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EFFECTS OF GAS-PHASE MASS TRANSPORT IN THE PYROTECHNIC SYSTEM RED LEAD–SILICON–POTASSIUM PERCHLORATE

S. R. Yoganarasimhan

IDL-NITRO NOBEL BASIC RESEARCH INSTITUTE, P.B. NO. 397,
SANKEY ROAD, MALLESWARAM, BANGALORE 560 003, INDIA

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The acceleratory effect of potassium perchlorate on the reactivity of the red lead–silicon system has been studied by employing DTA and DSC. Supporting investigations on pure potassium perchlorate and the binary system red lead–potassium perchlorate suggest that the complex decomposition kinetics of potassium perchlorate drastically influences the oxidation of silicon. Further, the ternary system also undergoes a transition from exothermic smooth decomposition to ignition at a certain critical mass, as noted in the red lead–silicon and iron(III) oxide system. The criticality should be a result of the rise in temperature expressed as a perturbation of the steady-state energy conservation conditions, as postulated by Gray.

The kinetics of decomposition of metal perchlorates is a complex process, as revealed by the extensive studies by Solymosi and coworkers [1–3]. The formation of chlorate was found to be an intermediate step, at least partially, during the thermal decomposition of potassium perchlorate ($KClO_4$). While chlorate formation seems to be a general occurrence in the decomposition of alkali metal perchlorates, it does not seem to be the general rule with other perchlorates, particularly transition metal and heavy metal perchlorates.

The oxidative reactions of $KClO_4$, which is extensively applied in several pyrotechnic devices, are of greater complexity, arising from the catalytic effect of the solid fuel oxide film on the decomposition of $KClO_4$, difficulty in the migration or diffusion of oxygen through the growing oxide layer, and the relative magnitudes of the rate of gaseous mass transport process and the rate of decomposition, which can result in non-steady-state conditions, leading to thermal ignition.

In this context, our interest is directed towards the effects of $KClO_4$ on the oxidation kinetics of the red lead–silicon system, which is used as a fast burning composition capable of providing millisecond delay intervals in detonators. The red lead–silicon system itself has been studied by Rees and coworkers [4–7], using DTA

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and combustion studies. The highest combustion rate was found at around 70% red lead and 30% silicon, though this proportion is oxygen–deficient. Yoganarasimhan and Josyulu [8] studied the system in greater detail, with the introduction of a combustion decelator, viz. Fe_2O_3. The overall reaction kinetics did not seem to change with the introduction of Fe_2O_3. They noticed an abnormal phenomenon of a critical mass, above which the reaction always led to ignition. This critical mass could be reproduced to within 1 mg in DTA experiments. Barton et al. [9] also found that the BaO–Mg system attained criticality above a certain mass, but the criticality regime was not defined by them to such a narrow range as in the red lead–silicon system. They did not offer a mechanistic interpretation of the criticality either.

We have now studied the ternary system red lead–silicon–$KClO_4$ in an attempt to understand the importance of the gas-phase mass transport of oxygen in enhancing the rate of reaction of the red lead–silicon system. We have also attempted to give a qualitative description of the ignition conditions at the critical mass in terms of the thermal explosion theory of Gray et al. [10], who postulated a phenomenological theory wherein the reactant consumption and varying ambient temperature are considered as determining characteristics leading to thermal explosion. The latter situation would be more appropriate in the dynamic temperature conditions existing in DTA/DSC. In order to be able to understand the ternary system, we have also investigated the relevant binary systems and $KClO_4$ itself.

Experimental

Materials

Potassium perchlorate was prepared through the double decomposition of sodium perchlorate and potassium chloride. The precipitate was washed free of chloride ions and was recrystallized from hot water by rapid cooling. Material passing 200 B SS was used for preparation of the mixtures. Some crystalline $KClO_4$ was also used for the DTA of pure $KClO_4$.

The silicon had a minimum purity of 98.5%, with less than 0.2% iron. The average particle size, as determined with a Seishin Micron Photo Sizer, was 5.8 μm, with less than 1.0% above 20 μm.

The red lead had a minimum purity of 97%, with an average particle size of 4 μm, and an insignificant portion above 30 μm.

Predetermined quantities of the ingredients were weighed and mixed by sieving as per standard practices employed in the handling of hazardous pyrotechnic materials.

Measurements

DTA curves of each mixture were recorded at different sample masses; all other conditions being kept constant. The instrument was built so as to be ideally suited for pyrotechnics and propellants. The features are described in [8]. All the measurements were made in air. DSC curves of the ternary and binary mixtures were recorded in the Perkin–Elmer Differential Scanning Calorimeter model DSC–2. Enthalpies were calculated by using indium as reference.

Results and discussion

1. Potassium perchlorate

Differential thermal analytical (DTA) curves of pure $KClO_4$ of three different particle sizes, viz. coarse ($> +150$ BSS), medium ($-240+300$ BSS) and fine (-300 BSS), are given in Fig. 1. The medium and fine samples were prepared by continued crushing of coarse crystalline $KClO_4$ and by sieve separation. The low-temperature range up to 773 K is not shown, as the well-characterized phase transition at around 573 K is the only prominent thermal change. One of the marked differences in the DTA curves of the three samples is that the melting point becomes sharper as the particles become finer. There is a fine structure of the melting endotherm, suggesting that in the case of finely ground materials the melting is also a multistage process. This cannot be attributed to sample size effects, as the sample mass was maintained at 64–65 mg in all cases. Melting sets in at 845, 832 and 828 K for coarse, medium and fine $KClO_4$, respectively. The first stage of the endothermic process occurs at 862, 861 and 873 K. The second stage becomes more prominent as the particle size decreases, until its intensity is greater than the peak intensity observed with the coarse $KClO_4$. Such fine resolution of the melting of $KClO_4$ was not reported either by Solymosi [1] or by Kovalenko, Ivanav and Usov [11]. If it is postulated that the relieving of the stresses and strains caused by the crushing of $KClO_4$ could liberate some heat during annealing prior to melting, only one shoulder or an aberration should be seen in an otherwise symmetric endothermic peak. Since three different endotherms are seen, it is proposed that the grinding process produces embryonic nuclei which lead to at least two endothermic reactions besides melting. One such reaction could be a partial conversion of $KClO_4$ to $KClO_3$ during the melting process. The enthalpy change of the reaction

$$KClO_4 \rightarrow KClO_3 + \frac{1}{2} O_2$$

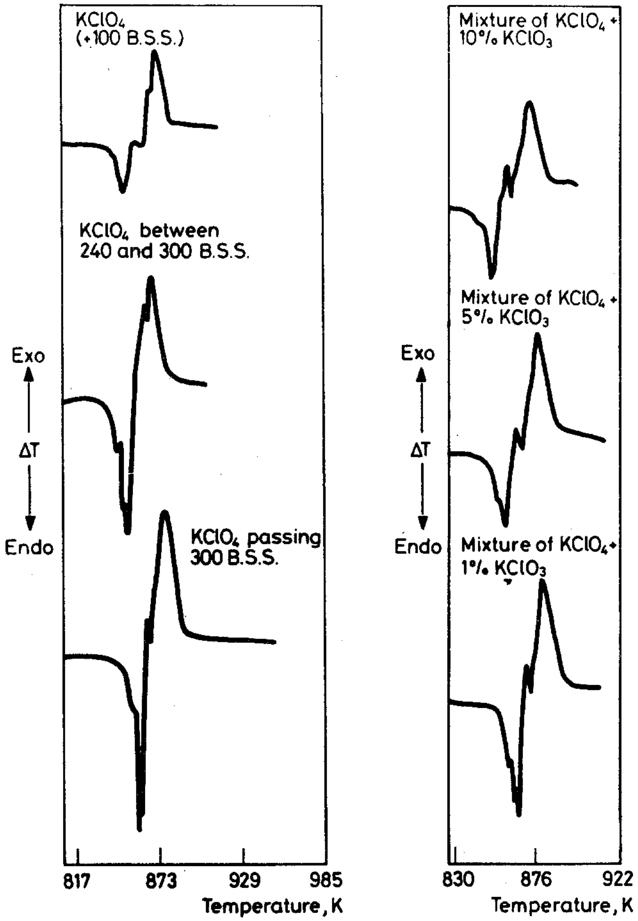

Fig. 1 DTA of potassium perchlorate in air as a function of (a) particle size and (b) admixture with potassium chlorate at 1.5 and 10% levels

should be +42.2 kJ mol^{-1}. A defect state which accelerates the conversion of $KClO_4$ to $KClO_3$ should increase in intensity as the powder is ground to a fine state. In order to verify such a postulate, DTA curvès of mixtures of $KClO_4$ and $KClO_3$ were recorded (Fig. 1); these show that the second reaction is probably associated with the conversion of $KClO_4$ to $KClO_3$. The other endotherm, apart from the one due to melting, cannot be unequivocally assigned, because a large number of reactions are possible, as predicted by Solymosi [1].

The main reaction exotherm shows certain singularities on the minor exotherm immediately after melting and a shoulder just before the peak. The intensity of the

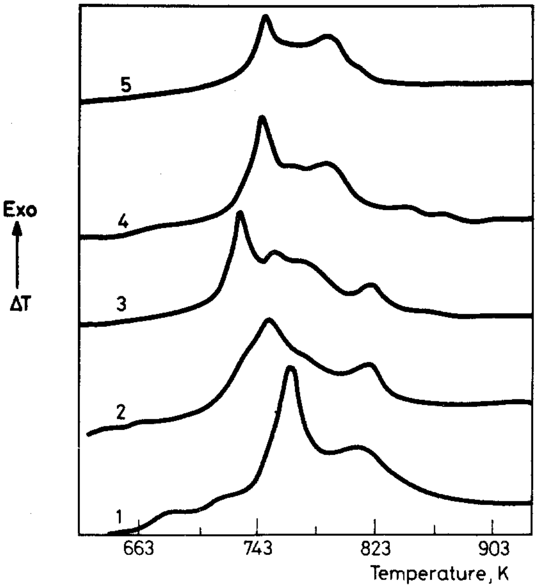

Fig. 2 DTA of red lead/silicon/$KClO_4$ in air, below the critical mass for ignition, as a function of $KClO_4$ content. (1, 2, 3, 4 and 5 relate to 5, 10, 20, 25 and 35 parts of $KClO_4$ added to the base composition of 70/30 red lead/silicon). Sample mass: 1: 22.0 mg, 2: 15.0 mg, 3: 14.8 mg, 4: 16.2 mg, 5; 12.3 mg

former increases as the proportion of $KClO_3$. It can reasonably be postulated that the conditions which favour the formation of $KClO_3$ during the melting and the minor exotherm mentioned above are interlinked. These reactions are expected to play the most dominant role in the oxidative reactions of $KClO_4$ discussed in the following section.

2. *Red lead–silicon–potassium perchlorate system*

Five different mixtures of the three ingredients were prepared by adding 5, 10, 20, 25 and 35 parts by weight of $KClO_4$ to a mixture of 70 : 30 parts by weight of red lead–silicon, and the mixtures were thoroughly "homogenized". DTA curves were recorded in the mass range from 10 mg to 25 mg. The results are shown in Figs 2 and 3. In the lower mass range, the DTA curves recorded in ambient atmosphere-show no endotherm due to the phase change near 573 K in samples 1 and 2, containing only 5 and 10 parts of $KClO_4$. This is due to the sensitivity of the instrument. As the mass of the sample is increased to 22.0 mg, sample 1 shows three exotherms, with peak temperatures at 692, 764 and 816 K. The more prominent third peak ranges between 816 and 834 K. Sample 3 behaves similarly to the first

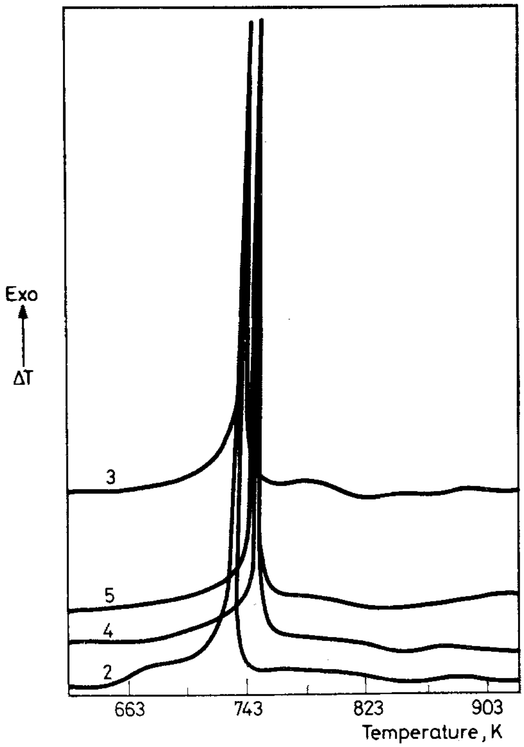

Fig. 3 DTA of red lead/silicon/$KClO_4$ in air under ignition conditions. (The nos 2 to 5 relate to the same as those in Fig. 2). Sample mass; 2: 25.1 mg, 3: 21.8 mg, 4: 20.8 mg, 5: 16.2 mg

two up to a sample mass of 15 mg. However, the inception temperature of the second exotherm marginally decreases further to 708 from 726 K for sample 1 and to 713 K for sample 2. As in the earlier cases, two shoulders are seen, suggesting the complexity of the oxidative reactions. At about 20 mg sample mass, the third exotherm at around 834 K is completely absent for sample 2, and the intensity of the second exotherm at a peak temperature of 747 K is considerably enhanced. The reaction takes place with a visible flame and gas emission. At higher mass (25.1 mg), much yellow smoke is liberated, accompanied by a flash and sound at 733 K. Similarly, in the case of sample 3, only one prominent exotherm is visible at a mass of 21.8 mg. A slow exothermic base line shift commences at 643 K, leading to a peak at 729 K. Dense fumes and a flame could be seen, accompanied by the report of a sound. Samples 4 and 5 also behave similarly, though the critical mass above which the reaction attains ignition conditions is lowered to about 16 mg. No endotherm due to the melting of $KClO_4$ was noted in any of the thermal curves.

We reported earlier [8] that a critical mass exists in the red lead–silicon system, which varied with the composition. The addition of iron(III) oxide invariably increased the critical mass. The addition of the reactive oxidant $KClO_4$ brings down the critical mass. Additionally, the reaction temperatures in the present system are markedly lower than the corresponding ones in the red lead–silicon system, which were 833, 913 and 1013 K. Secondly, a slow exothermic reaction starts at much lower temperature, in the form of a base line shift from 643 K. With a more reactive metal, e.g. Fe, such a reaction is reported to start at as low a temperature as 593 K [1]. That the lowering of the reaction temperature is mainly due to $KClO_4$ and not atmospheric oxygen is confirmed by the results of DSC carried out in nitrogen atmosphere.

DSC in nitrogen

DSC records in nitrogen atmosphere for all five samples are shown in Fig. 4. The complexity of the patterns indicates at least five different oxidative reactions in the following temperatures ranges (K): (i) 734–770, (ii) 799–806, (iii) 810–811, (iv) 820–829 and (v) 853–861.

These temperatures are certainly higher than the corresponding DTA temperatures at constant heating rate, but still much lower than those for the binary red

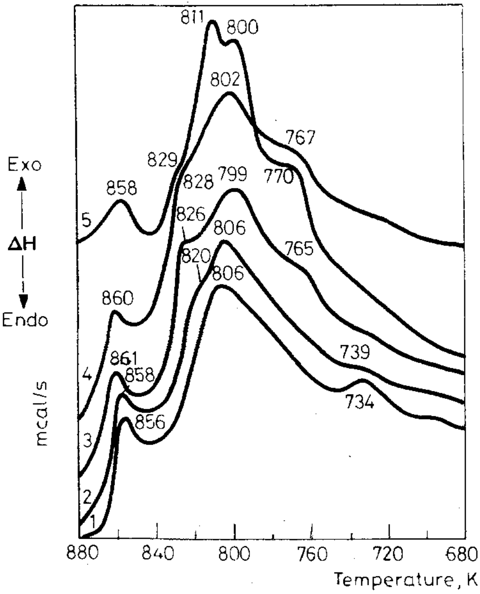

Fig. 4 DSC of red lead/silicon/$KClO_4$ in N_2 under non-ignition conditions. (The nos 1 to 5 relate to the same as those in Fig. 2)

lead–silicon system. This implies that, besides $KClO_4$, atmospheric oxygen also plays a certain role in the oxidation of silicon. This role, however, is possible only in the presence of $KClO_4$, as our earlier results [8] show that the temperatures recorded in the DTA in air and DSC in nitrogen are practically identical.

A unique characteristic of the decomposition of $KClO_4$ is that decomposition in the solid state is accompanied by the melting of $KClO_4$ much below the normal melting point. The surface mobility of the ions consequently gains increased importance in the reactivity of $KClO_4$ with fuels. The DTA studies presented in the earlier part of this paper showed the complexity of the decomposition of even pure $KClO_4$. $KClO_4$ decomposes by a series of decompositions and disproportionations:

$$KClO_4 \rightleftharpoons KClO_3 + \frac{1}{2}O_2$$

$$KClO_3 \rightleftharpoons KCl + \frac{3}{2}O_2$$

$$KClO_3 \rightleftharpoons \frac{3}{4}KClO_4 + \frac{1}{4}KCl$$

with instantaneous disproportionation of the transient chlorite:

$$KClO_3 \rightleftharpoons KClO_2 + \frac{1}{2}O_2$$

$$KClO_2 \rightleftharpoons \frac{2}{3}KClO_3 + \frac{1}{3}KCl$$

With all these reactions yielding either $KClO_3$ or gaseous oygen, it is reasonable to assume that gas-phase mass transport of oxygen plays the most crucial role in the oxidation of silicon. Further, the melting of $KClO_4$ associated with its decomposition will have the effect of spreading the molten phase over the fuel particles, where autocatalytic oxidation takes place. This phenomenon is expected to be the main cause of the behaviour observed in $KClO_4$-rich formulations. The oxidation rate is primarily determined by the rate of mass transfer between $KClO_4$ and Si through the silica layer which accumulates on the particle contact surface. The compositions in general are oxygen-deficient, and thus the inner cores of the fuel particles should remain unaffected. The large exotherms should therefore be ascribed to the rapid decomposition of $KClO_4$ relative to the mass transfer rate.

One question which arises relates to the possibility of the formation of lead perchlorate, which, being highly reactive, could accelerate the oxidation process. DSC curves of the binary system of red lead and $KClO_4$ were recorded in nitrogen

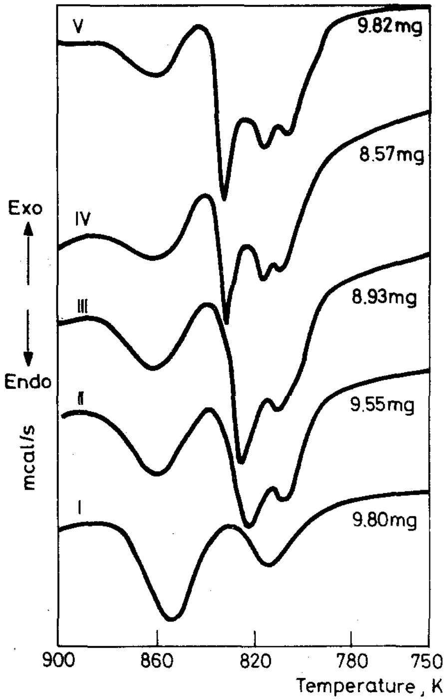

Fig. 5 DSC of the binary system red lead/$KClO_4$ in N_2 as a function of $KClO_4$ content. (The nos 1 to 5 represent increasing proportions of $KClO_4$)

atmosphere. Five binary mixtures were scanned by DSC. The DSC plots are given in Fig. 5. The composition with the minimum proportion of $KClO_4$ shows only two endotherms, with peak temperatures of 816 and 855 K. The former is asymmetric in shape. As the proportion of $KClO_4$ increases, the 816 K peak splits into two or three peaks centered around 812 and 827 K. The apparent fine structure observed in the DSC curves of ternary compositions with high proportions of $KClO_4$ should be attributed to the endotherms at 812 and 827 K, as these also occur at the same temperatures. The endotherm with its inception at around 840 K also lends itself to a similar interpretation when extended to the ternary system. The complete characterization of the binary system will be discussed separately.

However, one obvious conclusion which can be drawn from the above results is that the overall enthalpy change of the ternary reaction system should tend towards lower exothermicity as the proportion of $KClO_4$ increases beyond a certain value in the mixture. The measured values of heat change for the five mixtures are 1037, 1902, 2040, 1969 and 1634 Jg^{-1}, respectively, confirming the earlier deduction.

One question still remains as to why the pyrotechnic reactions of red lead–silicon, red lead–silicon–Fe_2O_3, Mg–BaO and red lead–silicon–$KClO_4$ attain combustion conditions above a critical mass. The answer probably lies in the fact that, in any thermal explosion, conditions which favour a rise in temperature due to a perturbation in the steady-state energy conservation equation should lead to ignition. As the rate of energy release due to reactant consumption coupled with an increase in ambient temperature (as exists in dynamic thermal analysis measurements) leads to just such a perturbation, thermal ignition should be a distinct feature above a critical mass, as observed in all the reactions mentioned above. It is relevant to recall Boddington [12], who stated that "The interrelationships which exist between combustion kinetics, heat transfer and burning velocity are complex, and simple cause and effect explanations are seldom tenable". A detailed mathematical analysis of such systems is in progress.

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Zusammenfassung — Mitsels DTA- und DSC-Methoden wurde der Beschleunigungseffekt von Kaliumperchlorat auf die Reaktivität des Systemes Mennige-Silizium untersucht. Ergänzende Untersuchungen an reinem Kaliumperchlorat und am binären System Mennige-Kaliumperchlorat lassen darauf schliessen, dass die komplexe Zersetzungskinetik des Kaliumperchlorates die Oxidation des Siliziums erheblich beeinflusst. Weiterhin kann im Deeikomponentensystem bei einem bestimmten kritischen Massenwert ein Übergang von einer leicht exothermen Zersetzung bis zur Entzündung stattfinden, wie dies im System Mennige-Silizium-Eisen(III)oxid beobachtet wird. Wie von Gray vorasugesetzt, sei die Kritikalität ein Ergebnis der Temperaturerhöhung, einer Veränderung der Bedingungen zur Erhaltung des stationären Energiezustandes.

Резюме — Методами ДТА и ДСК изучено ускоряющее действие перхлората калия на реакционную способность системы красный свинец–кремний. Дополнительные исследования, проведенные с чистым перхлоратом калия и двойной системой красный свинец–перхлорат калия, показали, что сложная кинетика разложения перхлората калия в значительной мере затрагивает окисление кремния. Кроме того, тройная система красный свинец–кремний–окись трехвалентного железа также подвергается переходу от плавного экзотермического разложения к взрыву при определенной критической массе. Критичным должен быть результат повышения температуры, выраженный как возмущение установившихся условий сохранения энергии.