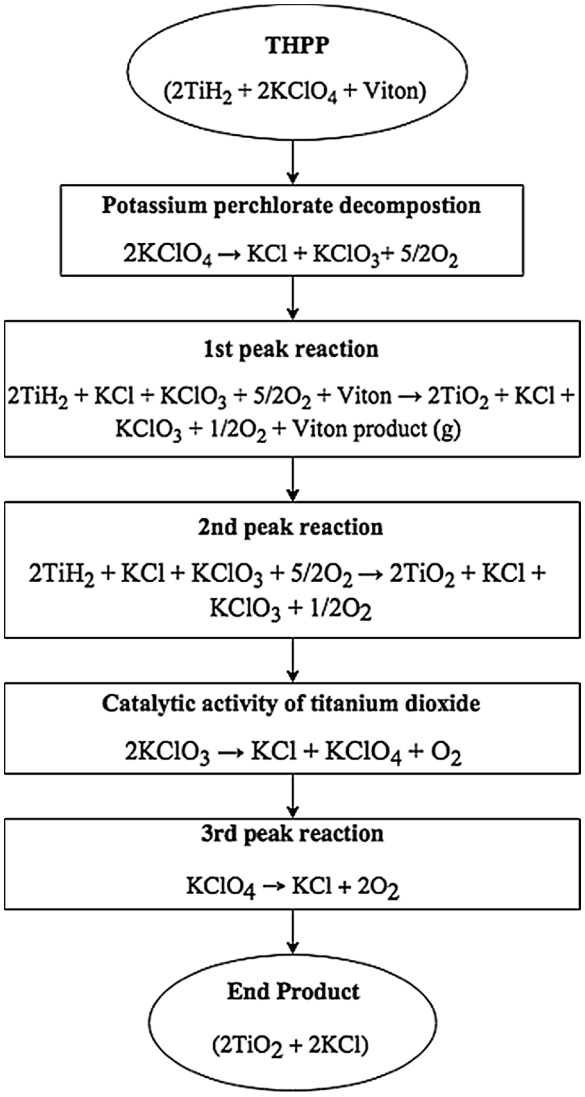

Fig. 2. Flow chart showing the THPP reaction scheme.

3.2. Kinetics analysis

The reaction kinetics parameters such as activation energy and pre-exponential factor corresponding to the DSC thermograms of each sample were calculated by employing the Friedman isoconversional method [12]. Kim et al. [10] adopted this method to obtain kinetics parameters with considerable accuracy for the complete range of reaction progress. A methodology similar to Kim et al. [10] has been employed in this paper to evaluate the values of baseline, reaction rate, pre-exponential factor and heat of reaction using AKTS software. The uncertainty of the activation energy and pre-exponential factor is standard deviation of the average values. The averaged values for kinetics parameters were obtained from the DSC experiments' data, which conducted for 3 times.

In this paper, kinetic parameters were obtained separately for the 1st and the 2nd peaks. The 2nd peak, attributed to the reaction of fuel and oxidants without Viton, was designated to be the prominent exothermic reaction of primary focus as it was related to the largest portion of the heat released. Therefore, the reaction progress and reaction rate have been explicitly reported for the 2nd peak.

Fig. 4 shows the extent of the reaction progress (α) as a function of the temperature for various heating rates for the 2nd peak. The reaction progresses for all samples have a rapidly increasing trend between the range of $0.25 < \alpha < 0.5$ while the reactions were observed to progress

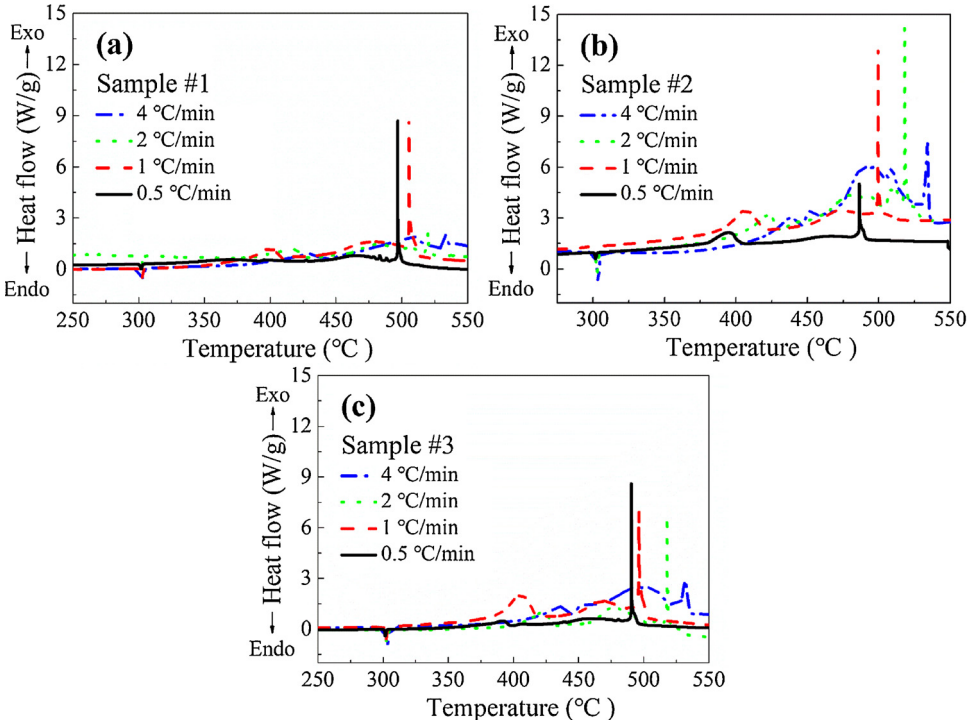

Fig. 3. Heating rate effect: (a) Sample #1, (b) Sample #2, (c) Sample #3.

slowly for $\alpha > 0.75$. In all three cases, the higher the heating rate, the higher the temperature required to have the same reaction progress. Therefore, at higher heating rates, the sample must be heated to a higher temperature to achieve the same value of reaction progress compared to the lower heating rate. The hygrothermally aged THPP sample demonstrated a lower reaction initiation temperature compared to the unaged sample and the temperature was further lowered with aging duration.

Fig. 5 shows the reaction rate corresponding to the 2nd peak in the thermograms of the THPP samples. All three cases exhibited an increase in the reaction rate with the heating rate. Additionally, as shown in Table 2, the peak reaction rate was also observed to occur at the higher temperature. With hygrothermal aging, the peak reaction temperature had generally decreasing trend when the samples were aged.

Fig. 6 shows the activation energy and pre-exponential factor as a function of reaction progress evaluated by employing the isoconversional Friedman method. In AKTS software program, each Arrhenius parameter is calculated with considerably narrow the interval of conversion, $\Delta\alpha = 0.0001$. In Fig. 6, however, to present both the uncertainty of each parameter and the tendency of parameter with the reaction progress, $\Delta\alpha = 0.02$ was adopted. The thermal decomposition of THPP was observed to consist of the chemical reaction with Viton (1st peak), chemical reaction without Viton (2nd peak), and $KClO_4$ decomposition process (3rd peak). The kinetics parameters for only the previous two reactions were obtained because $KClO_4$ decomposition peak was observed to be irregular depending to the heating rates and resulted in unreliable kinetic parameters.

Activation energy and pre-exponential factor at $0.2 < \alpha < 0.8$ tended to be higher for the 1st peak when hygrothermal aging was applied and the aging duration was longer. A slope change was observed at about $\alpha = 0.5$ in Fig. 5 for all samples. In the case of 1st peak process corresponding to the reaction of TiH_2, $KClO_4$ and Viton; the

Table 2
Thermal behavior of THPP samples at various heating rates.

Sample	β (°C/min)	T_p[a] (°C)			T_o[b] (°C)	$T_{r,s}$[c] (°C)	$T_{p,r}$[d](°C)	$R_{r,s}$[e](1/s)
		1st peak	2nd peak	3rd peak				
#1	0.5	368	466	496	347	430	467	0.00230
(unaged)	1	400	482	505	394	434	476	0.00083
	2	418	483	520	396	437	483	0.00053
	4	430	508	534	406	449	508	0.00027
#2	0.5	396	464	486	380	420	458	0.00210
(aged for 10 weeks)	1	407	473	500	392	429	470	0.00122
	2	424	479	518	403	440	476	0.00062
	4	438	495	534	432	454	485	0.00027
#3	0.5	392	460	490	379	398	453	0.00135
(aged for 12 weeks)	1	406	468	496	397	419	463	0.00102
	2	423	477	518	404	433	475	0.00048
	4	437	508	532	421	443	491	0.00019

[a]Exothermic peak temperature.
[b]Onset temperature.
[c]Reaction starting temperature.
[d]Peak reaction temperature.
[e]Peak reaction rate.

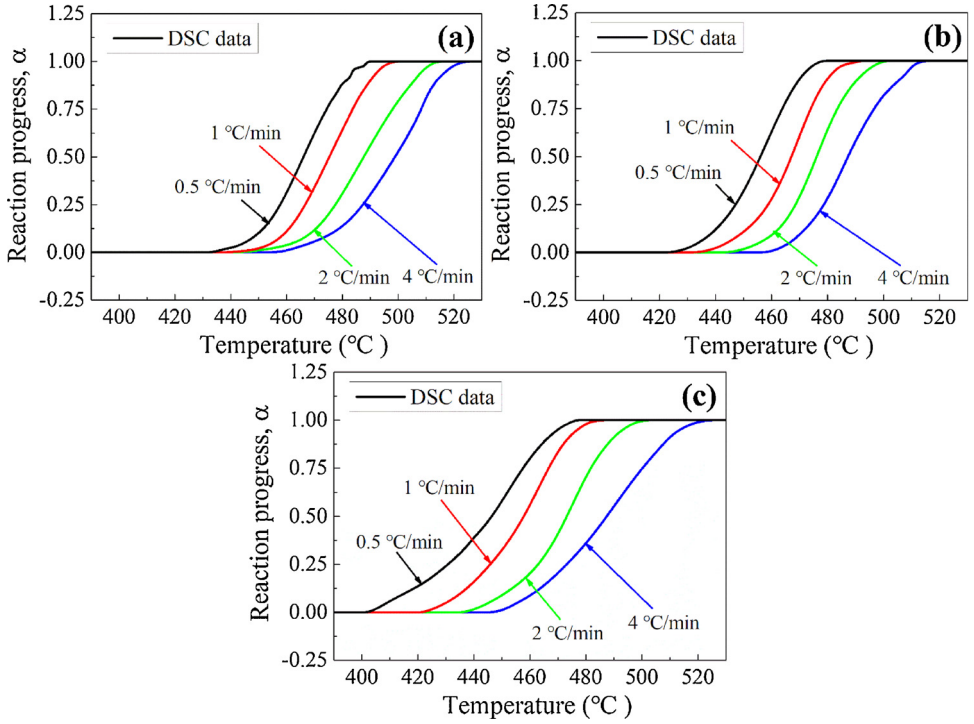

Fig. 4. Reaction progress of the 2nd peak process: (a) sample #1, (b) sample #2, (c) sample #3.

activation energy for sample #1 was observed to vary from 117 ± 8 kJ/mol to 167 ± 16 kJ/mol and the pre-exponential factor from 14 ± 1 s^{-1} to 20 ± 3 s^{-1}. Also, these factors increased gradually for $\alpha < 0.5$ and a relatively rapid increase was observed for $\alpha > 0.5$. In case of sample #2 the values tended to decrease for $\alpha < 0.4$ and maintained approximately constant activation energy and pre-exponential factor of 174 ± 10 kJ/mol and 24 ± 1 s^{-1} for $0.4 < \alpha < 0.7$. Sample #3 exhibited the constant state (168 ± 21 kJ/mol and 23 ± 4 s^{-1}) until $\alpha = 0.5$ and then showed slightly a decreasing trend for $\alpha > 0.5$. Based on these observation, it was inferred that a change in the reaction mechanism may have occurred at $\alpha \approx 0.5$.

In the case of the reaction corresponding to the 2nd peak, the tendencies of kinetics parameters of all samples had decreasing trend for $0.3 < \alpha < 0.7$. The hygrothermally aged THPP samples had lower parameter values than the unaged sample. Also, the aged samples had similar increasing tendency until $\alpha < 0.3$ and decreasing tendency for $0.3 < \alpha < 0.7$. Therefore, this results suggests that the hygrothermal aging can affect to the THPP sample's 2nd peak reaction. The kinetics

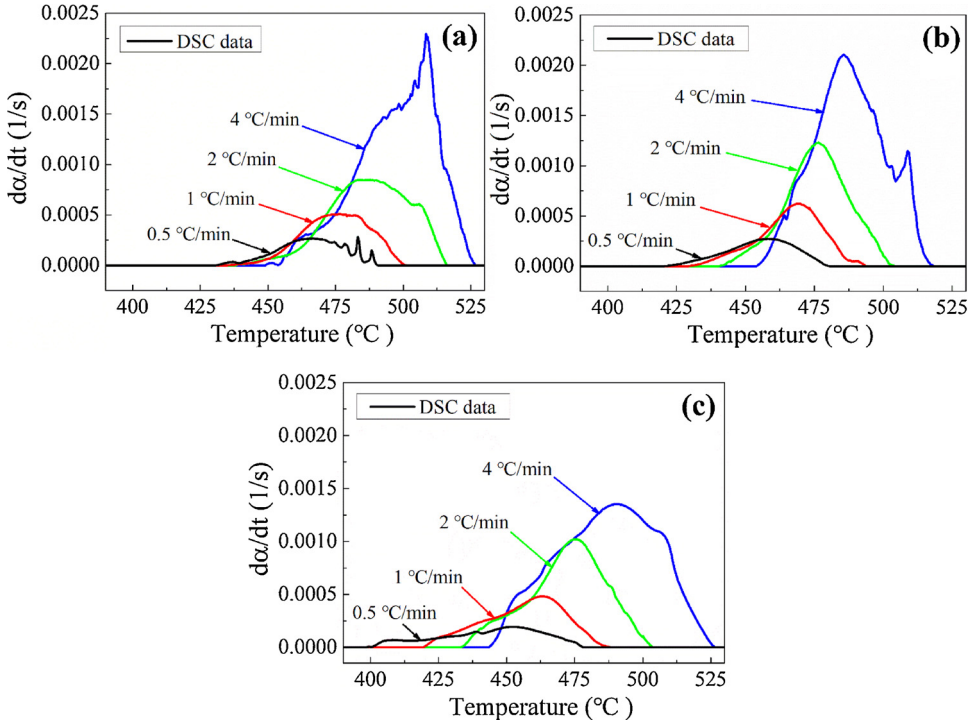

Fig. 5. Reaction rate of the 2nd peak process: (a) sample #1, (b) sample #2, (c) sample #3.

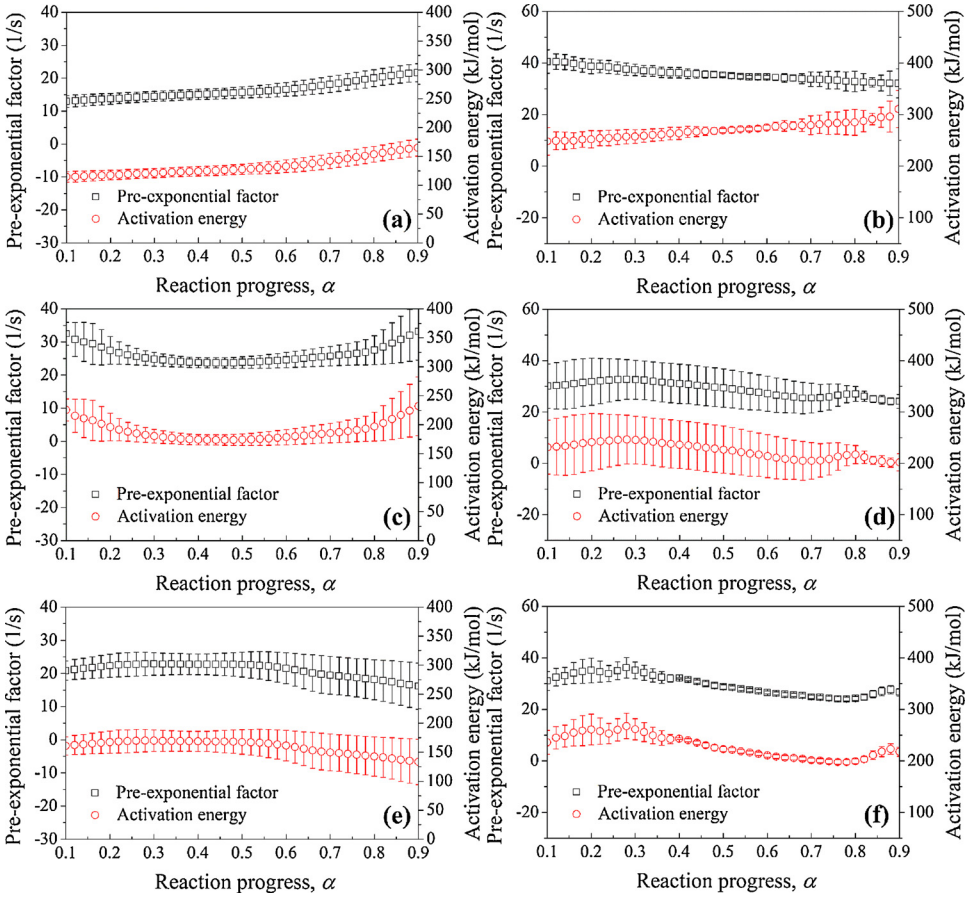

Fig. 6. Kinetics parameters of THPP: (a) sample #1 at 1st peak, (b) sample #1 at 2nd peak, (c) sample #2 at 1st peak, (d) sample #2 at 2nd peak, (e) sample #3 at 1st peak, (f) sample #3 at 2nd peak.

parameters had significantly low values for sample #3, and there was a small fluctuation in the range of $0.2 < \alpha < 0.4$, attributed to complex reactions occurring at the middle of the reaction. In 2nd peak reaction case, every sample had the extreme fluctuation at the beginning and end of the reaction process. This phenomenon also elucidated the 2nd peak reaction was composed of various reactions and accompanied a lot of process when the reaction started and finished.

In other words, the relatively large fluctuations in the kinetic parameters for $\alpha < 0.2$ and $\alpha > 0.8$ indicate the complex reactions in this range [28]. Also, the uncertainties of parameter values for each sample generally had the highest values at either extremes of the reaction progress. Therefore, the acceptable range of reaction progress value was fixed from 0.2 to 0.8, and the kinetic parameters presented in this range were summarized in Table 3. Additionally, the aged THPP samples' kinetics parameters had higher uncertainties than unaged sample. Especially, the 2nd peak reaction for sample #2 and the 1st peak reaction for sample #1 had large uncertainties compared with other cases. This tendency, thus, shows that the hygrothermal aging can affect strongly the THPP's kinetic characteristics.

To verify the validity of the kinetic parameters, comparison with the published data was proceeded. Shamsipur et. al [22] reported that titanium hydride-fueled binary pyrotechnic compositions' non-isothermal kinetic studies. They obtained the kinetic parameters from the non-isothermal decomposition data of pyrotechnic materials by using the Kissinger calculation method. We focused the two samples in the paper, $TiH_2 + KClO_4$ with the composition of 29/71 and $TiH_2 + KClO_3$ with the composition of 32.4/67.6. They had the similar composition of our sample, 32% of TiH_2, 63% of $KClO_4$ and 5% of Viton. Prior to comparison with the published data, each sample can be matched reaction process. In other words, kinetics parameters for $TiH_2 + KClO_3$ corresponded to the 2nd peak process. After all, by comparing 1st and 2nd peak process, the Viton's effect to the kinetic parameters for THPP

Table 3
Activation energy and pre-exponential factor of THPP.

Sample	Activation energy (kJ/mol)		Pre-exponential factor (1/s)	
	1st peak	2nd peak	1st peak	2nd peak
#1 (w/ Viton)	117 ± 8 ~ 154 ± 14	252 ± 17 ~ 285 ± 25	14 ± 2 ~ 20 ± 3	33 ±4 ~ 39 ± 3
#2 (w/ Viton)	174 ± 10 ~ 197 ± 25	205 ± 36 ~ 246 ± 47	24 ± 1 ~ 28 ± 4	25 ± 6 ~ 33 ± 8
#3 (w/ Viton)	143 ± 34 ~ 168 ± 21	198 ± 5 ~ 268 ± 25	18 ± 6 ~ 23 ± 4	24 ± 1 ~ 36 ± 4
$TiH_2 + KClO_4$ [22]	535.9		34.36	
$TiH_2 + KClO_3$ [22]	341.5		23.83	

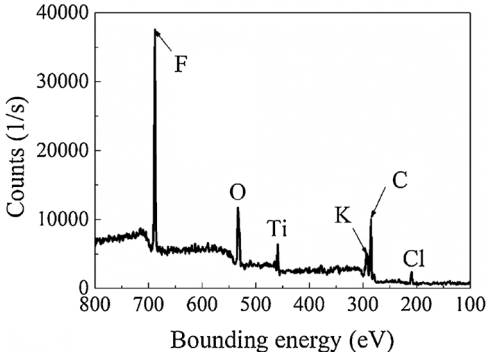

Fig. 7. The THPP composition from XPS data.

can be obtained also. The kinetic parameters at 2nd peak process for sample #1 were from 252 ± 17 to 285 ± 25 kJ/mol and from 33 ± 4 to 39 ± 3 s^{-1}. Meanwhile, the published data were 535.9 kJ and 34.36 s^{-1}. The activation energy was slightly lower, but the pre-exponential factor was higher than published parameter. By comparing the 1st and 2nd peak process, we can suppose that the Viton b affected the THPP to decrease the activation energy and pre-exponential factor. Also, by comparing $TiH_2 + KClO_4$ reaction parameters to $TiH_2 + KClO_3$ reaction values, it can be seemed that potassium perchlorate has higher activation energy and pre-exponential factor. Therefore, we can assume that the remained or created potassium perchlorate makes the activation energy and pre-exponential factor high.

3.3. Sample composition by XPS technique

Fig. 7 shows a scan from XPS experiment for unaged THPP sample showing all the atoms that form the THPP propellant. All THPP specimens were composed of the six main peaks of F, O, Ti, K, C, and Cl atoms corresponding to the composition of the THPP propellant. The fluorine peaks arise from the Viton, which is composed of carbon, hydrogen, and fluorine atoms ($[-C_5H_8F_{8-}]_n$) [29].

Based on the atomic ratio in the XPS data, quantitative analysis [30] was carried out and the chemical composition of each sample was obtained. Table 4 shows the molar ratio of the composition obtained for all samples. Samples were composed of mainly four molecules viz. TiH_2, TiO_2, $KClO_4$, and $KClO_3$. The sample #1 shows traces of titanium dioxide although it was not humidity aged. However, Zhang et al. [31] reported the XPS experiments with TiH_2 and identified a layer of TiO_2 on the outermost surface of TiH_2 particles. This could suggest that an oxidized film may surround the TiH_2 without aging the sample resulting in the measurements in the current study. Also, even though the original THPP sample had a small amount of potassium chlorate, the reaction scheme in the current study has been postulated based on the various observations extracted from the thermograms. Furthermore, the reactions in pyrotechnics are typically triggered by melting or decomposition of either the fuel or the oxidizer [32,33]. The small amount of potassium chlorate in the original sample can be observed to increase with aging.

As the THPP sample was composed of a mass ratio of 32% TiH_2, 63% $KClO_4$ and 5% Viton-b, the molar ratio of TiH_2 and $KClO_4$ was calculated to be 1:0.709. Calculating the molar ratio of Ti and KCl of each sample, sample #1, #2, and #3 had the values of 1:0.708, 1:0.709, and 1:0.734. Since the maximum error of molar ratio of each sample was below 3.54%, it could be seen that the XPS data was validated.

When the hygrothermal aging was applied to the THPP sample, TiH_2 and $KClO_4$ were prone to decrease, but TiO_2 and $KClO_3$ tended to increase. Moreover, as the aging duration was increased, the oxygenation rate of titanium hydride was higher. As shown in Table 4, when the THPP aged for 10 weeks and 12 weeks, the conversion rate to TiO_2 from TiH_2 of sample #2 was 12.13 ± 3.45%, but the rate of sample #3 was 33.76 ± 6. 55%. In the case of potassium perchlorate, the decomposition rate to $KClO_3$ was 1.05 ± 0.47% at sample #2 and 8.05 ± 0.19% at sample #3. Thus, the hygrothermal aging reaction could be expressed as eq. (1). Also, the prior results obtained from XPS data supposed that TiH_2 and $KClO_4$ reacted more with water and oxygen highly when the aging duration was longer. Therefore, the chemical composition results of THPP from XPS experiment can validate the below hygrothermal aging reaction of THPP.

$$TiH_2 + KClO_4 + H_2O + O_2 \rightarrow TiO_2 + KClO_3 + 2H_2O \quad (1)$$

3.4. Reaction phenomenology

Based on the observed changes in the heat generation of THPP samples with the aging duration, a prediction for heat performance was obtained. The value of heat of reaction (ΔH) was obtained using the AKTS software [10] with a sigmoidal baseline tangential on each side of the 2nd exothermic peak of the DSC signal. The experimental heat of reaction value showed the tendency to increase in the order of sample #3, #1, and #2 as shown in Table 5. The trend in the heat of reaction may be explained by looking at the fuel to oxidizer (F/O) ratio of each sample. The F/O ratio was calculated by dividing each sample's TiH_2 content by the sum of $KClO_4$ and $KClO_3$ content. The values used are represented in Table 4. The F/O ratio of sample #2 was 0.94 ± 0.04, which indicates an almost stoichiometric mixture while the F/O ratio for sample #3 was the lowest at 0.60 ± 0.02 leading to the observed trend.

In order to validate the experimental data, the idealized heat of reaction was evaluated using NASA CEA program [16] are also shown in Table 5. As the heat of reaction is one of the major performance characteristics in evaluating the aging effects of energetic materials, CEA was used to predict just that. A theoretical estimate of the heat of reaction was obtained by inputting the energetic material's composition, temperature, pressure, enthalpy, and O/F ratio into the NASA CEA program. Comparison of the trends obtained from NASA CEA with the composition of samples with different aging duration brings out the effect of aging.

The CEA program was run at a constant pressure of 1 atm and an initial temperature of 298.15 K. The values of heat of reactions for various samples with different aging duration were estimated based on their composition extracted by the XPS study. Thus giving a theoretical trend of change in heat of reaction, which was then compared with the DSC experimental data. The formation enthalpy of each sample was obtained from Chase et al. [34] and Zumdahl et al. [35] as shown in Table 6.

The heat of reaction values from experimental and CEA data changed with the similar tendency as the aging duration increased. Both data had the highest heat value in the case of sample #2, and the lowest heat in the case of sample #3. In this occasion, there exists the

Table 4
Chemical composition and Fuel to Oxidizer ratio of THPP.

Sample	TiH_2	TiO_2	$KClO_4$	$KClO_3$	$(F/O)_{molar}$
#1 unaged	44.50 ± 0.89	14.01 ± 0.28	33.46 ± 0.33	8.03 ± 0.80	1.07 ± 0.05
#2 aged	39.10 ± 0.78	19.42 ± 0.39	32.92 ± 0.33	8.60 ± 0.90	0.94 ± 0.04
#3 aged	25.52 ± 0.51	32.22 ± 0.64	30.71 ± 0.31	11.70 ± 0.12	0.60 ± 0.02

Table 5
A summary of heat of reactions – comparison.

Case	Sample	Heat of reaction (J/g)
Present experiment	#1	1848±102
	#2	2178±218
	#3	1749±175
NASA CEA	#1	190443
	#2	191217
	#3	186830

Table 6
Formation enthalpy of THPP composition.

Composition	Formation enthalpy (kJ/mol)
TiH_2	−144.35
$KClO_3$	−391.40
$KClO_4$	−430.12

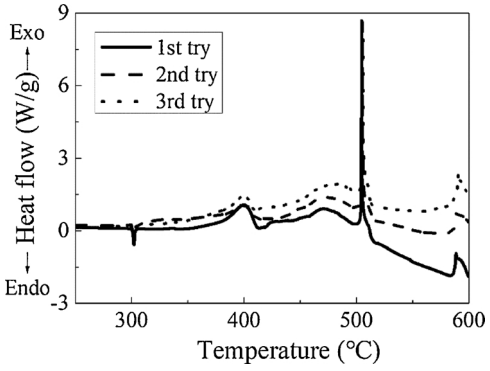

Fig. 8. Small variations of DSC thermograms.

difference between theoretical and experimental heat of reaction. This result comes from the following reason. The theoretical heat of reaction obtained from NASA CEA program was calculated equilibrium reaction products of THPP samples. However, the experimental heat of reaction data was affected by incomplete reactions and non-ideal conditions. Hence, the difference in the data could have occurred. Therefore, the similar tendency of heat values is important in this study. The trend of experimental and CEA data was similar, so the heat values of between 0 and 12 weeks could be predictable. Therefore, the heat released can be anticipated without any experiment for all the periods, suggesting that the method is quite remarkable for predicting the heat of reaction of the aged propellant.

4. Uncertainty analysis

Fig. 8 shows the DSC thermograms of unaged THPP with 1 °C heating rate. Each heat flow graph had almost identical endothermic and exothermic peak, but there existed small variation of the graph. However, the repetition of the DSC experiments yields approximately identical heat released value and major features. Moreover, kinetics parameters display a strong fluctuation in the range of $0.2 < \alpha$ and $\alpha < 0.8$ indicating a limitation in acquiring the exact kinetics parameters. Finally, as only three THPP samples were utilized with large gap between the duration of sample #1 and sample #2, the extrapolation of the data may not be reliable and further study with more samples is necessary.

5. Conclusion

In this paper, thermal behavior and kinetics parameters of hygrothermally aged THPP were obtained by using DSC and applying two-step isoconversional method, and the theoretical trend of change in heat of reactions for THPP propellants was predicted from XPS data and CEA program. These heat values were compared with the DSC experimental data, and confirmed that theoretical value and experimental data had similar trend.

The DSC thermograms under the effect of hygrothermal aging, showed a 1st peak which represents the combined reaction of Viton, fuel and oxidants. The reaction with Viton had a tendency of increasing onset temperatures as the hygrothermal aging was applied to the sample. On the other hand, the process corresponding to the 2nd and 3rd peaks remained in the similar temperature range.

The kinetic parameters for the 1st peak tended to increase with aging duration, but the peak value of the 2nd peak had both an increasing and a decreasing trend. By analyzing the kinetic parameters, it was found that complex reactions occurred for $\alpha < 0.2$ and $\alpha > 0.8$. Also, by comparing the results, Viton can affect THPP to have lower activation energy and pre-exponential factor but potassium perchlorate increased these values.

With longer duration of hygrothermal aging, the amounts of $KClO_4$ and TiH_2 decreased while the amounts of $KClO_3$, TiO_2 increased. Therefore, it can be assumed that hygrothermal aging catalyzes the $KClO_4$ decomposition and TiH_2 oxidation.

From the composition ratio of sample, we have obtained the heat of reaction of each sample. The sample #2′s heat of reaction had the highest value. This is because that the sample #2′s F/O ratio had the closest value to the stoichiometric ratio. By comparing the experimental heat of reaction data to NASA CEA data, the prediction of released heat of aged samples were obtained. Since the two data are similar, the prediction methodology outlined in this paper is reliable.

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