the values of λ obtained from these curves, and their relation to the potential and k_f.

TABLE I

VALUES OF λ AND k_f AS A FUNCTION OF POTENTIAL FOR THE REDUCTION OF IODATE (FIG. 1)

Curve	Potential (v. *vs.* S.C.E.)	λ	($k_f \times 10^4$)
A	−0.850	12.5	18.7
B	− .800	7.4	11.1
C	− .750	4.5	6.75
D	− .700	2.9	4.35
E	− .650	1.7	2.55
F	− .600	1.0	1.50
G	− .550	0.65	0.975

The slope of the plot of log k_f *vs.* E gave a value of 0.26 for αn_a, the same as obtained previously using voltammetry with linearly varying potential.[11]

These results indicate that the potentiostatic method should be very useful for characterizing slow electrode reactions using the hanging mercury drop electrode.

Experimental

The electrodes, cell assembly and potentiostat were the same as described previously.[6] The hanging mercury drop electrode was formed by collecting two drops from the capillary; the radius of the electrode was 0.0674 cm.

Materials were reagent grade and were used without further purification. Linde high purity nitrogen was used to remove oxygen from the cell. All experiments were carried out in a thermostat maintained at 25.0°.

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THE DIFFERENTIAL THERMAL ANALYSIS OF PERCHLORATES. V. THE SYSTEM $LiClO_4$-$KClO_4$

BY MEYER M. MARKOWITZ, DANIEL A. BORYTA AND ROBERT F. HARRIS

Foote Mineral Company, Research and Development Laboratories, Chemicals Division, P. O. Box 513, West Chester, Pa.

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The system $LiClO_4$-$KClO_4$ was determined to be of the simple eutectic type with the eutectic at 207° and 76.0 mole % $LiClO_4$. Some aspects of the thermal decompositions of the alkali metal perchlorates and of various alkali metal perchlorate mixtures were investigated by differential thermal analysis and by thermogravimetric analysis. These results are discussed from the points of view of polarization and of liquid phase formation effects.

Introduction

The previous phase investigations of binary systems involving lithium perchlorate as a component[1,2] have now been extended to include the anhydrous system $LiClO_4$-$KClO_4$. Some insight into the factors influencing the thermal decompositions of perchlorates was gained by differential thermal analyses (DTA) and by thermogravimetric analyses (TGA) carried out at higher temperatures. Thus, DTA and TGA data derived from the pure alkali metal perchlorates and from the salt pairs $LiClO_4$-$KClO_4$, $LiClO_4$-$NaClO_4$, $NaClO_4$-$KClO_4$ and $LiClO_4$-$LiCl$ have been interpreted to indicate two difficultly resolvable effects in the decomposition processes. One effect refers to the polarizing power of the cation atmosphere associated with the perchlorate group; the other effect deals with the relative ease of formation of a perchlorate-containing liquid phase.

Experimental

Equipment and Procedures.—The DTA instrumentation has been described earlier.[1] For the low temperature studies (up to 350°), a vertical crucible furnace-steel heating block arrangement was used.[3] A closed muffle furnace was adopted for all high temperature thermal decomposition investigations (up to 850°) in order to minimize objectionable heat transients during turbulent gas evolution reactions.[4,5]

The recording thermobalance developed for TGA was of the null deflection type with a linear variable differential transformer sensor and an electromagnetic coil restoring assembly[5] ("Recording Balance Accessory," Fisher Scientific Co., 717 Forbes St., Pittsburgh, Penna., catalog no. 13-940-190) attached to an analytical balance. A platinum wire fixed to one end of the balance beam passed into a muffle furnace some distance below the balance case; a circular platinum ring at the bottom of the wire held the sample crucible. The modulated signal from the control unit and a constant fraction of the e.m.f. from a Chromel-Alumel thermocouple placed directly beneath the sample crucible were passed alternately through a stepping switch ("Auto-Step Switch," Fisher Scientific Co., catalog no. 13-940-180) and then to a potentiometric recorder. In this manner, weight change and furnace temperature were recorded on the same time basis.

The numerical values of decomposition temperatures determined by DTA are not necessarily coincident with those obtained by TGA. This is due to the differences in sensitivities between the two techniques and to the fact that in DTA the actual sample temperature is measured whereas in TGA, it is the furnace temperature which is recorded. Nevertheless, trends in temperature-dependent behavior can be followed by consistent use of either technique.

All DTA and TGA runs were carried out at a constant heating rate of 10° per minute. This was achieved by use

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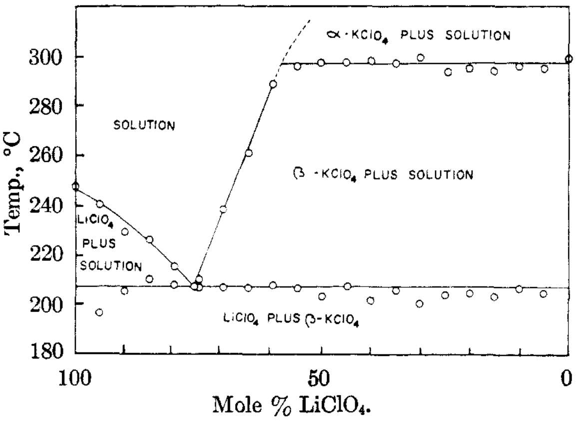

Fig. 1.—The system $LiClO_4$–$KClO_4$.

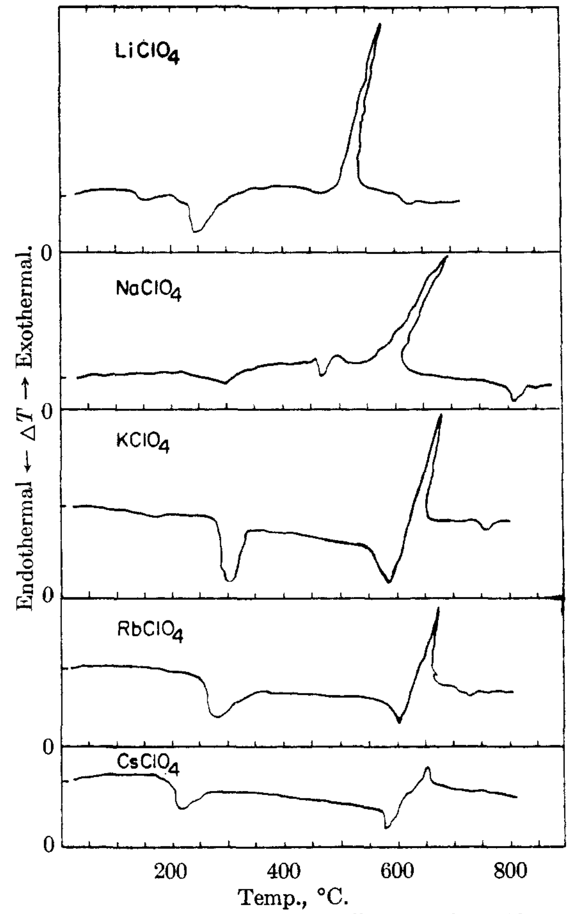

Fig. 2.—The DTA patterns of the alkali metal perchlorates.

of a motorized variable transformer to control the current to the furnace heating elements.[6]

Anhydrous lithium perchlorate, prepared as previously reported,[1] was analyzed by precipitation as nitron perchlorate. Analysis of product: ClO_4^-, 93.8 (calcd., 93.5). Reagent grade potassium and sodium perchlorates, dried under vacuum at 120° for 12 hours, were analyzed in a similar manner. Analyses of products: $KClO_4$:ClO_4^-, 71.7 (calcd., 71.9); $NaClO_4$:ClO_4^-, 81.4 (calcd. 81.2). Rubidium and cesium perchlorates were prepared by reaction of the C.P. carbonate and chloride salts, respectively, with dilute perchloric acid. The precipitated perchlorates, after drying at 120°, were analyzed by conversion to the chlorides through fusion with sodium carbonate in a platinum crucible. Analyses of products: $RbClO_4$:Cl, 18.93 (calcd., 19.18); $CsClO_4$:Cl, 14.87 (calcd., 15.27). Reagent grade lithium chloride was dried under vacuum at 150° for 12 hours. Analysis of product: Cl, 83.2 (calcd., 83.6).

The System $LiClO_4$-$KClO_4$.—Anhydrous lithium perchlorate when heated to about 350° showed but one DTA break, an endotherm corresponding to fusion at 247°. If a small amount of water is present an additional endotherm is introduced at about 150° due to dissociation of the monohydrate[1,7] (Fig. 2, $LiClO_4$). However, cycling of the sample under DTA conditions in a dry atmosphere eliminates this break by driving off the water. Potassium perchlorate evidenced a break at about 300° attributed to a reversible crystallographic transition[8] (Fig. 2, $KClO_4$).

Mixtures of the component salts (5 g.) were prepared and repeatedly subjected to DTA. Each liquidus temperature was determined by visual observation of a sample contained in a test-tube immersed in an oil-bath serviceable to about 275°. Subsequent TGA studies showed that the samples were all thermally stable at the temperatures and time durations encountered in this phase investigation. The persistence of the single eutectic break and of the break for the crystallographic transition of potassium perchlorate (samples containing 40–100 mole % $KClO_4$) indicate no complex interaction between the components. Accordingly, a plot of the data, given as Fig. 1, shows the system to be of the simple eutectic type with the eutectic occurring at 207° and 76.0 mole % $LiClO_4$.

The Thermal Decompositions of Perchlorate Salt Mixtures.—The mixtures (1 g.) of Table I were brought to constant weight during TGA runs carried out to 600–700°. The total weight losses indicated by the thermobalance generally checked to within several milligrams with the weight losses determined by manual weighing of the sample. For each mixture the total weight loss corresponded closely to the conversion of the perchlorate to the respective chloride and oxygen gas.[9] Similar TGA results were found for the decompositions of pure rubidium and cesium perchlorates in the present study.

The temperatures reported in Table I are those corresponding to the occurrence of 10% of decomposition. This criterion avoids misinterpreting slight weight losses due to volatile impurities as decomposition of the salts.

Table I

10% Thermal Decomposition Temperatures of Salt Mixtures

Compn., mole % salt A	Temp., °C.			
	(A)$LiClO_4$–$KClO_4$	(A)$LiClO_4$–$NaClO_4$	(A)$LiClO_4$–LiCl	(A)$NaClO_4$–$KClO_4$
100.0	485	485	485	576
90.0	494	495	454	580
80.0	496	492	446	580
70.0	500	499	433	587
60.0	504	505	434	585
50.0	512	511	433	589
40.0	516	519	435	589
30.0	527	526	438	596
20.0	530	533	438	598
10.0	543	549	435	604
0.0	634	576	..	635

Inspection of Table I shows that a mixture of any two component perchlorates decomposes at a lower temperature than that of the more stable salt, but never at a temperature lower than that of the less stable component. The decomposition temperature of lithium perchlorate is lowered by the presence of lithium chloride but attains a fairly constant value for mixtures containing 20 mole % and more of lithium chloride. For the pure alkali metal perchlorates, the 10% decomposition temperatures are in the order Li—485°, Na—576°, Cs—628°, K—635°, and Rb—640°.

The DTA Patterns of the Alkali Metal Perchlorates.—The thermograms of the alkali metal perchlorates were

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redetermined using the closed muffle furnace.[4,5] This was necessitated because of the spurious thermal effects present in earlier studies.[1,3] Recession of the sample from the thermocouple and consequent interaction with the cool, ambient atmosphere gives rise to extraneous endothermal breaks when DTA experiments involving turbulent condensed phase-gas evolution reactions are carried out in the open air. The newly-obtained curves are given in Fig. 2 and the pertinent data are summarized in Table II. Five gram samples were used.

TABLE II

THERMAL BEHAVIOR OF THE ALKALI METAL PERCHLORATES FROM DTA CURVES

Sample	Crystal transition, °C.	Fusion of $MClO_4$, °C., T_f	Onset of rapid decompn., °C., T_d	$T_d - T_f$, °C.	Fusion of MCl, °C.
$LiClO_4$	[a]	247	472	225	613
$NaClO_4$	305	461	561	100	810
$KClO_4$	300	588	588	0	764
$RbClO_4$	278	595	595	0	722
$CsClO_4$	221	571	571	0	646[b]

[a] The small endotherm at about 150° (Fig. 2, $LiClO_4$) corresponds to the dissociation reaction $LiClO_4 \cdot H_2O \rightarrow LiClO_4 + H_2O$. [b] An endotherm for the fusion of cesium chloride does not appear in the DTA curve (Fig. 2, $CsClO_4$) because the decomposition exotherm extends somewhat beyond the melting point of cesium chloride.

Only in the instances of lithium and sodium perchlorates are the fusion and rapid decomposition processes separated by an appreciable temperature interval. Inspection of Fig. 2 shows that for the potassium, rubidium and cesium salts, fusion and decomposition are essentially concomitant processes. For the latter compounds, the exotherms corresponding to rapid decomposition are continuous with the peaks of the fusion endotherms. Slow decomposition of these salts was observed to occur during fusion as evidenced by bubbling of the sample.

Discussion

From the present work the observed order of thermal stability of the alkali metal perchlorates as gauged by the temperatures of rapid decomposition is Li < Na < Cs < K < Rb. This sequence follows the fusion temperatures of the salts rather than the order based solely on consideration of anion distortion by cation polarization effects.[10,11] For the alkali and alkaline earth metals, the polarizing power frequently is equated with the ionic potential, *i.e.*, (cation charge/cation radius) and follows the order Li (r_{M^+} = 0.78 Å.) > Na (0.98 Å.) > K (1.33 Å.) > Rb (1.49 Å.) > Cs (1.65 Å.).[12,13] The importance of a liquid phase in increasing reaction rates has been demonstrated clearly for the thermal decomposition of potassium perchlorate[14-16] and for a number of metathetical reactions.[17] A similar kinetic effect due to liquefaction is believed to be responsible for the determined order of the thermal stabilities of the alkali metal perchlorates.

The decompositions of the mixtures of Table I are influenced by both the polarization and liquefaction effects. The introduction of lithium perchlorate to sodium or potassium perchlorate brings about early formation of a liquid phase during heating and increases the polarizing power of the cation atmosphere surrounding the perchlorate group. The thermal behavior of $NaClO_4$–$KClO_4$ mixtures may be interpreted in the same manner.

Preliminary data for the system $LiClO_4$–$NaClO_4$[18] indicate it to be of the simple eutectic type at liquidus temperatures with the eutectic at about 208° and 72.5 mole % $LiClO_4$. As expected, in this system, sodium perchlorate exhibits a crystallographic transition at about 305°.[8]

The lowering of the decomposition temperature of lithium perchlorate by addition of lithium chloride is believed to be primarily a polarization effect. The components form a simple eutectic at about 235° and 90 mole % $LiClO_4$[19] so that at the decomposition temperatures observed all the perchlorate is in solution. The fact that as the overall $[Li^+]/[ClO_4^-]$ ratio increases, the decomposition temperature reaches a steady value of about 435° might indicate that a maximum coördination and polarization effect of lithium ions about the perchlorate group occurs near the presence of 20 mole % lithium chloride.

There are some phenomena cited in the literature which might be explained on the basis of the previous discussions. Thus, the addition of barium nitrate to potassium perchlorate results in a lowered decomposition temperature for the perchlorate anion.[20 21] The two salts were found to form a eutectic at about 465°,[21] about 125° lower than the fusion temperature of potassium perchlorate as determined by DTA. Furthermore, the polarizing power of the divalent barium ion [$r_{Ba^{++}}$ = 1.43 Å.) can be anticipated to be higher than that of the monovalent potassium ion (r_{K^+} = 1.33 Å.), thereby increasing the net polarizing effect of the cation atmosphere in the melt. Similarly, liquid mixtures of barium nitrate and potassium chloride were found to decompose at higher temperatures than pure barium nitrate but lower than for pure potassium nitrate.[21] Here the presence of the less highly charged potassium ion appears to have resulted in a decrease of the over-all polarizing effects of the cation atmosphere on the nitrate ion over that of pure barium nitrate; the converse is to be expected for the addition of barium chloride to potassium nitrate and this has been reported to be the case.[21]

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