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

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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 (KClO₄). 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 KClO₄, 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 KClO₄, 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 KClO₄ 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
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 decelerator, viz. Fe$_2$O$_3$. The overall reaction kinetics did not seem to change with the introduction of Fe$_2$O$_3$. 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.

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