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Alkali Metal Perchlorates as Bases at Elevated Temperatures: The Depolymerization of Alkali Metal Condensed Phosphates

BY MEYER M. MARKOWITZ, HARVEY STEWART, JR., AND DANIEL A. BORYTA

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The normal course of pyrolysis of $LiClO_4$, $NaClO_4$, and $KClO_4$ to the metal chlorides is altered to varying degrees to yield effectively the metal oxides in the presence of the corresponding metaphosphates. This behavior reflects an acid displacement reaction which is accompanied by depolymerization of the metaphosphates to simpler anionic species. In this respect the perchlorates are bases relative to the isopolyphosphate anionic acids. The extent of metaphosphate depolymerization is found to be a function of the cationic environment such that for perchlorate–metaphosphate mixtures the order of extent of depolymerization is $Li > Na \gg K$. $NaClO_4$ and $KClO_4$, unlike $LiClO_4$, do not depolymerize their corresponding pyrophosphates to orthophosphates. Of interest is the fact that these elevated temperature reactions do not involve mutual oxidation and reduction of the perchlorate and condensed phosphate reactants. The stoichiometry and course of the reactions were studied by means of thermogravimetry, differential thermal analysis, Cl_2 evolution measurements, and chemical and X-ray analyses.

Introduction

As is common to all the discrete condensed phosphates and their mixtures, the depolymerization of the anhydrous alkali metal (M) poly- and metaphosphates ($2 \geq M_2O/P_2O_5 \geq 1$) is achievable by raising the ratio M_2O/P_2O_5 to the desired extent through reaction of the phosphate at elevated temperatures with the corresponding metal oxide.[1] The source of metal oxide is customarily an oxyanion-containing compound which upon thermal decomposition can yield the metal oxide as a reactive residue.[2,3] Thus, for example, NO_3^-, SO_4^{-2}, CO_3^{-2}, OH^-, and O_2^{-2} [4] can each ultimately serve as depolymerizing agents through participation in the simplified reaction scheme

$$M_yXO_x \longrightarrow y/2\ M_2O + XO_{x-y/2}\,(\text{gas}) \qquad (1)$$

$$y/2\ M_2O + (aM_2O)\cdot P_2O_5 \longrightarrow ((a + y/2)M_2O)\cdot P_2O_5 \qquad (2)$$

It is of interest to report that to varying degrees the alkali metal perchlorates are capable of acting as sources of oxide ions in the presence of condensed phosphates and to effect thereby their depolymerization. This is a surprising result inasmuch as the normal course of pyrolysis of these perchlorates is such as to produce the corresponding chloride as per reaction 3,[5] rather than the oxide according to reaction 4.[6]

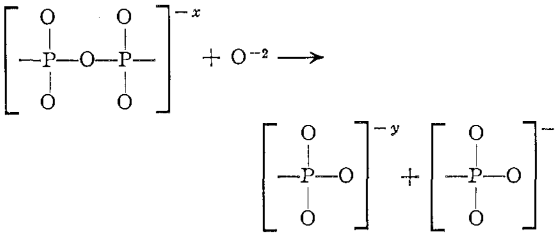
$$MClO_4 \longrightarrow MCl + 2O_2 \qquad (3)$$

$$MClO_4 \longrightarrow {}^1/_2M_2O + {}^1/_2Cl_2 + {}^7/_4O_2 \qquad (4)$$

This newly observed behavior is of further consequence because it represents, as far as can be determined, the only known type of interaction between a metal perchlorate and a co-reactant at elevated temperatures which does not involve a mutual oxidation–reduction process. Accordingly, under appropriate conditions, the alkali metal perchlorates can function as high-temperature bases in the presence of sufficiently strong acids, such as the condensed phosphates. As a result, the application of modern concepts of acid–base theory[7] to these reactions appears to be appropriate. In these terms, the reactions discussed here can be represented by an acid displacement process

$$\begin{array}{l}(aM_2O)\cdot P_2O_5 + b(M_2O\cdot Cl_2O_7) \longrightarrow \\ \qquad\qquad ((a + b)M_2O)\cdot P_2O_5 + bCl_2O_7 \quad (5) \\ \qquad\qquad\qquad 7b/2\ O_2 + bCl_2 \longleftarrow\!\!\lrcorner \end{array}$$

where $a = 1$ or 2, and $a + b \leq 3$. The accompanying oxide ion transfer reaction results in dissolution of the condensed phosphate isopolyanions through breaking of P–O–P linkages



$$\left[\begin{array}{c}\text{O}\quad\ \text{O}\\ |\qquad | \\ \text{—P—O—P—}\\ |\qquad |\\ \text{O}\quad\ \text{O}\end{array}\right]^{-x} + O^{-2} \longrightarrow \left[\begin{array}{c}\text{O}\\ |\\ \text{—P—O}\\ |\\ \text{O}\end{array}\right]^{-y} + \left[\begin{array}{c}\text{O}\\ |\\ \text{—P—O}\\ |\\ \text{O}\end{array}\right]^{-z} \qquad (6)$$

where $y + z = x + 2$. The additional bonds to P atoms in eq. 6 are each to O atoms which may be unbridged or which may be linked to other P atoms in a continuation of the polymeric structure as characterized by a succession of P–O–P bonds, tetracoördination of O to P, and no more than two O bridges per PO_4 tetrahedron.[1,8]

Experimental

Thermogravimetric Analyses.—Weight change–temperature profiles of accurately weighed (about 1 g.) samples of pure perchlorates or of perchlorate–phosphate mixtures were determined by thermogravimetric analyses (t.g.a.) at a heating rate of 4°/min. in a flowing, dry Ar atmosphere.[9] All t.g.a. runs were carried out to about 700°. Weight losses for $NaClO_4$–$NaPO_3$ and $KClO_4$–KPO_3 mixtures could not be determined by t.g.a. because of excessive sample loss due to splattering of the reacting materi-

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[1] M. M. Markowitz, *J. Chem. Educ.*, **33**, 36 (1956).

[2] L. F. Audrieth and T. Moeller, *ibid.*, **20**, 219 (1943).

[3] O. F. Hill and L. F. Audrieth, *J. Phys. Chem.*, **54**, 690 (1950).

[4] M. M. Markowitz and H. Stewart, Jr., unpublished results.

[5] M. M. Markowitz, D. A. Boryta, and R. F. Harris, *J. Phys. Chem.*, **65**, 261 (1961).

[6] M. M. Markowitz, *J. Inorg. Nucl. Chem.*, **25**, 407 (1963).

[7] L. F. Audrieth and J. Kleinberg, "Non-Aqueous Solvents," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 260–273.

[8] J. R. Van Wazer and E. J. Griffith, *J. Am. Chem. Soc.*, **77**, 6140 (1955).

[9] M. M. Markowitz and D. A. Boryta, *Anal. Chem.*, **33**, 940 (1961).

als in the relatively small containers used; rather, these samples were heated to about 700° in an Ar stream at 4°/min. in the larger apparatus used for the Cl_2 evolution studies using 2-g. quantities of these mixtures.

Differential Thermal Analyses.—Thermal effects during the course of heating were observed by differential thermal analyses (d.t.a.) in air using 2-g. samples, a heating rate of 8°/min., and ignited alumina as the reference material.[10] All d.t.a. experiments were carried out to about 900°.

Chlorine Evolution Studies.—During Cl_2 evolution studies, each sample was held in a long Vycor test tube contained in a heated quartz reaction chamber which was continuously flushed with dry Ar. Each sample was heated to about 700° at a heating rate of 4°/min. In accumulatory runs, aimed at accurately determining the total amount of Cl_2 liberated, the effluent gases were bubbled through two traps in series containing 10% KI solution which was titrated at the end of an experiment with 0.2 N $Na_2S_2O_3$ solution. In dynamic runs, aimed at determining the Cl_2 evolution–temperature profile, the liberated I_2 was continuously titrated in a single absorption trap and was correlated with simultaneous measurements of the sample temperature. Pure O_2 was found to have no effect on the KI solution.

Materials and Analytical Techniques.—All alkali metal perchlorates[5] and condensed phosphates[11,12] were of high purity and were rigorously dried prior to use. Perchlorate content was determined through precipitation as nitron perchlorate[13]; Cl^- content was determined gravimetrically as AgCl. Assays for $P_2O_7^{-4}$ and $P_3O_{10}^{-5}$ were performed using Bell's procedure[14] and total P content was found by the method of Jones.[15]

The crystalline metaphosphates used in these studies are represented as "MPO_3" for the sake of simplicity. They may be divided into two classes: the cyclic metaphosphates of exact formula $(MPO_3)_n$, where n indicates the number of metaphosphate groups in the ring, and the linear, long-chain polyphosphates of general formula $M_{n+2}(P_nO_{3n+1})$, where n, the chain length, is large so that the over-all composition closely approaches "MPO_3."[1,16] The various sodium metaphosphates show a tendency to revert to cyclic $(NaPO_3)_3$ on heating. Accordingly, it is likely that this is the reactive species in the $NaClO_4$–$NaPO_3$ system below fusion temperatures.

X-Ray diffraction powder patterns were obtained with a General Electric XRD-5 diffractometer using Ni-filtered Cu Kα radiation. Except where specifically indicated, X-ray and chemical analyses were consistently performed on reaction residues which had been heated up to about 700° at a rate of 4°/min.

Results

Stoichiometry of Reactions.—Equation 3[5] was confirmed as the primary mode of decomposition for $LiClO_4$, $NaClO_4$, and $KClO_4$ using t.g.a. The observed weight loss on heating was 103% of theoretical based on eq. 3 for $LiClO_4$, 102% of theory for $NaClO_4$, and 101% for $KClO_4$. About 1.6% of the available chlorine was lost on heating a separate sample of $LiClO_4$,[17,18] 0.1% on heating $NaClO_4$, and no detectable chlorine loss was suffered by $KClO_4$. On this basis, 98.4% of the $LiClO_4$, 99.9% of the $NaClO_4$, and 100.0% of the $KClO_4$ decompose as per eq. 3.

The weight losses occasioned by heating of mixtures of $LiClO_4$ and $LiPO_3$ (Table I) ensue at considerably lower temperatures than for pure $LiClO_4$ and are much larger than can be accounted for by eq. 3. Similar enhancement of weight losses over those anticipated from eq. 3 was found for $NaClO_4$–$NaPO_3$ and $KClO_4$–KPO_3 mixtures (Table II).

TABLE I

T.G.A. DATA FOR MIXTURES OF LITHIUM PERCHLORATE AND LITHIUM METAPHOSPHATE

Original mole % $LiClO_4$	Obsd. sample wt. loss, g.	Calcd. wt. loss for Li_2O, g.	% Decompn. $LiClO_4$ to Li_2O based on obsd. wt. loss
10	0.1126	0.1109	100.0
20	.2220	.2154	100.0
25	.2766	.2667	100.0
30	.3229	.3246	99.5
40	.4053	.4090	97.0
50	.4820	.4829	99.4
60	.5617	.5753	92.1
66.7	.5917	.6452	72.4
70	.5903	.6490	69.9
75	.5323	.6146	55.4
80	.6349	.7590	45.6

TABLE II

WEIGHT LOSS DATA FOR MIXTURES OF SODIUM AND POTASSIUM PERCHLORATES WITH CORRESPONDING METAPHOSPHATES

Original mole % $MClO_4$	Obsd. wt. loss, g.	Calcd. wt. loss for M_2O, g.	% Decompn. $MClO_4$ to M_2O based on obsd. wt. loss
		$NaClO_4$	
25	0.4008	0.4326	75.5
50	.7200	.8185	59.9
75	.9300	1.1676	32.2
		$KClO_4$	
25	.2820	0.3712	20.0
50	.5193	.7177	7.9
75	.7600	1.0332	11.9

The total P contents of the various types of heated $MClO_4$–MPO_3 samples (Tables I and II) were found to be conserved within the solid residual reaction products. On the other hand, resolution of the chlorine balance showed that the chlorine was distributed as MCl in the solid reaction residue and as appreciable amounts of Cl_2 in the evolved gaseous reaction products (Table III). X-Ray powder patterns of the lithium-containing mixtures of Table III showed the presence of $Li_4P_2O_7$ in each of the residues as well as poorly crystallographically oriented Li_3PO_4 in the 50 and 75 mole % $LiClO_4$-based residues; $Na_4P_2O_7$ but no Na_3PO_4 was found in the mixtures originally containing 50 and 75 mole % $NaClO_4$ (Table II). The 25 mole % $NaClO_4$–75 mole % $NaPO_3$ residue (Table II) had solidified to a glass but was found to contain both $Na_4P_2O_7$ and $Na_5P_3O_{10}$ by chemical analyses. $K_4P_2O_7$ was detected by chemical

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[10] M. M. Markowitz and D. A. Boryta, *J. Phys. Chem.*, **64**, 1711 (1960).

[11] R. K. Osterheld and M. M. Markowitz, *ibid.*, **60**, 863 (1956).

[12] M. M. Markowitz, R. F. Harris, and W. N. Hawley, *J. Inorg. Nucl. Chem.*, **22**, 293 (1961).

[13] F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., Ninth English Ed., 1942, pp. 183–184.

[14] R. N. Bell, *Anal. Chem.*, **19**, 97 (1947).

[15] L. T. Jones, *ibid.*, **14**, 536 (1942).

[16] E. Thilo in "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, pp. 33–49.

[17] M. M. Markowitz and D. A. Boryta, *Anal. Chem.*, **32**, 1588 (1960).

[18] M. M. Markowitz and D. A. Boryta, *J. Phys. Chem.*, **65**, 1419 (1961).

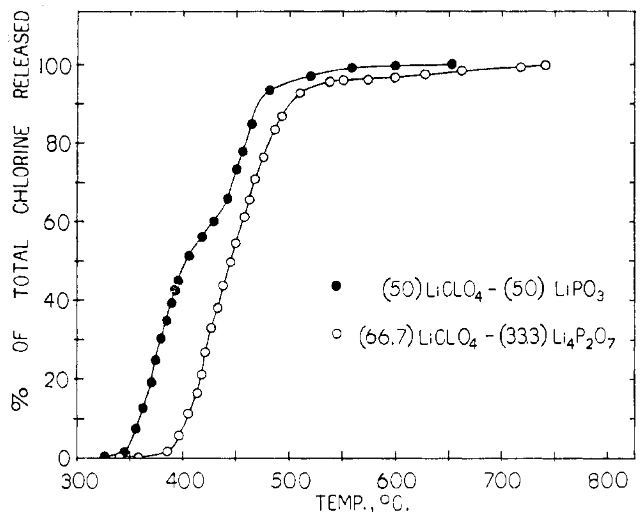

Fig. 1.—Dynamic chlorine evolution–temperature curves.

methods in each of the samples from the potassium-containing series (Table II). It appears then that the thermal decompositions of these alkali metal perchlorates in the presence of the metaphosphates are altered so as to follow reaction 4 to a greater extent and that a concomitant depolymerization of the metaphosphate component occurs. Such depolymerization can only take place in the presence of added MO_2 equivalents.

Table III

Chlorine Distribution from Heated Perchlorate–Metaphosphate Mixtures

Original mole % $MClO_4$	Total g. Cl in sample	G. Cl^- in solid residue	G. Cl_2 evolved	Total g. Cl found
		$LiClO_4$		
25	0.2015	0.0004	0.2015	0.2019
50	.3709	.0183	.3512	.3695
75	.5297	.2224	.2952	.5176
		$NaClO_4$		
75	.4528	.3039	.1336	.4375
		$KClO_4$		
75	.4006	.3546	.0378	.3924

The augmented weight losses found for the mixtures (Tables I and II) can be rationalized through the occurrence of reaction 4 to the degrees shown in the last columns of these tables. However, several stages of depolymerization are possible in the $MClO_4$–MPO_3 mixtures based on reaction of $MClO_4$ and MPO_3 in 1:1 and 2:1 mole ratios, *viz.*

$$MClO_4 + MPO_3 \longrightarrow {}^1/_2M_4P_2O_7 + {}^1/_2Cl_2 + {}^7/_4O_2 \quad (7)$$

$$2MClO_4 + MPO_3 \longrightarrow M_3PO_4 + Cl_2 + {}^7/_2O_2 \quad (8)$$

The weight loss and X-ray data indicate that the lithium-containing mixtures react to a large measure to the level of depolymerization represented by eq. 8, whereas the $NaClO_4$- and $KClO_4$-based mixtures tend to react primarily in the manner shown by eq. 7. In all instances, perchlorate in excess of that not reacting in accord with the stoichiometry required by eq. 7 and 8, of course, decomposes to the corresponding chloride (eq. 3).

Thermogravimetric data for 66.7 mole % $MClO_4$–33.3 mole % $M_4P_2O_7$ mixtures clearly demonstrate the non-reactivity of the sodium and potassium-containing samples in contrast to the ability of $LiClO_4$ to depolymerize $Li_4P_2O_7$ to Li_3PO_4 (reaction 5, $a = 2$, $b = 1$). X-Ray powder patterns of each of these residues indicated a high proportion of orthophosphate in the lithium samples but only unreacted pyrophosphate in the sodium and potassium counterparts.

Quantitative chemical analyses of reaction residues from various $MClO_4$–MPO_3 and $MClO_4$–$M_4P_2O_7$ mixtures substantiate the foregoing observations (Table IV). It should be noted that if the reaction product from the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ mixture is brought to a maximum temperature of only 700° during reaction, then upon cooling, the residue contains but 54.2% $Li_4P_2O_7$, though the weight loss would indicate an expected content of close to 95% $Li_4P_2O_7$. However, X-ray powder patterns showed the presence of unreacted $LiPO_3$ as well as the ultimate product of depolymerization, Li_3PO_4. If the ground residue is kept at 850° for several hours, both $LiPO_3$ and Li_3PO_4 disappear and virtually pure $Li_4P_2O_7$ results as

$$Li_3PO_4 + LiPO_3 \longrightarrow Li_4P_2O_7 \quad (9)$$

Accordingly, it appears that reaction 8 can occur even though reaction 7 has not gone to completion. Nevertheless, the over-all effect of these composite reactions is such as to yield an M_2O/P_2O_5 ratio close to 2 (reaction 7). A point of further interest in the residue from the 25 mole % $LiClO_4$–75 mole % $LiPO_3$ mixture is the presence of $Li_5P_3O_{10}$. This might indicate the partial occurrence of the subsidiary reaction

$$LiPO_3 + Li_4P_2O_7 \longrightarrow Li_5P_3O_{10} \quad (10)$$

Inasmuch as $Li_5P_3O_{10}$ was not found in the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ reaction residue, it seems likely that this higher polyphosphate also can be depolymerized as per the reactions

$$Li_5P_3O_{10} + 3LiClO_4 \longrightarrow 2Li_4P_2O_7 + {}^3/_2Cl_2 + 4O_2 \quad (11)$$

and

$$Li_5P_3O_{10} + 4LiClO_4 \longrightarrow 3Li_3PO_4 + 2Cl_2 + 7O_2 \quad (12)$$

Similar considerations probably also apply to the 25 mole % $NaClO_4$–75 mole % $NaPO_3$ mixture, which also was found to contain some $Na_5P_3O_{10}$ (Table IV). However, any Na_3PO_4 produced in mixtures successively richer in $NaClO_4$ must immediately react with additional $Na_5P_3O_{10}$ or $NaPO_3$. The lack of X-ray diffraction lines attributable to $Li_5P_3O_{10}$ might signify its presence as a glass and it is perhaps the higher polyphosphate conjectured to exist in the solidus region of the system $LiPO_3$–$Li_4P_2O_7$.[12]

Attempts at identifying Cl_2O_7 in the effluent gases from several reaction mixtures were unsuccessful. This is consistent with the known thermal instability of the compound at elevated temperatures.[19]

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(19) C. C. Addison in "Supplement to Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry," Supplement II, Part I, Longmans, Green and Co., New York, N. Y., 1956, pp. 541–542.

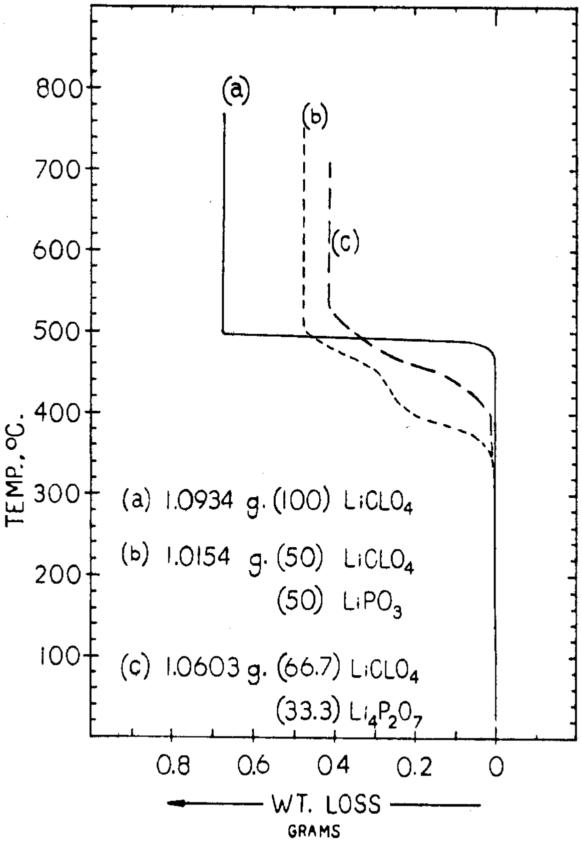

Fig. 2.—Weight loss–temperature curves.

TABLE IV

CHEMICAL ANALYSES OF PERCHLORATE–CONDENSED PHOSPHATE REACTION RESIDUES

Original sample compn., mole %	Wt. % MCl, found	Wt. % MCl, calcd.	Wt. % $M_4P_2O_7$, found	Wt. % $M_4P_2O_7$, calcd.
25 $LiClO_4$–75 $LiPO_3$[a]	0.0	0.0	. . .	. . .
50 $LiClO_4$–50 $LiPO_3$	2.1	1.9	92.4[b]	94.8
75 $NaClO_4$–25 $NaPO_3$	46.9	47.4	52.9	51.1
25 $KClO_4$–75 KPO_3	14.1	16.9	6.1	7.8
75 $KClO_4$–25 KPO_3	59.7	59.4	16.5	17.8
66.7 $LiClO_4$–33.3 $Li_4P_2O_7$[c]	8.3	10.2	23.0	24.2
66.7 $NaClO_4$–33.3 $Na_4P_2O_7$[d]	27.1	30.5	71.3	69.5
66.7 $KClO_4$–33.3 $K_4P_2O_7$	30.2	31.1	63.3	68.5

[a] Residue composition: 13.6% $Li_4P_2O_7$, 28.7% $Li_5P_3O_{10}$, 3.7% Li_3P_4, and 54.0% $LiPO_3$ (by difference). [b] After initial heating to 700°, grinding, and reheating for 2 hr. at 850°. [c] Cl balance: in residue, 0.0832; in evolved gas, 0.2522; total, 0.3354 g.; calcd., 0.3415 g.; 65.7% Li_3PO_4 (theory); 68.7% Li_3PO_4 (by difference). [d] Faint trace of chlorine evolved.

Reaction Sequence of Depolymerization Processes.—Inspection of the forms of the t.g.a., d.t.a., and dynamic Cl_2 evolution–temperature curves for the individual perchlorates and their mixtures with condensed phosphates yields considerable insight into the course of the reactions occurring during heating treatments. Pertinent to these studies, it is of consequence to note the close reproducibility of the weight losses and, hence, extents of depolymerization reactions characteristic of any particular sample heated under similar conditions. Thus, comparisons of results obtained from the three different techniques for the same sample composition appear to be justified.

For the $LiClO_4$–$LiPO_3$ mixtures, the thermal data for the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ samples contain aspects representative of the behavior found at both lower (25 mole % $LiClO_4$) and higher (75 mole % $LiClO_4$) perchlorate contents. Figure 1 illustrates the dynamic Cl_2 evolution curve for a 50 mole % $LiClO_4$–50 mole % $LiPO_3$ mixture. In Fig. 1, at the 100% level of total chlorine released, about 85–90% of the available chlorine is accounted for as elemental Cl_2 by this method. This is somewhat less than the Cl_2 determined in the earlier accumulatory runs (Table III) and probably is due to incomplete absorption of Cl_2 and incomplete retention of I_2 in the KI solution because of the very rapid flow of Ar carrier gas used. A large gas flow is required in order to keep the sample temperature measurements and the Cl_2 evolution determinations in phase due to the considerable volume of the system. Chloride analyses of the residues from these dynamic experiments, however, indicate the loss of at least 95% of the available chlorine. Despite this possible shortcoming, it is felt that the dynamic Cl_2 evolution curves represent the reaction sequence. Clearly seen is the onset of Cl_2 release at about 340°, a diminution in the rate of Cl_2 evolution at about 405° after 45% of the total Cl_2 evolution had occurred, and at about 445° the rate of Cl_2 rises again to diminish at about 470°.

Figure 1 also depicts the Cl_2 evolution–temperature profile for a mixture of 66.7 mole % $LiClO_4$–33.3 mole % $Li_4P_2O_7$. Of the available chlorine, about 70% appears as Cl_2 by the dynamic evolution technique. This is consistent with the results of Table IV which indicate about 25% conversion of the $LiClO_4$ content of the mixture to LiCl and thus incomplete reaction with the $Li_4P_2O_7$. For this sample, it is evident that Cl_2 release becomes significant above 400° and can only involve depolymerization of the $Li_4P_2O_7$ to Li_3PO_4. It appears reasonable then that the lower portion of the Cl_2 evolution curve for the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ mixture must correspond to the formation of $Li_4P_2O_7$ plus some small extent of reaction of the latter with $LiClO_4$ to yield some Li_3PO_4; the upper portion of the curve for this mixture is attributed to the depolymerization of the $Li_4P_2O_7$ formed at the lower temperatures to Li_3PO_4 plus some additional reaction between $LiClO_4$ and $LiPO_3$.

The above considerations are in harmony with the forms of the t.g.a. curves characterizing these mixtures as seen in Fig. 2. It seems clear that the decline in Cl_2 evolution in the range 405–445° noted above is associated with the decrease in weight over the same range (Fig. 2b) after 48% of the aggregate weight loss; the increase in rate of weight loss starting at about 445° must correspond to the rapid conversion of $Li_4P_2O_7$ to Li_3PO_4, further depolymerization of unreacted $LiPO_3$, and some slight decomposition of $LiClO_4$ to LiCl. The weight losses from the 66.7 mole % $LiClO_4$–33.3 mole % $Li_4P_2O_7$ mixture (Fig. 2c) extend smoothly over the entire course of reaction with no successive diminution

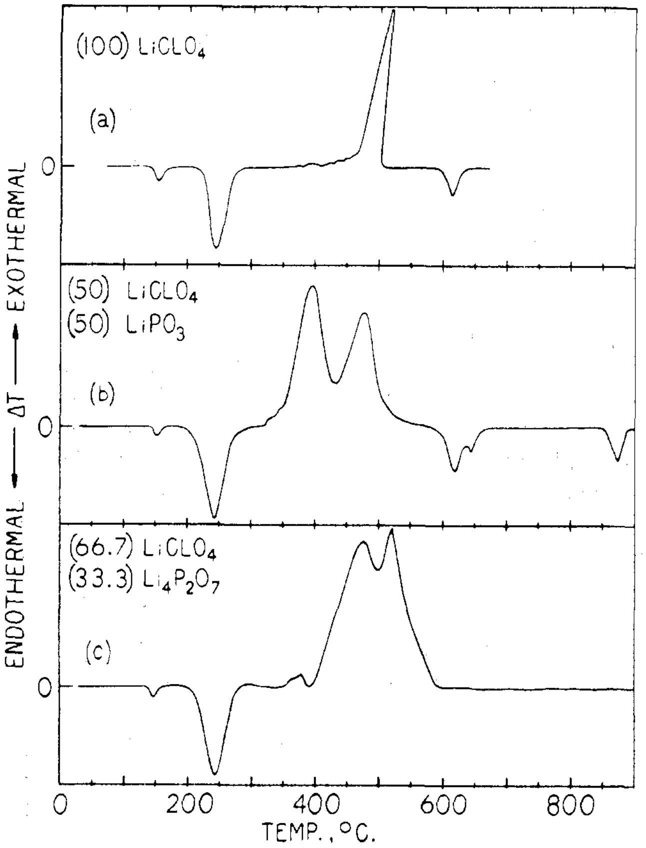

Fig. 3.—Differential thermal analysis curves.

and acceleration in rate as with the $LiClO_4$–$LiPO_3$ mixture. Curve 2c in conjunction with the corresponding Cl_2 evolution curve indicates that the decomposition of $LiClO_4$ to LiCl and reaction of $LiClO_4$ with $Li_4P_2O_7$ occur simultaneously at the higher temperatures. The excess $LiClO_4$ appears to be more thermally stable in the $LiClO_4$–$Li_4P_2O_7$ mixture than in the pure state. From Fig. 2a, it is found that pure $LiClO_4$ is completely decomposed at 505° whereas $LiClO_4$ is still present in the $LiClO_4$–$Li_4P_2O_7$ mixture considerably beyond this temperature (Cl_2 evolution continues even at 600°, Fig. 1). The explanation for this phenomenon lies in the fact that the thermal decomposition of $LiClO_4$ is catalyzed by the LiCl pyrolysis product.[17,20] In the $LiClO_4$–$Li_4P_2O_7$ sample, little or no LiCl forms at the lower temperatures due to preferential reaction of $LiClO_4$ with $Li_4P_2O_7$. Only at the higher temperatures, when the rate of reaction of $LiClO_4$ with $Li_4P_2O_7$ diminishes because of diffusional and concentration effects, can LiCl start to accumulate as a result of the competing self-decomposition of the $LiClO_4$. Apparently, once this occurs the thermal decomposition of $LiClO_4$ to LiCl is favored over reaction with $Li_4P_2O_7$. This is in accord with the analytical data which always showed incomplete conversion of the available $Li_4P_2O_7$ content to Li_3PO_4 for these mixtures.

The d.t.a. curves for pure $LiClO_4$ and for the two mixtures under discussion are presented in Fig. 3. In each case the small endothermic break at about 150° corresponds to the transition $LiClO_4 \cdot H_2O \rightarrow LiClO_4 + H_2O$, occasioned by small amounts of moisture absorption from the air atmosphere in which these runs were made[21,22]; the larger endotherm at 247° corresponds to the melting point of $LiClO_4$.[5] As noted, each mixture manifests two large exotherms in the temperature region of interaction. The first exotherms, as do the temperatures corresponding to the onset of weight loss and Cl_2 evolution, occur appreciably below the temperature of onset of rapid decomposition of pure $LiClO_4$. For the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ mixture, the order of these exotherms must refer to the reaction sequences: (a) $LiPO_3 + LiClO_4 \rightarrow {}^1/_2Li_4P_2O_7 + {}^1/_2\ Cl_2 + {}^7/_4O_2$ (*ca.* 340–420°), followed by (b) ${}^1/_2\ Li_4P_2O_7 + LiClO_4 \rightarrow Li_3PO_4 + {}^1/_2Cl_2 + {}^7/_4O_2$ (*ca.* 440–500°) with accompanying further depolymerization as per reaction a. The succeeding pair of endothermic breaks probably correspond to eutectic and liquidus formation between $Li_4P_2O_7$ and unreacted $LiPO_3$; the final endotherm, peaking at about 878°, is the melting point of pure $Li_4P_2O_7$.[12] Cooling and reheating of this residue shows the presence of the endotherm signifying the crystallographic transition of $Li_4P_2O_7$ (646°)[12] and the reappearance of the fusion endotherm. The reaction $Li_3PO_4 + LiPO_3 \rightarrow Li_4P_2O_7$, as indicated by other d.t.a. studies, does not appear to occur rapidly below about 800°. The pair of exotherms found for the 66.7 mole % $LiClO_4$–33.3 mole % $Li_4P_2O_7$ mixture is ascribed, respectively, to depolymerization of $Li_4P_2O_7$ followed by the decomposition of unreacted $LiClO_4$ to LiCl. No clear endotherm was found for the fusion of LiCl (m.p. 614°), probably due to the considerable turbulence of the preceding reactions which prevented formation of an appreciable amount of coherent residue.

Because of the disparities in melting points between $LiClO_4$ (247°), $LiPO_3$ (658°), $Li_4P_2O_7$ (878°), and Li_3PO_4 (1225°),[23] it seems unlikely that these phosphates and $LiClO_4$ will manifest any appreciable degree of mutual solubility at the low reaction temperatures encountered here, particularly at the onset of reaction. Furthermore, at reaction temperatures (*ca.* 350–500°) liquid phase formation between $LiPO_3$ and $Li_4P_2O_7$ (eutectic 603)[12] is not possible and solution between $Li_4P_2O_7$ and Li_3PO_4 appears unlikely at these temperatures. Thus, for the most part the depolymerization processes must proceed topochemically between the heterogeneous components, *i.e.*, solid condensed phosphate and liquid $LiClO_4$. Accordingly, the reaction product residue of the $LiClO_4$–$LiPO_3$ mixture below 603° must be a layered composite consisting of an inner core of unreacted $LiPO_3$, a center layer of $Li_4P_2O_7$, and an outer thickness of Li_3PO_4. The coexistence of all these compounds in the residue from the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ sample has been confirmed by chemical and X-ray analyses. In the succession of chemical

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[20] M. M. Markowitz and D. A. Boryta, *J. Phys. Chem.*, **66**, 358 (1962).

[21] J. P. Simmons and C. D. L. Ropp, *J. Am. Chem. Soc.*, **50**, 1650 (1928).

[22] M. M. Markowitz, *J. Phys. Chem.*, **62**, 827 (1958).

[23] T. Y. Tien and F. A. Hummel, *J. Am. Ceram. Soc.*, **44**, 206 (1961).

changes from $2LiPO_3$ (density 2.467) $\xrightarrow{Li_2O}$ $Li_4P_2O_7$ (density 2.352) $\xrightarrow{Li_2O}$ $2Li_3PO_4$ (density 2.537), the corresponding equivalent molar volume sequence is: 69.7 cc. $\longrightarrow$ 85.8 cc. $\longrightarrow$ 91.3 cc. Thus, it appears that the conversion of $Li_4P_2O_7$ to Li_3PO_4 should proceed relatively unhampered by reactant diffusion through the product layer, whereas the large difference in volume between $LiPO_3$ and the equivalent quantity of $Li_4P_2O_7$ would be expected to introduce diffusional difficulties beyond a certain thickness of $Li_4P_2O_7$, as conjectured by an extension of the Pilling–Bedworth rules.[24,25] On this basis, the reaction halts found for the mixtures containing 40 mole % or more of $LiClO_4$ become reasonable. From the data depicted in Fig. 1 and 2 and supplemental chemical analyses, the first reaction stage for the 50 mole % $LiClO_4$–50 mole % $LiPO_3$ mixture involves the conversion of approximately one-half the $LiPO_3$ content to $Li_4P_2O_7$ and the second stage of reaction concerns the conversion of about one-half this $Li_4P_2O_7$ to Li_3PO_4 accompanied by re-formation of $Li_4P_2O_7$ through depolymerization of one-half of the remaining $LiPO_3$ content; thus, close to one-quarter of the original $LiPO_3$ content remains unreacted.

Dynamic Cl_2 evolution and t.g.a. studies for the 25 mole % $LiClO_4$–75 mole % $LiPO_3$ composition show smooth curves with no halts evident during the interval of reaction; over 90% of the total Cl_2 evolution and weight losses occur in the temperature range 335–420°. The d.t.a. curve for this mixture has but one exotherm (340–425°). These results, in combination with chemical and X-ray analyses, substantiate the primary reaction to be depolymerization of $LiPO_3$ to $Li_4P_2O_7$. On the other hand, the behavior of the 75 mole % $LiClO_4$–25 mole % $LiPO_3$ mixture is more complex. For this composition, halts are clearly obtained in the Cl_2 evolution and t.g.a. curves for successive stages of condensed phosphate depolymerization. Though Cl_2 evolution virtually ceases at 460°, significant weight losses continue to about 500°. Over this temperature range, decomposition of unreacted $LiClO_4$ to LiCl must occur in these samples. The d.t.a. curve was found to contain three exothermic bands. These regions are attributed to the sequential occurrence of $Li_4P_2O_7$ formation, $Li_4P_2O_7$ depolymerization and further $LiPO_3$ depolymerization, and, finally, decomposition of excess $LiClO_4$.

The reaction sequences of $NaClO_4$–$NaPO_3$ and $KClO_4$–KPO_3 mixtures are less complex than those related to the lithium compounds. For the former materials, reaction does not proceed beyond the pyrophosphate stage. All dynamic Cl_2 evolution curves from samples containing 25, 50, and 75 mole % $NaClO_4$ or $KClO_4$ show no alternations in slope in intermediate stages of reaction. As is the case with the lithium compounds, Cl_2 evolution ensues at a lower temperature than that characteristic of the thermal decomposition of the pure perchlorate to metal chloride. The temperatures corresponding to the onset of rapid depolymerization in $MClO_4$–MPO_3 mixtures are 340° (Li), 480° (Na), and 540° (K) as compared to 443° (Li), 498° (Na), and 556° (K) for the decompositions of the pure perchlorate salts. Thus, in the instances of $NaClO_4$ and $KClO_4$, which fuse close to their temperatures of rapid decomposition,[5] thermal decomposition to the chlorides is a seriously competing reaction in the temperature ranges at which metaphosphate depolymerization occurs. On this basis, $LiClO_4$ is kinetically a more effective depolymerizing agent than the other alkali metal perchlorates.

Discussion of Results

The standard free energy changes at 25° characterizing the conversions of mole quantities of $MClO_4$ to MCl (ΔF_3^0) or to M_2O (ΔF_4^0) are presented in Table V.[6,26–28] The preponderant occurrence of the chloride route during perchlorate pyrolysis is readily understandable in terms of the greater thermodynamic stabilities of the chlorides in comparison to the oxides. Nevertheless, in the instance of $LiClO_4$, decomposition to the oxide is also thermodynamically feasible and was demonstrated to occur to the extent of 1.6% under a slowly rising temperature program. It is instructive to look at the pyrolysis of the metal perchlorates in another light. The perchlorate thermal decomposition process actually refers to an oxidation–reduction reaction involving a redistribution of electron density among the various charged species. If the alkali metal perchlorates are regarded as existing in the most extreme state of polarization, *i.e.*, aggregates of M^+, Cl^{+7}, and O^{-2} ions, then the competition for negative charge rests with the univalent metal cations and the more highly positively polarized chlorine particles. With each $MClO_4$ salt but $LiClO_4$, the metal cation is apparently insufficiently acidic, in the Usanovich sense,[29,30] to compete successfully with the positively polarized chlorine for electrons so that the chlorine, being more acidic, is virtually completely reduced to Cl^-. However, in the case of Li^+, the acidities or electrophilic natures of Li^+ and the positively polarized chlorine are more comparable and the result is an incomplete transfer of negative charge from O^{-2} to cationic chlorine with the consequent formation of some Cl_2 and solid Li_2O. This approach is consistent with the observed highly electrophilic character of Li^+ in aqueous[31] and non-aqueous[32] solvent systems which results

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(24) N. B. Pilling and R. E. Bedworth, *J. Inst. Metals*, **29**, 577 (1923).

(25) M. M. Markowitz and D. A. Boryta, *J. Chem. Eng. Data*, **7**, 586 (1962).

(26) F. D. Rossini, D. D. Wagman, W. H. Evans, B. Levine, and J. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Govt. Printing Office, Washington, D. C., 1952.

(27) J. P. Coughlin, "Contributions to the Data on Theoretical Metallurgy. XII. Heats and Free Energies of Formation of Inorganic Oxides," Bureau of Mines Bulletin 542, U. S. Govt. Printing Office, Washington, D. C., 1954.

(28) Dow Chemical Co., "Joint Army–Navy–Air Force Thermochemical Data," Thermal Laboratory, Midland, Michigan, 1960.

(29) M. Usanovich, *J. Gen. Chem. USSR*, **9**, 182 (1939).

(30) W. F. Luder and S. Zuffanti, "The Electronic Theory of Acids and Bases," John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 13–14.

(31) M. M. Markowitz and D. A. Boryta, *J. Chem. Eng. Data*, **6**, 16 (1961).

(32) M. M. Markowitz, W. N. Hawley, D. A. Boryta, and R. F. Harris, *ibid.*, **6**, 325 (1961).

in extensive solvation effects and in the generally lower thermal stabilities of lithium compounds of decomposable oxyanions as compared to the corresponding compounds of the other alkali metals.[33] For the alkali metals, the increasing order of thermal stability usually follows the decreasing order of polarizing power or ionic potential.[34]

Table V

Standard Free Energy Changes (Kcal./Mole at 25°) for Alkali Metal Perchlorate Decompositions

Salt	$\Delta F_3{}^0$	$\Delta F_4{}^0$
$LiClO_4$	-31.4	$-\ 6.4$
$NaClO_4$	-32^a	$+15^a$
$KClO_4$	-25.0	$+34.2$
$RbClO_4$	-25.3	$+38.4$
$CsClO_4$	-26.2	$+41.3$

[a] Estimated, see ref. 6.

Clearly demonstrated in the present work is the behavior of the more common alkali metal perchlorates as sources of oxide ions in the presence of the strong, high-temperature polyanionic acid, metaphosphate. This behavior is manifested as a degradation of the polymeric metaphosphate structure through scission of the P–O–P bonds to form less condensed phosphate species. The rupture of these O bridges in the condensed phosphates must possess exceedingly favorable free energy increments to counterbalance the usual tendencies of these perchlorates to decompose to chlorides. The depolymerization process may be regarded as the result of an acid displacement reaction (eq. 5) which incorporates the transfer of the oxide ion (Lewis base) to the metaphosphate group (Lewis acid) or in the Lux–Flood formulation[35]: PO_3^- (acid) + $O^{-2} \rightarrow PO_4^{-3}$ (base).

The extent of depolymerization, *i.e.*, the number of P–O–P bridges broken per mole of perchlorate present, is a function of the complementary metal cation. It is readily seen that for the metaphosphate–perchlorate mixtures, the order of extent of metaphosphate depolymerization under the conditions employed is Li > Na >> K, and that for the pyrophosphate–perchlorate mixtures, the order is Li >>> Na, K = 0. Other studies[36,37] have shown that O bridges in isopolyanions decrease in stability with increasing polarizing power of the associated cations. Thus, it can be anticipated that the O bridges in $LiPO_3$ will be the most readily ruptured of all the alkali metal metaphosphates, *i.e.*, $LiPO_3$ is the strongest acid of all the alkali metal metaphosphates. The effect of the cation on the basicity of the alkali metal perchlorates or their tendency to yield O^{-2} is discernible but relatively small due to the overriding acidity of the positively polarized Cl atoms. Accordingly, the extent of depolymerization of a metaphosphate, it is felt, will be most strongly controlled by the acidity of the metaphosphate. On this basis, the observed order of extent of depolymerization of MPO_3 by $MClO_4$ is rationalized.

The condensed phosphate structures considered here are composed of two types of PO_4 tetrahedra.[38] One structural unit consists of a singly-charged tetrahedron in which there are two O bridges (middle groups) and the other unit consists of a double-charged tetrahedron in which there is but one O bridge per tetrahedron (end groups). The present studies allow for some distinction to be made in the acidic strengths of these two classes of acidic groups as influenced by their complementary cationic environment. Readily evidenced is the fact that with the corresponding perchlorates, the order of acid strengths of pyrophosphates (contain only two end groups) is $Li_4P_2O_7 >>> Na_4P_2O_7, K_4P_2O_7 = 0$, and that generally the metaphosphates (composed primarily of middle groups) are stronger acids than the pyrophosphates. In this context it can be predicted that the triphosphates (two end groups and one middle group) will be stronger acids than the pyrophosphates though not as strong as the metaphosphates. The perchlorates of metals of high ionic potential and polarizing power (*e.g.*, Mg, Al, Fe, etc.) normally decompose to yield preponderantly the corresponding oxide rather than the chloride.[6,39] Thus, these perchlorates might be expected to act as particularly strong bases toward condensed phosphates. On the other hand, the heavier alkali metal perchlorates (Rb and Cs) because of the low polarizing powers of the large cations probably will serve as very poor bases with respect to their condensed phosphates.

It is interesting to note that $LiClO_4$ starts to react with $LiPO_3$ about 60° lower than does pure Li_2O itself (onset of reaction at about 400° as determined by d.t.a. experiments with accompanying temperature rises of 300–400° for $LiPO_3$–Li_2O mixtures in 1:1 and 2:1 mole ratios). Accordingly, it is conjectured that the perchlorates may provide the synthetic chemist with new methods for the preparation of polyphosphates at relatively low temperatures. In addition, the alkali metal perchlorates as well as other halates may also prove to be useful in the general study of depolymerization reactions involving oxygen-bridge scission due to the acidic nature of the polymeric substances.

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[33] R. T. Sanderson, "Chemical Periodicity," Reinhold Publishing Corp., New York, N. Y., 1960, pp. 162–166.

[34] G. H. Cartledge, *J. Am. Chem. Soc.*, **50**, 2855, 2863 (1928); *ibid.*, **52**, 3076 (1930).

[35] T. Moeller, "Inorganic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 260–273.

[36] H. Flood and T. Förland, *Acta Chem. Scand.*, **1**, 582, 781, 790 (1947).

[37] H. Flood and A. Muan, *ibid.*, **4**, 364 (1950).

[38] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 421–425.

[39] A. A. Zinov'ev and L. J. Cludinova, *Zh. Neorgan. Khim.*, **1**, 1722 (1956).