Thermochimica Acta, 13 (1975) 293–304

THERMAL DECOMPOSITION OF ALKALI METAL PERCHLORATES

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(Received 18 June 1975)

ABSTRACT

The effect of past mechanical history on the subsequent thermal decomposition kinetics of sodium, potassium, rubidium and caesium perchlorates, has been investigated. At low temperatures the decomposition of all these salts is significantly sensitized by pre-compression. At high temperatures, however, prior compression results in a lowered decomposition rate in the case of potassium, rubidium and caesium perchlorates and in an increase in the thermal reactivity of sodium perchlorate. The high temperature behaviour is shown to be an indirect consequence of the low temperature behaviour. The difference in behaviour between sodium perchlorate and the other alkali metal perchlorates is explained on the basis of the stability of the respective chlorates, formed during the low temperature decomposition. This is substantiated by experiments which show that the addition of sodium chlorate to sodium perchlorate brings about a sensitization while potassium perchlorate admixed with potassium chlorate results in a desensitization at high temperatures.

INTRODUCTION

The thermal decomposition of alkali metal perchlorates has been studied by a number of investigators in recent years[1–12]. The general picture about the stability of these materials, about the role of structural and physical properties in determining the stability and the possible mechanism of the decomposition, has been investigated in detail. Solymosi[2] has reported that the decomposition of alkali perchlorates takes place at high temperatures and with the exception of lithium perchlorate, the decompositions occur in a relatively narrow temperature range (500–575 °C). The decompositions have been found to be autocatalytic and proceed concomittantly with melting of the perchlorates probably due to the chlorides forming a eutectic with the undecomposed materials. The decompositions are believed to consist of the following steps:

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$$MClO_4 \overset{k_1}{\rightleftarrows} MClO_3 + \tfrac{1}{2}O_2 \qquad (1)$$

$$MClO_3 \overset{k_2}{\rightleftarrows} MCl + \tfrac{3}{2}O_2 \qquad (2)$$

(M = Na, K, Rb and Cs)

the rate determining step being reaction (1).

An examination of the literature shows a wide variation in the reported values of the activation energies and pre-exponential factors for the decomposition of these materials. Most of the investigators report chloride and oxygen as the major decomposition products. Significantly enough, Cordes and Smith[4] report alkali chlorate as a major decomposition product. Some of the variations in the kinetic data are undoubtedly due to the differences in the age, particle size, method of preparation and previous mechanical and thermal history of the materials. A systematic investigation has therefore been undertaken with a view to establish the role of these factors in the control of the decomposition rates of these materials. This paper reports results of the effect of the mechanical history on the decomposition kinetics of sodium, potassium, rubidium and caesium perchlorates. The effect of age, method of preparation, prior thermal treatment and particle size, will be published in subsequent papers.

EXPERIMENTAL

Potassium perchlorate (Laboratory Chemicals, India, AR grade) was recrystallized twice from hot distilled water. Rubidium and caesium perchlorates were prepared from the corresponding carbonates (BDH, AR grade). The materials were recrystallized twice from hot distilled water. Sodium perchlorate (Fluka, Switzerland, AR grade) was used as received. All the materials studied were polycrystalline and the materials in all the cases, were stored in powder form over phosphorus pentoxide. All comparative runs were done on materials of the same particle size (149–177 μ) and age.

Compression of the materials was effected uniaxially on a hydraulic pellet press using a stainless-steel die for holding the materials. After compression, the material was crushed in a mortar (avoiding circular motion of the pestle) and then sieved to the same particle size as the uncompressed material.

Differential thermal analysis (DTA) was carried out on an apparatus similar to that described by Savant and Patel[13]. The DTA assembly was housed in a tubular quartz furnace which was programmed to a constant heating rate of 10°C min^{-1}. The temperature were measured on a calibrated chromel–alumel thermocouple connected in series with the block thermocouple and immersed in an ice–water mixture so as to maintain 0°C as the reference temperature. Ignited powdered alumina was used as the reference material. Thermogravimetric analysis (TG) was carried out on a conventional McBain-Baer type quartz-spring balance[14]. The sample was heated in a quartz furnace whose temperature could be controlled to ±1 °C of the required temperature. A convenient sample size for decomposition studies was found to be fifty milligrams.

Ageing studies were carried out on samples kept in sealed tubes maintained at appropriate storage temperature.

RESULTS

Figure 1 (A, B, C and D) shows the DTA traces of sodium, potassium, rubidium and caesium perchlorates compared with those of the materials subjected to prior uniaxial compression. The DTA traces of the pre-compressed samples show an enhanced decomposition at low temperatures prior to fusion.

The isothermal decomposition of potassium perchlorate and that of the material pre-compressed at 300 kg cm^{-2} was studied in the temperature range 500–600°C. The α–t curves were found to be of the sigmoid type with a short time-lag in

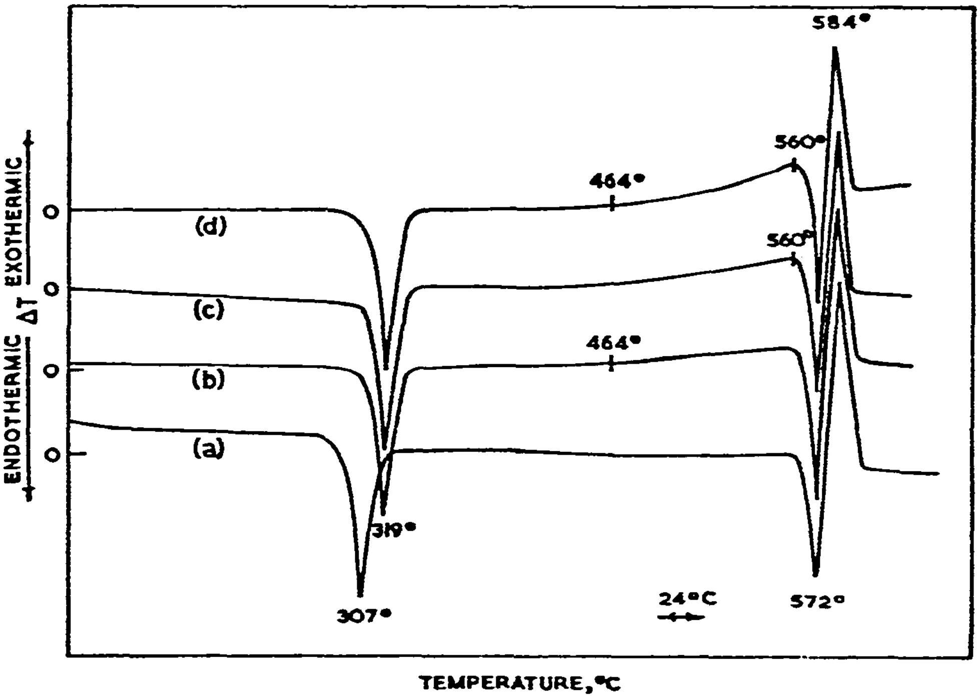

Fig. 1.(A). DTA in air of potassium perchlorate compared with that of the same material pre-compressed at different pelletting pressures. (a) Uncompressed material; (b) material pre-compressed at 100 kg cm^{-2}; (c) material pre-compressed at 200 kg cm^{-2}; (d) material pre-compressed at 300 kg cm^{-2}. (B). DTA in air of rubidium perchlorate (a); compared with that of the material pre-compressed at 300 kg cm^{-2} (b). (C). DTA in air of caesium perchlorate (a); compared with that of the material pre-compressed at 300 kg cm^{-2} (b). (D). DTA in air of sodium perchlorate compared with that of the material pre-compressed at different pelletting pressures (a) Uncompressed material; (b) material pre-compressed at 100 kg cm^{-2}; (c) material pre-compressed at 200 kg cm^{-2}; (d) material pre-compressed at 300 kg cm^{-2}.

the initial stages of the decomposition. The data were fitted to the Prout-Tompkin's equation[15]:

$$\log_e\left(\frac{\alpha}{1-\alpha}\right) = kt+C \qquad (3)$$

Two straight lines were obtained in the plot of $\log_e(\alpha/1-\alpha)$ versus time—one for the acceleratory portion of the decomposition and one for the deceleratory portion. The rate constants in the two regions (k_a and k_d) for the uncompressed and pre-compressed materials are listed in Table 1. The activation energies were found to be unaltered on pre-compression and were 60 kcal mol^{-1} both for the acceleratory and the deceleratory portions of the decomposition. The activation energies were also calculated from the plots of $\log_e t_{\frac{1}{2}}$ ($t_{\frac{1}{2}}$ is the half-time for the decomposition) against the

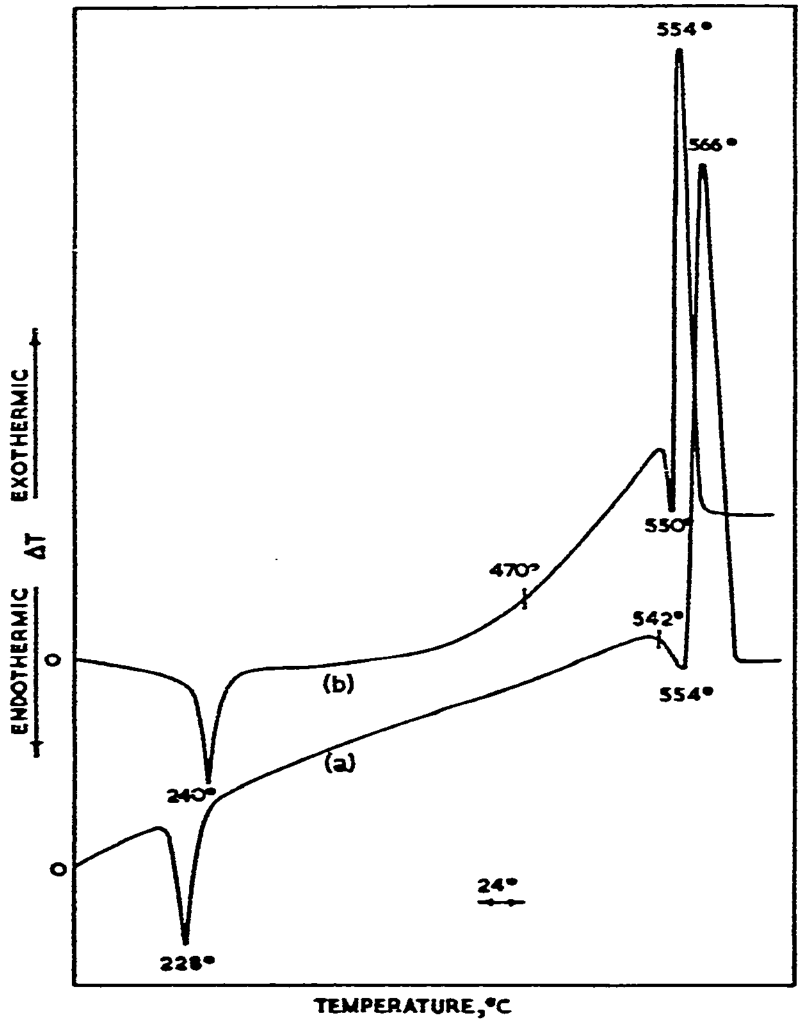

Fig. 1 (B).

TABLE 1

KINETIC DATA ON THE ISOTHERMAL DECOMPOSITION OF POTASSIUM PERCHLORATE PRECOMPRESSED AT 300 kg cm^{-2}

Temp. (°C)	*Half-times (min)*		*Rate constants*			
			10^2 K_a min^{-1}		*10^2 K_d min^{-1}*	
	KP[a] 0	*KP 300*	*KP 0*	*KP 300*	*KP 0*	*KP 300*
524	14	19	9.30	6.00	2.10	0.96
536	9	12	12.00	10.70	3.60	1.70
550	5	7	24.00	17.30	6.00	2.80
572	2	3	60.00	42.00	15.00	7.50

[a] KP stands for potassium perchlorate and the number signifies the pressure in kg cm^{-2} at which the samples were pre-compressed.

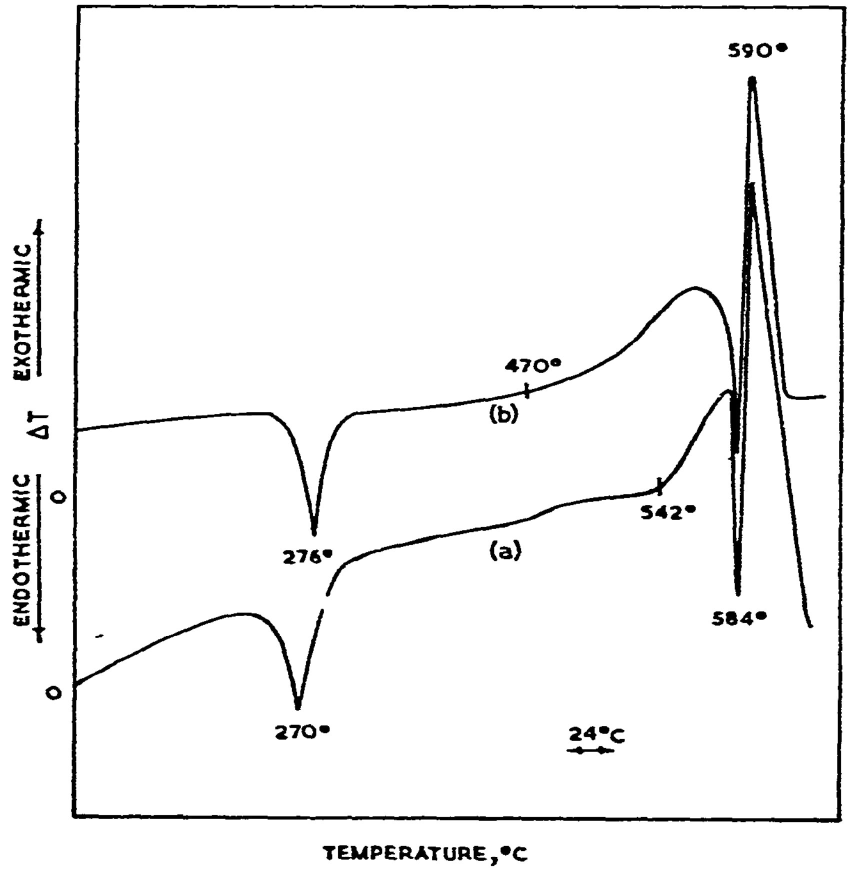

Fig 1 (C).

reciprocal of the absolute temperature and were found to be 54 kcal mol^{-1} both for the uncompressed and the precompressed materials. An examination of Table 1 shows, surprisingly enough, a lower decomposition rate for the pre-compressed material. Similar isothermal studies on rubidium and caesium perchlorates at temperatures above 500°C also reveal a lowered decomposition rate in the case of the pre-compressed materials.

Figure 2 shows the results of the isothermal decomposition at 540°C of sodium perchlorate and of the material pre-compressed at different pelletting pressures. The α–t curves were found to give a good fit of the Prout-Tompkins equation. The rate constants and the half-times for the decomposition of the different samples are shown in Table 2. The data reveal an increase in the decomposition rate for the materials subjected to prior compression. The decomposition of the materials was studied at different temperatures and the Arrhenius plots for the uncompressed and pre-compressed materials were compared (Fig. 3). The activation energies were found to remain unaltered at 45 kcal mol^{-1} for the acceleratory region and 55 kcal mol^{-1} for the deceleratory portion of the decomposition. The activation energies were also

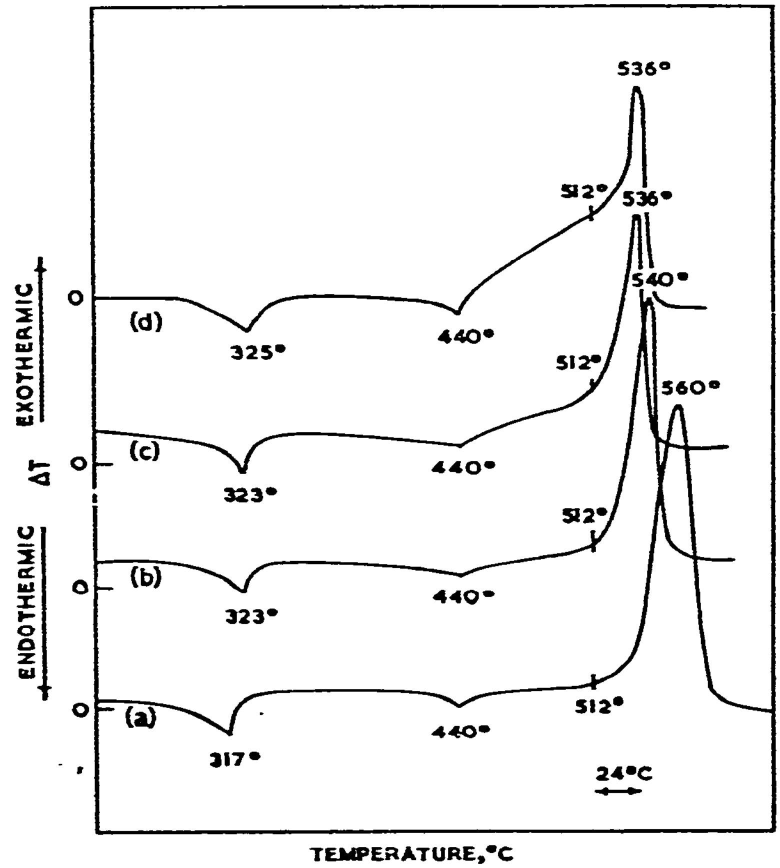

Fig. 1 (D).

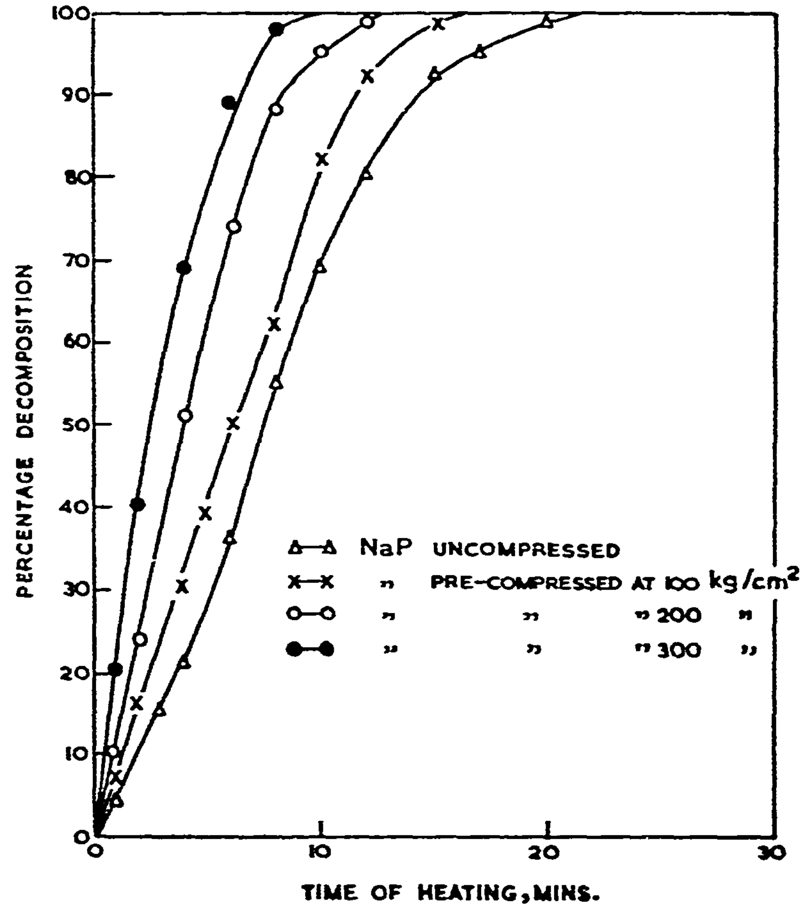

Fig. 2. Isothermal decomposition (540 °C) in air of sodium perchlorate and of sodium perchlorate pre-compressed at different pressures.

TABLE 2

EFFECT OF PRE-COMPRESSION ON THE ISOTHERMAL DECOMPOSITION OF SODIUM PERCHLORATE (NaP) AT 540 °C

Material	*Half-times (min)*	*Rate constants* ($\times 10$ *min*$^{-1}$)	
		K_a	K_d
NaP 0[a]	8	1.78	1.40
NaP 100	6	2.80	1.75
NaP 200	4	3.20	2.20
NaP 300	2.7	3.50	3.00

[a] The number signifies the pressure in kg cm^{-2} at which the sample was pre-compressed.

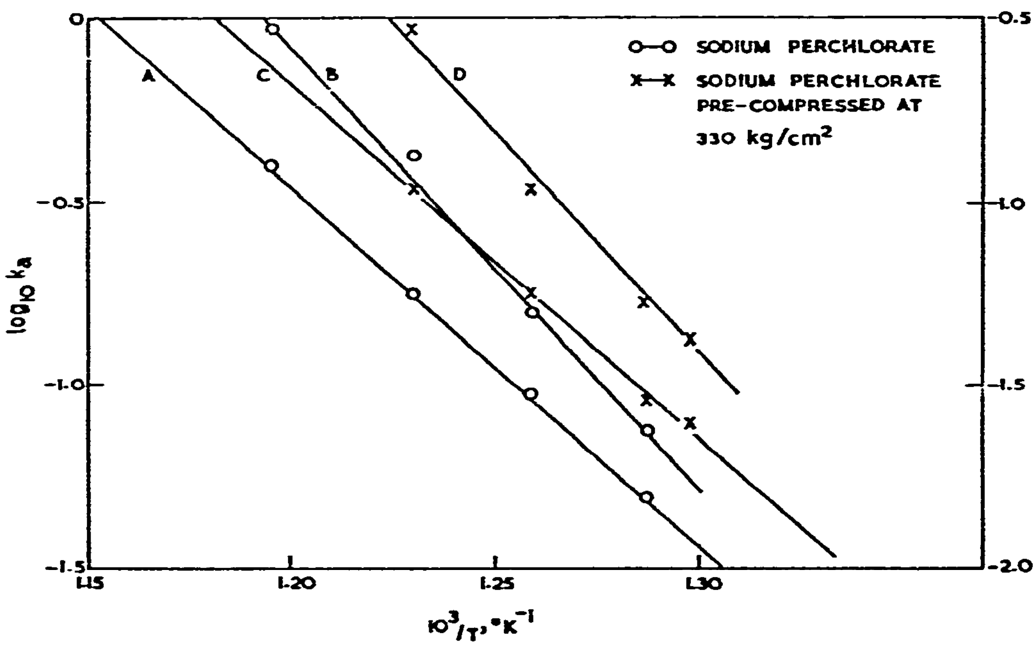

Fig. 3. Arrhenius plots of (A) sodium perchlorate (NaP) (acceleratory region); (B) NaP (deceleratory region); (C) NaP pre-compressed at 300 kg cm^{-2} (acceleratory region); and (D) NaP pre-compressed at 300 kg cm^{-2} (deceleratory region).

calculated by plotting $\log_e t_{\frac{1}{2}}$ against the reciprocal of the absolute temperature. They were found to be 58 kcal mol^{-1} both for the uncompressed and the pre-compressed samples.

The time dependence of the pre-compression effect was studied for potassium perchlorate by carrying out the isothermal decomposition of the pre-compressed material at various intervals of days after the pre-compression treatment. The results are shown in Fig. 4. A gradual decrease in the thermal reactivity is evident with storage of the pre-compressed material. After twelve days, however, there is an increase in the decomposition rate with age. Figure 5 shows the effect of the storage temperature on the thermal reactivity of potassium perchlorate subjected to prior compression. An increase in the rate and the extent of ageing with an increase in the storage temperature is evident.

DISCUSSION

The results of the present investigation show that the decomposition rates of alkali metal perchlorates are sensitive to the preceding mechanical history of the materials. Prior compression results in a lowered decomposition rate in the case of potassium, rubidium, caesium perchlorates and an increase in the thermal reactivity of sodium perchlorate at temperatures above 500°C. The DTA results at the same time show an enhanced decomposition at temperatures below the fusion points for all the materials studied. Studies on the isothermal decomposition of these materials at low temperatures (below the fusion points) will be reported elsewhere[16]. Thermal analysis data in conjunction with infrared spectra and X-ray diffraction employed in these studies[16] indicate the important role played by crystal defects in controlling the decomposition rates of these materials at low temperatures. Thus the enhancement in the decomposition rates at low temperatures observed in the DTA traces of the materials subjected to prioı compression, can be attributed to the additional defects introduced in them as a result of the prior treatment[16]. The behaviour of these materials at high temperatures may be an indirect consequence of the low temperature decomposition which in turn is influenced by pre-compression.

The data on sodium perchlorate reveal a marked increase in the decomposition rate as a result of prior mechanical treatment throughout the temperature range investigated. The desensitization of the decomposition observed at high temperatures in the case of the other alkali perchlorates is absent here. This anomalous behaviour

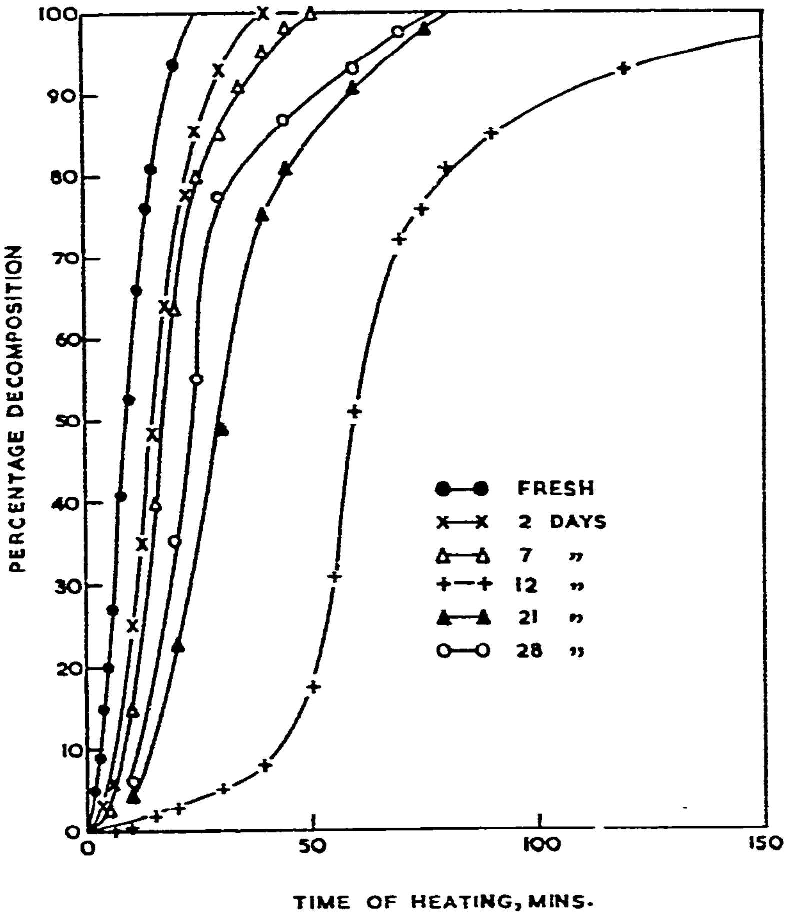

Fig. 4. Effect of storage time on the isothermal decomposition (536 °C) of potassium perchlorate pre-compressed at 300 kg cm^{-2}.

can probably be explained by comparing the relative stabilities of the alkali chlorates formed in the course of the decomposition. The increased amount of the highly unstable sodium chlorate in the pre-compressed material as a result of its low temperature decomposition probably forms sodium chloride which in turn, accelerates the subsequent high temperature decomposition. In the case of potassium, rubidium and caesium perchlorates, the relative tendency for the respective chlorate to form the corresponding chlorides is much less[17]. Thus potassium perchlorate to which a small amount of potassium chlorate is added, decomposes at a lower rate whereas sodium perchlorate containing sodium chlorate shows an enhancement in the decomposition rate (Fig. 6).

The effect of prior compression on the thermal reactivity of these materials, shows a complex dependence on the time of storage of the material and suggests that diffusion and recrystallization processes in the pre-compressed materials on storage may be important factors. The dependence of the pre-compression effect on the storage temperature can possibly be attributed to the temperature dependence of these processes on the subsequent decomposition kinetics.

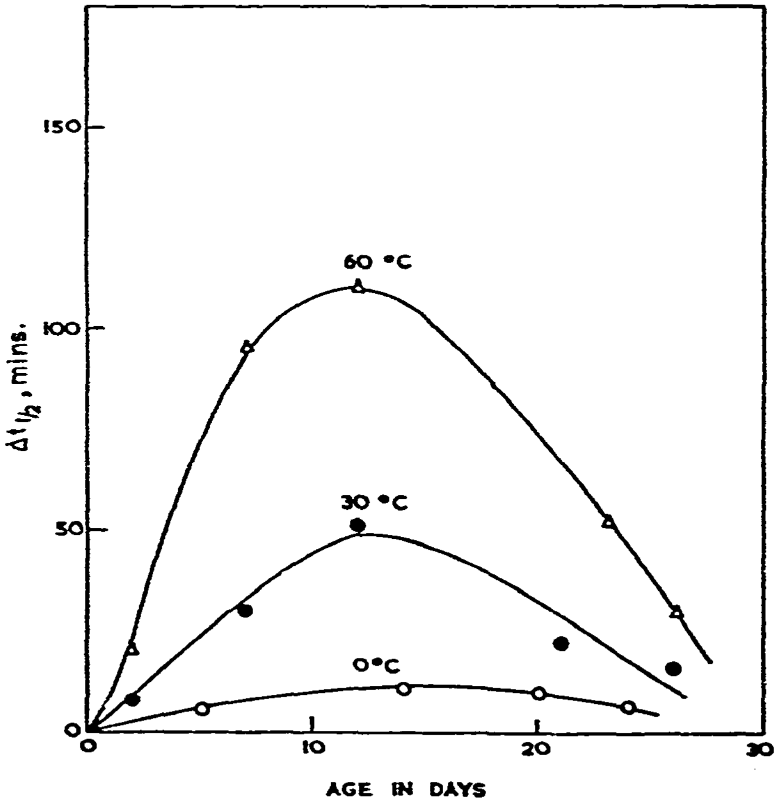

Fig. 5. Effect of storage temperature on the thermal reactivity of potassium perchlorate pre-compressed at 300 kg cm^{-2}.

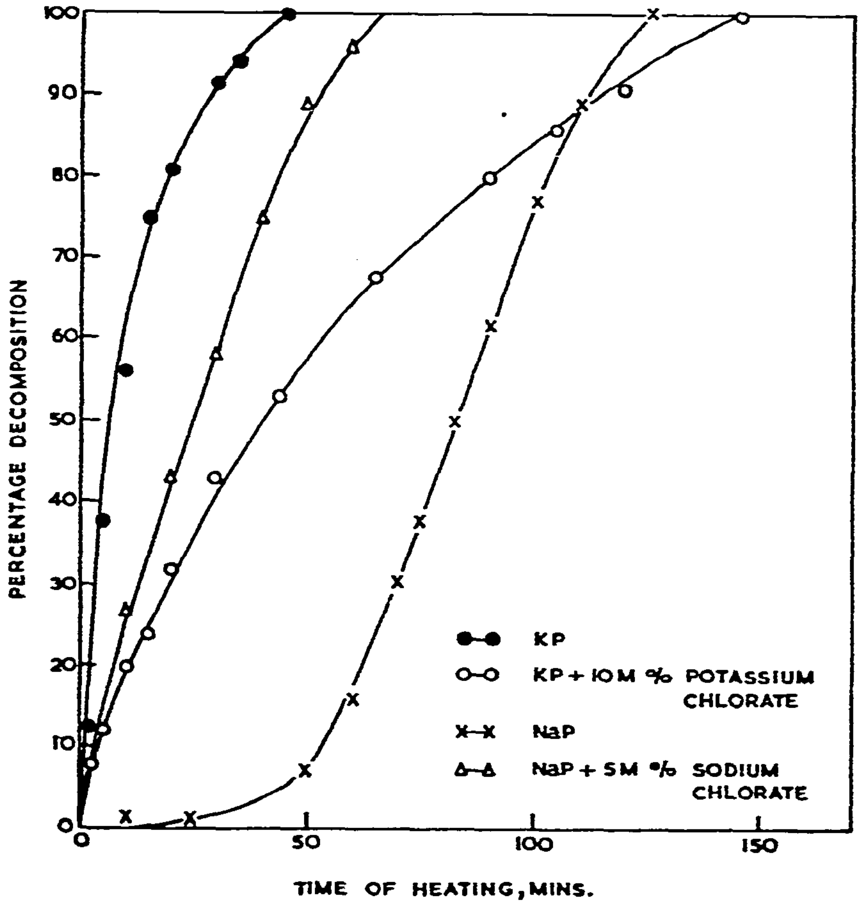

Fig. 6. Isothermal decomposition in air (536°C) of sodium perchlorate (NaP) and of potassium perchlorate (KP) compared with that of the same materials admixed with the corresponding chlorates.

REFERENCES

1 M. M. Markowitz, *J. Phys. Chem.*, 62 (1958) 827; 61 (1957) 505; *J. Inorg. Nucl. Chem.*, 25 (1963) 407.
2 F. Solymosi, *Acta Chim. Akad Sci. Hung. Tom.*, 57 (1968) 11.
3 M. M. Markowitz, and D. A. Boryta, *J. Phys. Chem.*, 64 (1960) 1711; 65 (1961) 1419; 69 (1965) 1114.
4 H. Cordes and R. Smith, *J. Phys. Chem.*, 72 (1968) 2189.
5 J. Cabane' and J. Benard, *Bull. Soc. Chim.* (*France*), 3 (1961) 36.
6 K. G. Il'in and B. I. Khorunzhii, *Zh. Fiz. Khim.*, 46 (1972) 1457.
7 A. Glasner and L. Weidenfeld, *J. Am. Chem. Soc.*, 74 (1952) 2467.
8 A. E. Harvey, M. T. Edmison, E. O. Jones, R. A. Seybert and K. A. Catto, *J. Am. Chem. Soc.*, 76 (1954) 3270.
9 T. A. Rogers and A. Wassinck, *Final Summary Report*, University of Arkansas, No. DA 23-072-ORD (1958).
10 A. E. Simchen, *J. Phys. Chem.*, 65 (1961) 1092.
11 A. Glasner and A. E. Simchen, *Bull. Soc. Chim.* (*France*), (1951) 273.
12 L. L. Bircumshaw and R. T. Phillips, *J. Chem. Soc.*, (1953) 703.
13 V. V. Savant and C. C. Patel, *Ind. J. Technol.*, 6 (1968) 231.
14 J. W. McBain and A. M. Baer, *J. Am. Chem. Soc.*, 48 (1926) 600.

15 P. W. M. Jacobs and F. C. Tompkins, in W. E. Garner (Ed.), *Chemistry of the Solid State*, Butterworths, London, 1955, Ch. 7.
16 V. R. Pai Verneker and K. Rajeshwar, *J. Phys. Chem. Solids*, 1 (1975) 1107.
17 M. M. Markowitz, D. A. Bortyta and H. J. Stewart, Jr., *J. Phys. Chem.* 68 (1964) 2282.