0.04% change in C. A shift of 1:1000 of the P_j caused only a 0.05% change in B and a 0.13% change in C. Thus, a small systematic error in the piston area does not make an important change in the virial coefficients when the direct method is used.

In the apparatus constant method the value of the constant at zero pressure must be determined very precisely. Errors in this constant introduce an error in the compressibility factor which increases as the number of expansions increase. The method of determining the constant using helium in a pressure range where fourth virials are negligible is shown in Figure 1. The proper selection of the zero pressure constant is indicated by a linear relationship resulting. Unfortunately, the deviations from linearity are shown most sensitively by the low pressure points and these points are most influential in determining the constants as shown in Figure 1. As has been discussed above these points are the least accurate and may have a systematic error. The scatter in these points is considerably dampened in the apparatus constant method since the compressibility factors at which they are determined are calculated from higher pressures in the expansion. However, even a small systematic error in these points will cause a significantly erroneous choice of the apparatus constant necessary to linearize them. Since the lower pressures are generally too high, this causes the second virial coefficient, as given by the intercept in Figure 1, to be too large. In almost every case the second virials of the apparatus constant method are larger than those predicted by the direct method.

Because many of the difficulties in the apparatus constant method are avoided, the direct method proposed here is the more accurate procedure for the determination of virial coefficients from Burnett data. The data obtained by Canfield are very accurate over a wide pressure range and the pressure at which the systematic errors begin is quite low. Consequently the results of the two methods for these data are very close. If all pressures could be determined with equal relative accuracy with no nonrandom deviations at low pressures, then the results of the two methods should be identical.

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Thermoanalytical Study of Lithium Chlorate

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ELUCIDATION of the trends in thermal stability and of those chemical and physical processes occurring during the pyrolysis of the alkali metal (M) perchlorates has been facilitated through application of differential thermal analysis (DTA) and of thermogravimetric analysis (TGA) (*39*). In contrast, the alkali metal chlorates appear not to have been studied systematically by the use of these techniques. Accordingly, the present investigation of the thermal decomposition of $LiClO_3$ was undertaken with the views in mind of gauging the applicability of DTA and of TGA in this area, of defining the order of thermal stability of the lithium compounds of chlorine-containing oxyanions (ClO_x^-, x = 1, 2, 3, 4), and ultimately, of determining the pyrolysis relationships among the alkali metal chlorates in general.

EXPERIMENTAL

Thermoanalytical Techniques. DTA experiments to about 700° were performed in a closed muffle furnace with equipment previously described (*35, 39, 44*) in conjunction with calibrated chromel-alumel thermocouples (24 B. and S. gage) and quartz sample tubes (3 inches × ½ inch o.d.

The pyrolysis of $LiClO_3$ was studied by differential thermal analysis and thermogravimetry at a heating rate of 4°/min., and by isothermal experiments at 339°. The decomposition was shown to follow the sequence: (rapid; ca. 365–430°) $LiClO_3 \rightarrow LiCl + 3/2O_2$ concomitant with $LiClO_3 \rightarrow 3/4LiClO_4 + 1/4LiCl$, and (slow; ca. 430–490°) $LiClO_4 \rightarrow LiCl + 2O_2$. Estimates are presented for ΔH_f° ($LiClO_3$) and ΔF_f° ($LiClO_3$) at 25°, thereby permitting tabulations of the standard enthalpy and free energy changes at 25° for a number of the processes occurring during the pyrolysis of the alkali metal chlorates in general. These data suggest the occurrence of internal oxygenation effects in decomposing chlorate melts leading to the formation of the more thermodynamically and kinetically stable perchlorates, viz., $MClO_3 + \frac{1}{2}O_2 \rightarrow MClO_4$. Trends in the thermal stabilities of the alkali metal compounds of chlorine-containing oxyanions ($MClO_x$, x = 1, 2, 3, 4) are detailed and the following order of stabilities is demonstrated: $MClO_4 > MClO_3 > (MClO_2, MClO)$.

× 1 3/32 inch i.d.) concentric with larger Pt tubes used to provide more uniform heat distribution. For those runs carried out to only 180°, a method used earlier (*32*) was adopted in combination with a liquid heat transfer medium (550 Silicone Fluid, Dow-Corning Corp., Midland, Mich.). Visual observation of the sample was possible during these heatings.

TGA determinations were made with apparatus already detailed (*33, 44*) using Vycor sample tubes. Appropriate corrections were applied to all measured temperatures (*34*) to approximate the sample temperature from the furnace temperature.

Each DTA and TGA experiment was conducted under a dry, flowing Ar atmosphere and, unless otherwise specified, one gram samples were used and subjected to a linear heating rate of 4°/minute (*38*).

Materials and Chemical Analytical Procedures. Anhydrous $LiClO_3$ was prepared by the method of Potilitzin (*52*) involving the double decomposition of equivalent quantities of Li_2SO_4 and $Ba(ClO_3)_2$ in aqueous solution. The solid product obtained after evaporation of water was dried at 100° under 1 micron Hg pressure for two days. The material was stored over P_2O_5 and all handling and manipulation of the highly deliquescent $LiClO_3$ was performed in a glove box under dry Ar or N_2. Analyses: Cl as ClO_3^-: found, 39.08% (calcd., 39.24%); Cl as Cl^-: found, 0.02%. Spectrographic examination showed the presence of <5 p.p.m. Al, <5 p.p.m. Ca, <1 p.p.m. Cu, <1 p.p.m. Mg, <0.5 p.p.m. Mn, and <1 p.p.m. Ni; B, Cr, Pb, Sn, Ti, and V were absent.

Partially decomposed residues of $LiClO_3$ were analyzed for Cl^-, ClO_3^-, ClO_4^-, and O^{-2} contents, except for several instances where ClO_4^- was taken by difference. Cl^- was determined gravimetrically as AgCl; ClO_3^- was assayed as additional Cl^- after reduction of the sample aliquot with aqueous SO_2. ClO_4^- was analyzed by precipitation as nitron perchlorate (*58*) after reduction of ClO_3^-. O^{-2} content was found by titration to the phenolphthalein end-point with 0.1*N* HCl.

The total Cl_2 evolved from various reacting samples was determined by absorption in KI solution as described previously (*44*).

X-ray diffraction powder patterns of products from $LiClO_3$-condensed phosphate reaction mixtures were obtained with a General Electric XRD-5 diffractometer using Ni-filtered Cu-K_α radiation.

RESULTS

Thermal Behavior of $LiClO_3$ up to 180°. The polymorphism of $LiClO_3$ has been a matter of some dispute in the literature. Some workers (*29*) have claimed the reversible crystallographic changes $\gamma \rightleftarrows \beta$, $\beta \rightleftarrows \alpha$ at 44.5° and 106.4°, respectively, whereas others (*3, 10*) have reported but a single crystallographic transition at about 100°. Accordingly, in the present study, DTA patterns of $LiClO_3$ on an expanded scale were obtained over the temperature range from ambient to about 180°. Only a single transition occurring at 111.1° was ever found upon repeated heating and cooling cycles. A second endotherm was identified by visual observations as the melting point of α-$LiClO_3$ and agrees (129.2°) with previously reported values (*3, 10, 8, 48, 52*). These changes are seen as the first two endotherms in the DTA curves of Figures 1 and 2. Supercooling of liquid $LiClO_3$ and of α-$LiClO_3$ by as much as 50° was observed in the course of the present experiments.

The $LiClO_3$ samples subjected to the above DTA studies showed no changes in composition after the runs as determined by chemical analyses; this, of course, was also indicated by the reproducibility of the invariant points despite repeated thermal cycling. Maintaining fused $LiClO_3$ at 135° for two days under an Ar atmosphere at ambient pressure resulted in no measurable degree of decomposition as revealed by chemical analyses. These observations would indicate the feasible use of $LiClO_3$ as a stable component in phase studies of anhydrous salt systems at moderately elevated temperatures as have been performed with $LiClO_4$ (*32, 36, 39, 41*).

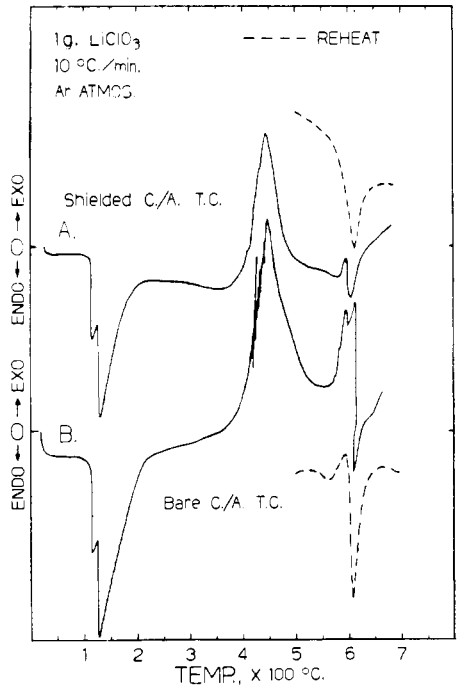

Figure 1. DTA curves of $LiClO_3$ heated at 10° /Min.

The density of α-$LiClO_3$ at room temperature was measured as 2.631 by a gas pycnometer method.

Isothermal Decomposition Studies of $LiClO_3$ at 339°. Some preliminary information on the thermal decomposition of $LiClO_3$ was secured by maintaining 4–5 gram samples at 339° ± 1° under flowing Ar for varying periods of time. The analyses of these residues are presented in Table I in terms of the extents of decomposition (x_i) of $LiClO_3$ as per the reactions:

$$LiClO_3 \rightarrow \tfrac{1}{2}Li_2O + \tfrac{1}{2}Cl_2 + \tfrac{5}{4}O_2 \quad (1)$$

$$LiClO_3 \rightarrow \tfrac{3}{4}LiClO_4 + \tfrac{1}{4}LiCl \quad (2)$$

$$LiClO_3 \rightarrow LiCl + \tfrac{3}{2}O_2 \quad (3)$$

Equation 2 is customarily used to account for $MClO_4$ formation in $MClO_3$ melts (*1, 12, 13*), although an alternate formulation of the reaction will be suggested in a later section of this paper.

The data of Table I indicate a number of interesting aspects of the pyrolysis of $LiClO_3$. Both Reactions 2 and 3 appear to be catalyzed as the degree of $LiClO_3$ decomposition increases. This autocatalytic behavior is akin to that observed for the disproportionation of $KClO_3$ (*21, 50*) and for oxygen evolution from various $KClO_3$–KCl mixtures (*21*). For $LiClO_3$, Reactions 2 and 3 seem to occur at approximately the same rates as suggested by the relative constancy of the ratio $1.5 > x_2/x_3 \geq 1.0$ up to 12 hours of heating. After 12 hours, the decomposition residue is substantially a mixture of LiCl and $LiClO_4$ in a 5:3 mole ratio. Thus, the pyrolysis of $LiClO_3$ after this interval can be closely represented by the overall equation:

$$8LiClO_3 \rightarrow 5LiCl + 3LiClO_4 + 6O_2 \quad (4)$$

which is the sum of Equations 2 and 3. About one-half of the oxygen loss occurs subsequently through the considerably slower reaction:

$$LiClO_4 \rightarrow LiCl + 2O_2 \quad (5)$$

when the melt is devoid of any appreciable $LiClO_3$ content.

The rate of decomposition of $LiClO_4$ in a saturated solution of LiCl in $LiClO_4$ at 339° may be computed (*36*) and is found to be only 0.41% per hour, so that the augmenting LiCl content due to Reaction 5 becomes significant only after the longer heating periods. In Table I, Reaction 5 was not considered to cause any alterations in x_2 and x_3 although it clearly plays a role after the 12-hour heating period when the $LiClO_4$ content has reached a maximum. This effect is manifested in the steadily decreasing magnitude of x_2/x_3 beyond the 12 hour interval. Indeed after this point, the thermal decomposition of $LiClO_3$ is essentially complete so that the succeeding values of x_i are merely formal in nature and the changes in the system are best represented by Equation 5.

The values of x_3 calculated from the chemical analyses agreed closely with those values computed from the weight losses. This would be expected because of the generally small magnitude of x_1. Other studies (*16, 20*) have shown the occurrence of small degrees of Cl_2 evolution from $KClO_3$ and from various $KClO_3$-catalyst mixtures as well as from combusting $NaClO_3$-Fe compositions (*54*). It is clear then that full kinetic scheme for the pyrolysis of these $MClO_3$ compounds would have to take into account a reaction such as that represented by Equation 1.

When $LiClO_4$ was heated under flowing Ar at 399° ± 1° for 72 hours 0.38% decomposed following Equation 5 and 0.20% decomposed as per:

$$LiClO_4 \rightarrow LiClO_3 + \tfrac{1}{2}O_2 \quad (6)$$

These results together with those obtained previously show that $LiClO_4$ is appreciably more thermally stable than is $LiClO_3$. Consequently, it was anticipated that this marked difference in decomposition rates would be reflected in the DTA and TGA patterns for $LiClO_3$.

High Temperature DTA Patterns of $LiClO_3$. DTA patterns were obtained for $LiClO_3$ at a heating rate of 10°/minute using thermocouples shielded in an outer, close-fitting quartz tube. A typical curve is presented in Figure 1a. The exothermal decomposition band starts to depart appreciably from the baseline at about 376° and consists of only a single, smooth peak. There are no discontinuities in this band indicative of the occurrence of reactions. of widely differing rates, e.g., Reactions 2 and 3 as compared with Reaction 5. Accordingly, an attempt was made to secure better resolution in the DTA curves by the use of bare thermocouples (*2, 18*); the behavior found by this procedure is shown in Figure 1b. Here, the steadily rising baseline after fusion would indicate the occurrence of slow decomposition at lower temperatures than in the previous experiment with the rate becoming appreciable at about 370°. As seen in Figure 1b, again only a single large exotherm was recorded. However, through use of a heating rate of 4°/min. (Figure 2a), a knee appeared on the decomposition exotherm; a similar effect occurred with the use of a bare thermocouple (Figure 2b). It was felt that this discontinuity was associated with the final portion of the decomposition sequence of $LiClO_3$, *i.e.*, Reaction 5. As in the instance of the higher heating rate, the use of bare thermocouples resulted in the onset of rapid decompo-

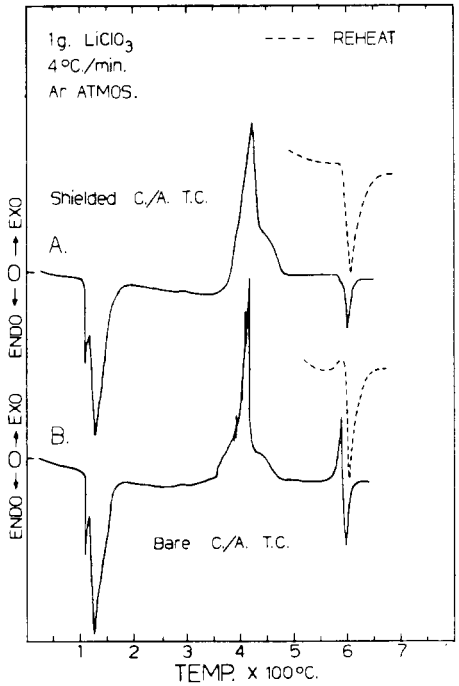

Figure 2. D.T.A. curves of $LiClO_3$ heated at 4°/min.

Table I. Decomposition Paths of $LiClO_3$ at 339 ± 1°

Time, Hrs.	Mole Fraction $LiClO_3$ Remaining	x_1	x_2	x_3	x_2/x_3
1	0.9483	0.0000	0.0260	0.0257	1.012
3	0.8700	0.0000	0.0769	0.0531	1.448
5	0.6693	0.0008	0.1899	0.1400	1.356
7	0.4794	0.0012	0.2861	0.2333	1.226
8	0.3807	0.0046	0.3184	0.2963	1.075
10	0.2972	0.0032	0.3558	0.3438	1.035
12	0.2401	0.0064	0.3807	0.3728	1.021
16	0.0294	0.0066	0.3828	0.5812	0.659
24	0.0041	0.0026	0.3590	0.6343	0.409
64	0.0057	0.0088	0.2452	0.7403	0.331

sition at lower temperatures (355°) than with the shielded thermocouples (367°). It is pertinent to note the considerable oscillations in ΔT shown in the decomposition regions of Figures 1b and 2b.

The explanation for the differences observed for the two types of thermocouple arrangements was traced to the attack of the bare metals by the sample melt. Qualitative analyses (*17*) of decomposed residues from DTA runs showed the presence of soluble Cr and Ni compounds as well as black solid particles of metal oxides in only those samples in which bare thermocouples had been immersed. Thus, the use of unshielded thermocouples in these experiments must give rise to both homogeneous and heterogeneous catalysis of the decompositions of $LiClO_3$ and of $LiClO_4$, thereby introducing additional experimental complications. The application of bare thermocouples is feasible when there is no likelihood of sample-thermocouple interactions (*42*). The promotion of the pyrolysis of $LiClO_3$ by chromel-alumel couples was also demonstrated by isothermal studies in $LiClO_3$ melts with and without the presence of composite wire spirals.

A partial cause of the poor development of the second exotherm in the decomposition region of $LiClO_3$ may be found by examination of the final endotherms in Figures 1 and 2 attributable to the fusion of the major residual reaction product, LiCl (m.p., 614°). In each of these curves, the fusion endotherm is much smaller during the first heating than during the second heating and, in some instances, is actually preceded by an exotherm in the initial heating. This type of behavior would indicate that the thermocouple is initially in contact with only a fraction of the LiCl formed as a result of decomposition and that after the initial fusion, the amount of LiCl in the region of the thermocouple is augmented. Visual observations of the samples in the temperature interval between the beginning and the end of rapid decomposition (*i.e.*, after complete conversion to solid LiCl) showed that the turbulence of the pyrolysis reactions had caused the sample to overflow the holder and to be distributed over the entire inner surface of the containing tube. This resulted in a diminution of the mass of material in the vicinity of the thermocouple and in poor thermal contact between sample and sensor (*35*). These effects appeared to be more pronounced at the higher heating rate (Figure 1); at the lower heating rate (Figure 2), there was sufficient sample retained in the bottom of the quartz holder after the first stage of $LiClO_3$ decomposition (Reaction 4) to give indications of the second exotherm (Reaction 5). The use of still lower heating rates (1° and 2°/min.) or of a smaller sample size (0.5 g.), and a wider sample holder (one inch) at a heating rate of 4°/min. somewhat improved the development of the second exotherm but also decreased the areas bounded by all the breaks. The exotherms prior to LiCl fusion are due to enhanced thermal conductivity because of liquid phase formation causing better thermocouple-sample contact and furnace-sample heat transfer. This type of behavior has been observed in other systems undergoing fusion phenomena during DTA (*5*).

An interrupted DTA run was carried out to the first peak temperature indicated in Figure 2a (425°) and the quenched residue was analyzed. It contained (mole %) 0.88% $LiClO_3$, 0.55% Li_2O, 68.24% LiCl, and 30.33% $LiClO_4$ (by difference). Clearly then the second exotherm (Figure 2a) could be associated with the thermal decomposition of $LiClO_4$ (Reaction 5). The mole ratio of LiCl to $LiClO_4$ at this point was 2.25 rather than 1.67 as expected from the isothermal runs at 339°. However, as will be seen subsequently, the complementary TGA experiments on $LiClO_3$ closely fulfilled the anticipation of two distinct stages in the pyrolysis of $LiClO_3$ under these experimental conditions (viz., Equations 4 and 5). A sharper resolution of these two levels of reaction was not possible by DTA because of the combined effects of sample turbulence, of large thermal gradients, and perhaps most importantly, of the overlapping of exothermic breaks due to successive reaction. This last occurrence causes a continuation of the first peak due to the start of the second succeeding exotherm. As will be shown later, a large degree of thermal overlap probably occurs at the higher heating rate, which in addition to increased sample turbulence over the lower heating rate, causes virtually complete obscurity of the heat release from Reaction 5.

TGA Pattern of $LiClO_3$. Figure 3a illustrates a typical TGA curve for $LiClO_3$. The rate of weight loss becomes appreciable at about 370° and is followed by a marked decrease in rate at about 430° where the aggregate weight loss is 27.7%. This weight loss corresponds closely to that expected for Equation 4, *i.e.*, $8LiClO_3 \rightarrow 5LiCl + 3LiClO_4 + 6O_2$ (calcd. weight loss, 26.6%). The subsequent reaction period (ca. 430–490°) would then be related to Reaction 5, *i.e.*, $LiClO_4 \rightarrow LiCl + 2O_2$. This latter reaction proceeds more rapidly than for pure $LiClO_4$ due to autocatalysis provided by the LiCl from the preceding reaction (*33, 36, 37*). TGA experiments with pure $LiClO_4$ show rapid decomposition to ensue at about 445°.

A 1.0905 gram sample of $LiClO_3$ was heated in the TGA apparatus to the loss of 0.2925 gram (calcd. for 50% loss of available O_2, 0.2896 gram). The quenched residue was analyzed for $LiClO_3$ and LiCl contents and in conjunction with the weight loss data the following assay was obtained (mole %): 2.40% $LiClO_3$, 1.97% Li_2O, 57.25% LiCl, and 38.37% $LiClO_4$. The mole ratio of LiCl to $LiClO_4$ is thus 1.49, in fairly good agreement with that (1.67) to be predicted from the occurrence of Reactions 2 and 3 to equal extents, *i.e.*, Equation 4.

The total weight loss suffered by $LiClO_3$ (Figure 3a) is 102.6% of that based on completion of Reaction 3, *i.e.*, $LiClO_3 \rightarrow LiCl + \frac{3}{2}O_2$. Inasmuch as earlier experiments had indicated the presence of Li_2O in decomposed $LiClO_3$ residues, the augmented weight loss could be accounted for by the occurrence of Reaction 1, $LiClO_3 \rightarrow \frac{1}{2}Li_2O + \frac{1}{2}Cl_2 + \frac{5}{4}O_2$, to the extent of 3.8%. Direct determination of the total amount of Cl_2 evolved from the decomposition of $LiClO_3$ indicated Reaction 1 to occur to the extent

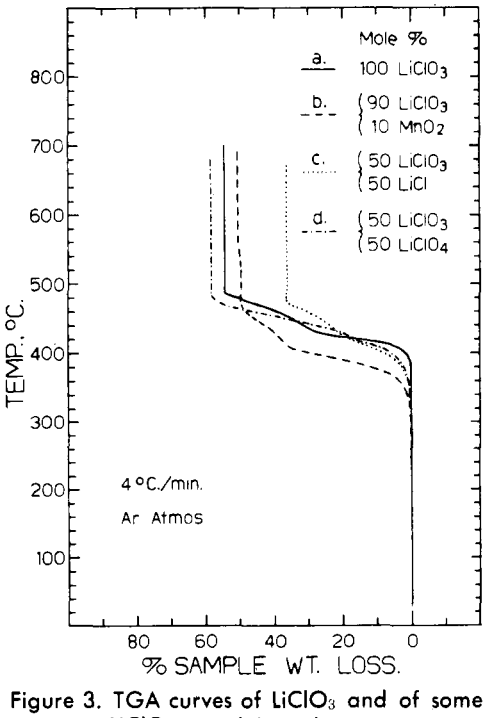

Figure 3. TGA curves of $LiClO_3$ and of some $LiClO_3$-containing mixtures

of 4.5%. As will be demonstrated later, the ability of $LiClO_3$ to yield Li_2O on thermal decomposition constitutes the foundation for its use as an elevated temperature base in reactions with acidic or oxide ion deficient materials.

Note that the TGA curve for $LiClO_3$ up to 430° reflects principally the occurrence of Reaction 3 because Reaction 2 does not engender any change in sample weight, whereas the DTA curve over the same temperature range manifests the composite results of the heat release from both Reactions 2 and 3.

Thermal Behavior of Some $LiClO_3$-Containing Mixtures. 90 Mole % $LiClO_3$–10 Mole % MnO_2. As is known for $KClO_3$ (*7, 9, 20*), it was found for $LiClO_3$ that MnO_2 causes the acceleration of O_2 evolution. This effect may be seen from Figures 3b and 4a where the onset of rapid decomposition of $LiClO_3$ occurs at about 330°. From both the DTA and TGA curves it appears that the quantity of $LiClO_4$ formed by Reaction 2 is diminished by the presence of the MnO_2. Thus, the second exothermic break in Figure 4a is smaller than for pure $LiClO_3$ and the inflection at 406° in the TGA curve (Figure 3a), attributable to the onset of rapid pyrolysis of $LiClO_4$, occurs at a weight loss (72.8% of that based on Reaction 3) indicative of about 25% conversion of $LiClO_3$ to $LiClO_4$, rather than 50% as for Reaction 2. It appears then that the effect of MnO_2 is to catalyze chloride formation over perchlorate formation.

The catalytic action of a 10 mole % addition of MnO_2 to $LiClO_4$ results in the lowering of the start of rapid decomposition to about 402°.

50 Mole % $LiClO_3$–50 Mole % LiCl. Both the DTA (Figure 4b) and TGA (Figure 3c) patterns indicate that the onset of rapid decomposition of $LiClO_3$ is lowered to about 343° by the presence of the LiCl. From the TGA curve it is seen that the LiCl appears to catalyze both O_2 evolution and $LiClO_4$ formation inasmuch as the inflection in rate of weight loss at 422° corresponds to the completion of Reaction 3 to 55.5%; the succeeding portion of the TGA curve is, of course, attributed to the decomposition of the $LiClO_4$ content (Reaction 5).

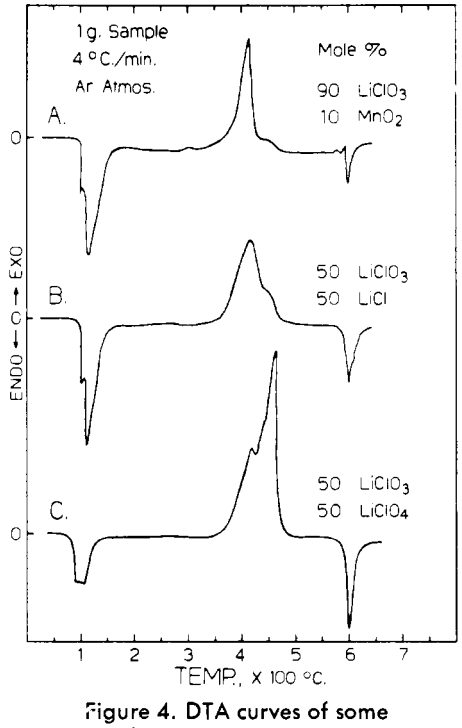

Figure 4. DTA curves of some $LiClO_3$-containing mixtures

50 Mole % $LiClO_3$–50 Mole % $LiClO_4$. Decomposition phenomena are seen to ensue at about 350° from both the DTA (Figure 4c) and TGA (Figure 3d) runs. The DTA curve shows the second exotherm to be considerably augmented over pure $LiClO_3$ as would be expected from the increased $LiClO_4$ content of the sample. The initial endotherm at about 100° corresponds to liquid phase formation in this binary mixture as observed visually with a separate sample.

$LiClO_3$–Condensed Phosphate Mixtures. It was thought that as in the instance of $LiClO_4$ (*44*), $LiClO_3$ might prove effective as a depolymerizing agent for condensed lithium phosphates (*e.g.*, $Li_4P_2O_7$ and the polymeric $LiPO_3$) through its decomposition as per Reaction 1 which yields O^{-2} ions. Total Cl_2 evolution and preliminary DTA and TGA studies showed reaction to become measurable at about 250° for the mixtures of Table II which also summarizes the extents of conversion of the $LiClO_3$ contents to Li_2O.

The formation of Li_2O in the mixtures of Table II is reflected in the disruption on the polyphosphate ions to yield simpler anionic species (*30*). Thus, x-ray powder patterns of the heated residues from samples 1, 2, and 3 showed the presence of $Li_4P_2O_7$ and Li_3PO_4 in samples 1 and 2 and Li_3PO_4 in sample 3; each residue showed a considerable decrease in line intensities attributable to the original condensed phosphate reactant. These x-ray data in combination with the results of Table II demonstrate the occurrence of the reactions:

$$2LiClO_3 + 2LiPO_3 \rightarrow Li_4P_2O_7 + Cl_2 + \tfrac{5}{2}O_2 \quad (7)$$

$$2LiClO_3 + Li_4P_2O_7 \rightarrow 2Li_3PO_4 + Cl_2 + \tfrac{5}{2}O_2 \quad (8)$$

Consequently, acid-displacement reactions of the type: $Li_2O \cdot Cl_2O_5 + Li_2O \cdot P_2O_5 \rightarrow (2Li_2O) \cdot P_2O_5 + Cl_2 + \tfrac{5}{2}O_2$ are suggested. Reactions 7 and 8 ensue at considerably lower temperature than does the thermal decomposition of $LiClO_3$ itself (365°), or condensed phosphate depolymerization using $LiClO_4$ (*44*), or Li_2O, LiOH, Li_2CO_3, and Li_2O_2 as bases (*40*).

Corresponding types of depolymerization reactions with $KClO_3$ are implied by noting the increased Cl_2 evolution found in $KClO_3$-$K_2S_2O_7$ (*16*) and in $KClO_3$-Cr_2O_3 (*47*) mixtures. In addition, Mellor (*46*) and others (*20*) have observed the general increase in evolved Cl_2 from decomposing $KClO_3$ in the presence of acidic oxides.

DISCUSSION OF RESULTS

Some significant insights into the pyrolysis of $MClO_3$ salts in general and of $LiClO_3$ in particular may be gained by consideration of some of the thermodynamic quantities (ΔF_f°, ΔH_f°) associated with the observed chemical changes. However, as in the instances of the corresponding $MClO_4$ compounds (*31*), there is a paucity of thermodynamic data for chlorates. Accordingly, some of these values will have to be estimated (*31*).

ΔH_f° values at 25° are available for $NaClO_3$, $KClO_3$, and $RbClO_3$ (*53*) and the approximate values of ΔH_f° at 25° for $LiClO_3$ and $CsClO_3$ may be derived from the former data by use of a method proposed by Hoppe (*27*). He

Table II. Some $LiClO_3$-Condensed Phosphate Reactions

Sample No.	Initial Composition, Mole %	% Conversion of $LiClO_3$ to Li_2O	
		TGA data	Cl_2 evolution
1	50 $LiClO_3$–50 $LiPO_3$	99.7	94.8
2	66.7 $LiClO_3$–33.3 $LiPO_3$	61.0	57.8
3	66.7 $LiClO_3$–33.3 $Li_4P_2O_7$	48.8	50.8

established the existence of a linear relationship between the equivalent heats of formation of oxyanion compounds of noble gas-type cations (*e.g.*, the alkali and alkaline earth metals) from the corresponding metal oxides and acid anhydrides $[\Delta R_f^\circ(M_yXO_z)]$ and the difference in equivalent heats of formation between the metal chlorides and oxides. Thus, for the alkali metals:

$$\Delta R_f^\circ(M_yXO_z) = [\Delta H_f^\circ(M_yXO_z)]_{equiv.} - [\Delta H_f^\circ(M_2O)]_{equiv.} - [\Delta H_f^\circ(X_aO_b)]_{equiv.} \quad (9)$$

$$\Delta R_f^\circ(M_yXO_z) = A[\Delta H_f^\circ(MCl) - \tfrac{1}{2}\Delta H_f^\circ(M_2O)] + B \quad (10)$$

Close linearity was found to hold among various nitrates, orthophosphates, carbonates, sulfites, sulfates, and perchlorates where the appropriate data were available. Thus, knowledge of $\Delta R_f^\circ(M_yXO_z)$, $\Delta H_f^\circ(MCl)$, and $\Delta H_f^\circ(M_2O)$ for some members of a particular class of oxyanion compounds at a given temperature permits an estimate to be made of the unknown $\Delta H_f^\circ(M_yXO_z)$ for a specific compound of that class. The application of this approach to $MClO_4$ salts gives the data of Table III (*26, 27*), where $\Delta H_f^\circ(MClO_4)_{calcd.}$ at 25° was obtained from the equation:

$$\Delta R_f^\circ(MClO_4) = 1.124\,[\Delta H_f^\circ(MCl) - \tfrac{1}{2}\Delta H_f^\circ(M_2O)] - 22.91 \quad (11)$$

Table III shows the close agreement secured between the literature and the calculated values for $\Delta H_f^\circ(MClO_4)$ at 25°.

Inasmuch as there is no known acid anhydride of $HClO_3$, it will be necessary to utilize as the basis for the calculation of $\Delta R_f^\circ(MClO_3)$ for $LiClO_3$ and $CsClO_3$, the reaction (*55*):

$$ClO_3 + \tfrac{1}{2}M_2O \rightarrow \tfrac{1}{2}MClO_4 + \tfrac{1}{2}MClO_3 \quad (12)$$

$\Delta H_f^\circ(ClO_3)$ and $\Delta H_f^\circ(MClO_4)$ are known as well as $\Delta H_f^\circ(MClO_3)$ for $NaClO_3$, $KClO_3$, and $RbClO_3$. These data are incorporated in Figure 5 which corresponds to the equation:

$$\Delta R_f^\circ(MClO_4, MClO_3) = 1.34[\Delta H_f^\circ(MCl) - \tfrac{1}{2}\Delta H_f^\circ(M_2O)] - 11.08 \quad (13)$$

Therefore,

$$\Delta H_f^\circ(MClO_3) = 2.68\,\Delta H_f^\circ(MCl) - 0.34\,\Delta H_f^\circ(M_2O) - \Delta H_f^\circ(MClO_4) + 2\Delta H_f^\circ(ClO_3) - 22.16 \quad (14)$$

The computed values at 25° of $\Delta H_f^\circ(MClO_3)$ are given in Table IV and are found to be in good agreement with the corresponding literature values where these are known (*53*).

ΔF_f° data at 25° are available for $NaClO_3$ (−59.1 kcals./mole) (*28*), $KClO_3$ (−69.3 kcals./mole) (*53*), and $RbClO_3$ (−67.8 kcals./mole) (*53*). These values yield an average entropy change ($\Delta\bar{S}^\circ$) of 64.2 ± 3.4 e.u. for the conversion of $MClO_3$ to MCl (Reaction 3). Thus, $\Delta F_f^\circ(MClO_3)$ may be computed for $LiClO_3$ and $CsClO_3$ from the equation:

$$\Delta F_f^\circ(MClO_3) = T\Delta\bar{S}^\circ + \Delta F_f^\circ(MCl) - (\Delta H_f^\circ(MCl) - \Delta H_f^\circ(MClO_3) \quad (15)$$

and were calculated to be −45.1 and −72.9 kcals./mole, respectively, at 25°.

From the aggregate data on $\Delta H_f^\circ(MClO_3)$ and $\Delta F_f^\circ(MClO_3)$ at 25°, the entries in Table V were derived to characterize the decompositions of $MClO_3$ salts via the oxide (Reaction 16) or the chloride (Reaction 17) routes:

$$MClO_3\,(solid) \rightarrow \tfrac{1}{2}M_2O\,(solid) + \tfrac{1}{2}Cl_2\,(gas) + \tfrac{5}{4}O_2\,(gas) \quad (16)$$

$$MClO_3\,(solid) \rightarrow MCl\,(solid) + \tfrac{3}{2}O_2\,(gas) \quad (17)$$

Thus,

$$\Delta F^\circ(16) = \tfrac{1}{2}\Delta F_f^\circ(M_2O) - \Delta F_f^\circ(MClO_3), \text{ and } \Delta F^\circ(17) = \Delta F_f^\circ(MCl) - \Delta F_f^\circ(MClO_3)$$

Inspection of Table V clearly shows that the chloride route yields the more thermodynamically favored final reaction state for the thermal decompositions of $MClO_3$ compounds. As was demonstrated with the corresponding perchlorate salts (*31*), the ultimate product distribution is determined by the relative thermodynamic stabilities of the chlorides and oxides on an equivalent basis. $LiClO_3$, like $LiClO_4$, can decompose so as to yield Li_2O as well as LiCl, and this is undoubtedly indicated by the Cl_2 contents of their evolved gaseous decomposition products.

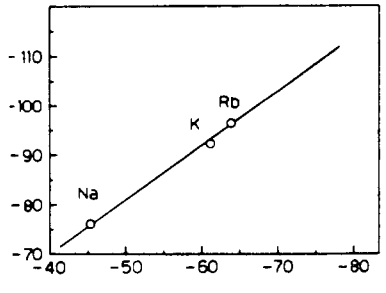

Figure 5. Plot of ΔR_f° ($MClO_4$-$MClO_3$) = $[\frac{1}{2}\Delta H_f^\circ(MClO_4) + \frac{1}{2}\Delta H_f^\circ(MClO_3) - \Delta H_f^\circ(ClO_3) - \frac{1}{2}\Delta H_f^\circ(M_2O)]$, *y* axis *vs.* $[\Delta H_f^\circ(MCl) - \frac{1}{2}\Delta H_f^\circ(M_2O)]$, *x* axis

Table III. Method of Hoppe (*27*) as Applied to the Alkali Metal Perchlorates (25°)

Compound	$\Delta H_f^\circ(MClO_4)_{lit.}$[a]	$\Delta H_f^\circ(MClO_4)_{calcd.}$[a]
$LiClO_4$	−91.7 (*43*)	−92.2 (*26*)
$NaClO_4$	−92.2 (*53*)	−95.4 (*27*)
$KClO_4$	−103.6 (*53*)	−103.0 (*27*)
$RbClO_4$	−103.9 (*53*)	−102.1 (*27*)
$CsClO_4$	−103.9 (*53*)	−106.9 (*27*)

[a] Kcals./mole.

Table IV. $\Delta H_f^\circ(MClO_3)$ at 25° (Kcals./Mole)

Compound	$\Delta H_f^\circ(MClO_3)_{lit.}$ (*53*)	$\Delta H_f^\circ(MClO_3)_{calcd.}$
$LiClO_3$	...	−70.0
$NaClO_3$	−85.7	−85.4
$KClO_3$	−93.5	−94.4
$RbClO_3$	−93.8	−93.5
$CsClO_3$	...	−96.0

Table V. Thermodynamic Parameters (Kcals./Mole at 25°) for the Final Decomposition States of $MClO_3$ Compounds

Compound	ΔF_f°[a]	ΔH_f°[a]	ΔF_f°[b]	ΔH_f°[b]
$LiClO_3$	−21.8[c]	−1.2[c]	−46.8[c]	−27.7[c]
$NaClO_3$	14.2	36.0	−32.7	−12.5
$KClO_3$	31.1	53.0	−28.3	−10.7
$RbClO_3$	33.0	54.4	−30.7	−9.1
$CsClO_3$	40.4[c]	58.0[c]	−26.6[c]	−7.5[c]

[a] Reaction 16. [b] Reaction 17. [c] Estimated values.

Of interest in resolving the reaction sequences of $MClO_3$ compounds are the two additional general reactions, viz.,

$$MClO_3\ (solid) \rightarrow \tfrac{3}{4}MClO_4\ (solid) + \tfrac{1}{4}MCl\ (solid) \quad (18)$$

$$MClO_3\ (solid) + \tfrac{1}{2}O_2\ (gas) \rightarrow MClO_4\ (solid) \quad (19)$$

The pertinent thermodynamic data for these reactions are given in Table VI.

The close similarity in numerical values for $\Delta F_?^\circ$ (18) and $\Delta H_?^\circ$ (18) is to be expected for a completely solid phase reaction inasmuch as there is little or no loss in the number of degrees of vibrational freedom contributing to the heat capacity of the system as a result of the chemical change, *i.e.*, $\Delta S_?^\circ$ (18) $\cong 0$. However, the most surprising result of Table VI is the indication that direct oxygenation of chlorates to perchlorates appears possible (Reaction 19). Reaction 18 may be resolved into two simpler processes, viz.,

$$MClO_3 \rightarrow MCl + \tfrac{3}{2}O_2 \quad (20)$$

$$3MClO_3 + \tfrac{3}{2}O_2 \rightarrow 3MClO_4 \quad (21)$$

$$4MClO_3 \rightarrow 3MClO_4 + MCl \quad (22)$$

Thus, from Table VI a thermodynamic basis is available to support the contention that reversible interconversion of $MClO_3$ and $MClO_4$ compounds as per:

$$MClO_3 + \tfrac{1}{2}O_2 \rightleftarrows MClO_4 \quad (23)$$

might be a significant step in the thermal decompositions of these materials (*21, 56, 57*). This assumes that $\Delta F_?^\circ(MClO_3)$ and $\Delta F_?^\circ(MClO_4)$ maintain the same relative values from 25° to reaction temperatures.

Measurable quantities of the lower halates ($MClO$, $MClO_2$) have never been reported from decomposition studies of $MClO_3$ and $MClO_4$ salts, thereby suggesting that reactions such as:

$$MClO_{3\ or\ 4} \rightarrow MClO + O_2 \text{ or } \tfrac{3}{2}O_2 \quad (24)$$

$$MClO_{3\ or\ 4} \rightarrow MClO_2 + \tfrac{1}{2}O_2 \text{ or } O_2 \quad (25)$$

probably do not play an important role; rather the reverse reaction type seems to be true inasmuch as the pyrolysis of $MClO$ and $MClO_2$ compounds usually follow a course leading to transient $MClO_3$ formation (*1, 24*). The latter would therefore indicate substantially irreversible internal oxygenation effects like those indicated below:

$$2MClO \rightarrow 2MCl + O_2 \quad (26)$$

$$MClO + O_2 \rightarrow MClO_3 \quad (27)$$

$$3MClO \rightarrow MClO_3 + 2MCl \quad (28)$$

$$MClO_2 \rightarrow MCl + O_2 \quad (29)$$

$$2MClO_2 + O_2 \rightarrow 2MClO_3 \quad (30)$$

$$3MClO_2 \rightarrow 2MClO_3 + MCl \quad (31)$$

The present studies show that $LiClO_3$ melts (maintained at some temperature T_1) can accumulate considerable quantities of $LiClO_4$ during thermal decomposition; on the other hand, $LiClO_4$ achieving a measurable rate of pyrolysis (at some temperature T_2, $T_2 > T_1$) yields only a small $LiClO_3$ content at any stage of decomposition (*36*). Similar results have been found in investigations of the decompositions of $KClO_3$ (*20, 21, 23, 25, 50*) and of $KClO_4$ (*4, 21, 22, 23, 25, 49, 56*). These observations undoubtedly stem from the greater thermodynamic stabilities of $MClO_4$ salts as compared to the corresponding $MClO_3$ compounds (Table VI), *i.e.*, the forward of Reaction 23 is favored over the reverse reaction, and from the greater kinetic stabilities of perchlorates over chlorates. The latter point was readily demonstrated in the present work for $LiClO_3$ in comparison with $LiClO_4$ and has been found to be true for $MClO_3$ and $MClO_4$ compounds in general (*40*). The ultimate pyrolysis of $LiClO_4$ to LiCl which produces $LiClO_3$ as an intermediate (*36*) through the rate-controlling reaction $LiClO_4$ (liquid) $\rightarrow$ $LiClO_3$ (liquid) + $\tfrac{1}{2}O_2$ (gas) is due to the rapid irreversible decomposition of $LiClO_3$ to LiCl (Reaction 17). The trends in the available thermodynamic and kinetic data would suggest that the behavior observed with $LiClO_3$ and $LiClO_4$ also prevails for the other $MClO_3$ and $MClO_4$ compounds. The preparation of pure chlorates from decomposing perchlorates though apparently possible at low partial pressure of oxygen for the heavier alkali metals (Table VI) does not appear feasible because of the simultaneous intervention of Reaction 17 with the reverse of Reaction 19. Similarly, the complete conversions of chlorates into perchlorates as per the composite Reaction 22 seems unlikely unless the rate of oxygen production (Reaction 20) is less than the rate of chlorate oxygenation (Reaction 21), a circumstance which does not appear to hold for either $LiClO_3$ or $KClO_3$ (*16, 25*).

Despite the indications from Table VI that direct oxygenation by molecular oxygen of $MClO_3$ to $MClO_4$ is thermodynamically possible at low temperatures and partial pressures of oxygen, this conversion has not been observed by mere exposure of $MClO_3$ to O_2. Thus, the treatment of $KClO_3$ at 475° with 1200 atmospheres O_2 pressure did not result in formation of $KClO_4$ (*14*). In the present study, maintaining samples of pure $LiClO_3$, 80 mole % $LiClO_3$–20 mole % $LiClO_4$, and 80 mole % $LiClO_3$–10 mole % $LiClO_4$–10 mole % LiCl at 150° for two days under 100 atmospheres O_2 pressure resulted in no change in the compositions of these samples. Thus, it seems likely that the $MClO_3$–$MClO_4$ conversion (Reaction 23) is achieved through atomic oxygen (*21, 22, 23, 57*). As a result the circumstances prevailing in a melt of decomposing chlorate cannot be readily duplicated in the laboratory. However, it is of interest to note that up to 350°, the rate of decomposition of $KClO_3$ to KCl and O_2 in $KClO_3$–MnO_2 mixtures was greatly retarded by application of high O_2 pressures (*45*). Decomposition of the $KClO_3$ had apparently only been followed by analyses for KCl, so that the possibility of enhanced $KClO_4$ formation under these conditions by Reaction 23, unfortunately, could not be tested.

The exothermic decomposition portion of the DTA curve of $LiClO_3$ (Figure 2a) can be resolved into its component parts by further consideration of the TGA and the heat of formation data for this compound. As seen, the TGA pattern (Figure 3a) delineates two major stages of weight loss and it is to be anticipated that these overall changes

Table VI. Thermodynamic Parameters (Kcals./Mole at 25°) for $MClO_4$ Formation from $MClO_3$ Compounds

Compound	$\Delta F_?^\circ$[a]	$\Delta H_?^\circ$[a]	$\Delta F_?^\circ$[b]	$\Delta H_?^\circ$[b]
$LiClO_3$	−23.3[c]	−23.2[c]	−15.4[c]	−21.7[c]
$NaClO_3$	−8.6	−8.0	−0.5	−4.1
$KClO_3$	−9.5	−10.3	−3.4	−10.1
$RbClO_3$	−11.7	−9.8	−5.4	−10.1
$CsClO_3$	−7.0[c]	−7.7[c]	−0.4[c]	−7.9[c]

[a] Reaction 18. [b] Reaction 19. [c] Estimated values.

will also be manifested in the DTA curve of $LiClO_3$ in terms of the following reactions:

$$8LiClO_3 \text{ (liquid)} \rightarrow 2LiCl \text{ (solid)} + 3LiCl \text{ (liquid)} + 3LiClO_4 \text{ (liquid)} + 6O_2 \text{ (gas)} \quad (32)$$

$$3LiClO_4 \text{ (liquid)} \rightarrow 3LiCl \text{ (solid)} + 6O_2 \text{ (gas)} \quad (33)$$

A saturated solution of LiCl in $LiClO_4$ at about 425° is of approximately a 1:1 mole ratio of components (*36*) and this composition was used to estimate the phase distribution resulting in Reaction 32. Assuming that the changes represented by Equations 32 and 33 occur at an average temperature of 425°, values of $\Delta H_?$ may be computed for these reactions. In the calculations, enthalpy changes due to solution effects are neglected. $\Delta H_?(LiClO_3)_{liquid}$ is taken to be −68.0 kcals./mole on the assumption that the entropy of fusion of $LiClO_3$ is 5 e.u. and, therefore, $\Delta H^\circ_{fusion}(LiClO_3) = T_{m.p.}, \Delta S^\circ_{fusion}(LiClO_3) = 2.0$ kcals./mole (*60*). Values of $\Delta H_?(LiCl)_{liquid\ and\ solid}$ and $\Delta H_?(LiClO_4)_{liquid}$ are available for 425° (*15*). The calculations show $\Delta H_?$ (Reaction 32) = −175.2 kcals. and $\Delta H_?$ (Reaction 33) = −46.2 kcals. which coincide roughly with the relative sizes of the two exothermic breaks found in the DTA curve of $LiClO_3$ (Figure 2a). The high degree of heat loss caused by sample dispersal and decreased sample mass in contact with the thermocouple can be gauged by comparing the second exotherm in Figure 2a with the corresponding exotherm from the DTA of 0.73 grams of a mixture of LiCl and $LiClO_4$ in 5:3 mole ratio, *i.e.*, the residual product produced by reaction (32) during the DTA of one gram $LiClO_3$. It was found that this mixture yielded a rather coherent reaction residue with little sample splattering evident, and that the final LiCl fusion endotherm agreed well in area with that obtained by DTA of 0.47 gram LiCl. Thus, the ratio of areas of the second exotherm in Figure 2a to that from the synthetic $LiClO_4$–LiCl mixture was about 1:3.

The effects of thermal overlap of successive reactions during DTA and the role that the heating rate plays in this phenomenon are of interest. At 10°/min. heating rate (Figure 1a), no resolution of the decomposition sequence was found, but such a differentiation did appear at 4°/min. heating rate (Figure 2a). Observe that the peak exothermal temperature recorded in Figure 1a is about 445°, whereas that in Figure 2a is only about 425°. Apparently, at the higher heating rate, during decomposition, the sample can attain higher temperatures than at the lower heating rate, so that Reactions 32 and 33 can occur simultaneously at appreciable rates. However, at the lower heating rate there is less sample selfheating and thus a clearer definition of reactions of differing rates. Therefore, the degree of thermal overlap is greater at the higher heating rate than at the lower heating rate (Figure 6). At the proper heating rate, the TGA method does not appear to suffer appreciably from the shortcoming of overlapping of the effects of successive reactions (Figure 3a). Those approaches developed for securing quantitative kinetic data from dynamic DTA (*6*) and TGA (*19*) experiments do not seem applicable to chlorate salts due to the factors of large thermal transients and to the occurrence of multiple reaction paths.

Analyses of the Cl–O bonding characteristics in ClO_x^- ions (x = 1, 2, 3, 4) have shown the extent of π-bonding, originating from the 3d orbitals of chlorine, to be in the order (*11, 51, 59*): $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$. For the $LiClO_x$ compounds, as well as for $MClO_x$ compounds in general, the observed order of thermal stabilities is $MClO_4 > MClO_3 > (MClO_2, MClO)$. It has been found that the pyrolyses of $MClO_3$ salts results in the intermediate

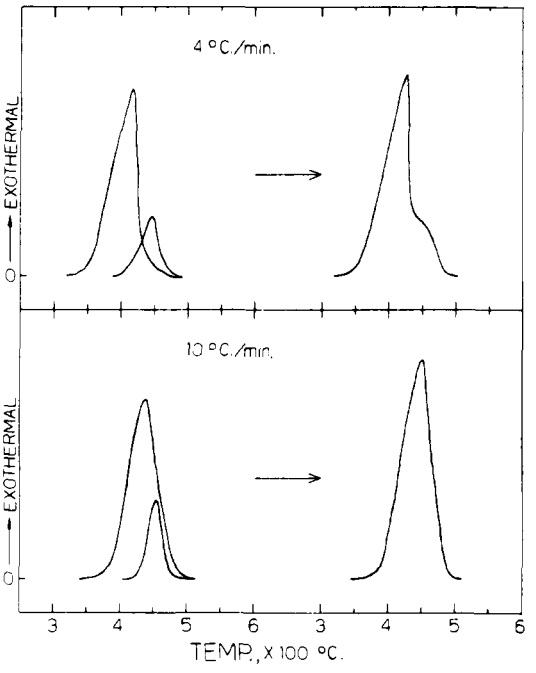

Figure 6. Thermal overlap of successive reactions during DTA

formation of $MClO_4$ and that the decompositions of $MClO_2$ and MClO involve transient $MClO_3$ formation. Thus, a portion of the thermal breakdown of the lower $MClO_x$ compounds ($x < 4$) is accompanied by a transition of these oxyanions to states of higher degrees of π-bonding.

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Isomeric Bis(Vinylphenyl)borinic Acids

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The synthesis of bis(*o*-, *m*-, and *p*-vinylphenyl)borinic acids, isolated as their 2-aminoethyl esters, is reported. The bis(*o*- and *m*-vinylphenyl)borinic acids were obtained as uncrystallizable oils by hydrolysis of their esters. The para isomer could not be isolated in monomeric form.

THE AUTHORS described, in a recent paper (*1*), the synthesis of the isomeric vinylbenzeneboronic acids and now wish to report the synthesis of the corresponding bis(*o*-, *m*-, and *p*-vinylphenyl)borinic acids.

Both bis(*o*-vinylphenyl)borinic acid and the corresponding meta isomer were prepared by allowing 2 moles of *o*(or *m*)-vinylphenylmagnesium bromide to react with 1 mole of butyl borate at low temperature. The reaction mixture was hydrolyzed with dilute hydrochloric acid, and the product was isolated from the ethereal solution as the 2-aminoethyl ester. This method of isolation was more advantageous than attempts to isolate the free acid.

Both esters were readily hydrolyzed in the presence of dilute hydrochloric acid, yielding the free acids as viscous oils which could not be induced to crystallize. All attempts to dehydrate the acids led to polymer formation exclusively.

An initial attempt to synthesize bis(*p*-vinylphenyl)-borinic acid by the method employed for the ortho and meta isomers met with remarkable success; a 58% yield of the crude 2-aminoethyl ester was obtained, which melted at 170–175° C. This result could not be repeated, however; only polymeric material was isolated in each additional attempt. However, when hydrolysis was effected with an aqueous solution of ammonium chloride, a 35% yield of the ester was obtained. Alternately, this ester could be obtained (35%) by treating the reaction mixture with an excess of 2-aminoethanol rather than with aqueous ammonium chloride. No attempt was made to isolate the free acid.

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