THE DIFFERENTIAL THERMAL ANALYSIS OF PERCHLORATES. II. THE SYSTEM LiClo₄-LiNO₃

BY MEYER M. MARKOWITZ

Foote Mineral Company, Research and Development Department, Berwyn, Penna.

Received February 24, 1958

The phase system $LiClO_4-LiNO_3$ was found to be of the simple eutectic type with the eutectic at about 172° and at a composition of 53.5 mole % $LiClO_4$, 46.5 mole % $LiNO_3$. In contrast with the other alkali metal perchlorates, which display but a short temperature interval between fusion and rapid decomposition, lithium perchlorate is thermally stable at and above its melting point. Like many other metal salts of oxyacids, the ease of thermal decomposition of perchlorates generally increases as the size of the cation decreases.

A review of the literature reveals that there is a paucity of phase studies of anhydrous systems involving perchlorate salts. This lack of data can be attributed to the thermal instability of most perchlorates at fusion temperatures.¹ In the course of an investigation of the thermal behavior of lithium perchlorate, it was found that this substance exhibited considerable stability at its melting point (247°) and to some temperature beyond. However, differential thermal analyses (DTA),² and thermogravimetric analyses,³ show that lithium perchlorate decomposes at a lower temperature than the other alkali metal perchlorates. Nevertheless, there exists a sufficiently long temperature interval between the melting point and the onset of rapid decomposition of the salt to permit a high temperature phase study involving this compound.

Experimental Procedures

DTA curves were obtained using the arrangement of chromel-alumel thermocouples described by Gordon and Campbell.² The recording system consisted of a 10 millivolt span Leeds-Northrup X-Y recorder which allowed for the simultaneous plotting of sample temperature *versus* the temperature differential between the 3.0-g. sample and a similar quantity of ignited alumina, the reference material. By diverting the e.m.f. from the temperature measurement through a 1000-ohm potentiometer which acted as a voltage divider, it was possible to achieve a variable range for the instrument. Because of the small magnitude of the e.m.f.'s originating from the temperature differentials, these were amplified by a Leeds-Northrup zero-center, stabilized d.c. amplifier before passage to the recorder. All temperatures reported here have been corrected by the individual calibrations of the thermocouples used.

Inasmuch as the individual salts and their mixtures have fairly low melting points, a convenient heating arrangement was constructed of an electrically heated 500-ml. threenecked flask containing Mobiltherm 600 as the heating medium. The sample and alumina were contained in small test-tubes held in the side necks of the flask; a mechanical stirrer was inserted in the center neck. The linear heating rate of 5° per minute used in the phase studies was obtained by manual adjustment of the current to the heater.

Anhydrous lithium perchlorate was prepared by neutralization of a solution of lithium hydroxide monohydrate with aqueous perchloric acid followed by prolonged drying of the resulting solution in an oven at 250°, and then final vacuum (1-3 mm.) dehydration of the solid for 8 hours at 160°. The resultant material was analyzed by precipitation as nitron perchlorate.⁴ Qualitative tests were negative for the presence of chloride by the addition of silver nitrate, and of chlorate by reduction with sulfurous acid and addi-

tion of silver nitrate. Analysis of product: ClO_4 , 92.3 (calcd., 93.5).

(catca., 93.5). Reagent grade lithium nitrate, dried under vacuum for 6 hours at 160° was analyzed by precipitation as nitron nitrate.⁴ Analysis of product: NO_8^- , 87.7 (calcd., 89.9). The Thermal Behavior of Lithium Perchlorate.—DTA

The Thermal Behavior of Lithium Perchlorate.—DTA curves of lithium perchlorate extending to about 275° reproducibily showed the appearance of but one endothermic break at 247°, reversible upon cooling. Visual observation confirmed the correspondence of this temperature to fusion of the salt. On occasion a small, reversible endothermic break was evident at about 146°. However, by allowing a continuous stream of dry nitrogen to play on the sample during the DTA run, the 146° break disappeared. X-Ray powder patterns of the salt at 170° in a helium atmosphere showed that no change in structure over that prevailing at room temperature was occasioned past 146°. Apparently then the 146° break must be attributed to the presence of a small amount of lithium perchlorate monohydrate which is known to undergo the transition LiClO₄-H₂O. The X-ray patterns and DTA curves of the water-free salt failed to reveal any crystallographic change in lithium perchlorate. This verifies the early microscopic and thermometric work of Vorlaender and Kaascht.⁶ Such transitions are, however, characteristic of the other alkali metal perchlorates.¹ This behavior tends to show a similarity of lithium perchlorate to the non-polymorphic, anhydrous alkaline earth perchlorates.

The melting point of 247° found for lithium perchlorate in the present study agrees well with that of 247.7° as reported by Gluyas.⁷ The oft-quoted value of 236° probably stems from determinations made with water-contaminated samples.⁸

Maintaining fused lithium perchlorate at 275° for three days gave no indications of decomposition through the absence of chloride and chlorate. This is consistent with the results of Richards and co-workers^{9,10} who prepared the compound in a state of high purity by dehydrating the trihydrate during prolonged heating at 300° in a dry air current.

By carrying the DTA of lithium perchlorate to about 725° in a high temperature furnace, the phenomenon of reaction product crystallization in the DTA of inorganic perchlorates¹ was demonstrated. At a heating rate of 15° per minute, the rate of decomposition became appreciable at about 502° . The aspect of the DTA curve was akin to the upper portion of the curve obtained for lithium perchlorate trihydrate by previous workers² except that an additional, endothermic break appeared at about 610° . This corresponds closely to the melting point of lithium chloride (614°). No other breaks were observed by cooling and reheating of the final product of the DTA run.

The only heat effect found during the DTA of lithium nitrate carried out to about 275° was that associated with fusion at 257°.

(10) T. W. Richards and M. W. Cox, ibid., 36, 819 (1914).

⁽¹⁾ M. M. Markowitz, This Journal, 61, 505 (1957).

⁽²⁾ S. Gordon and C. Campbell, Anal. Chem., 27, 1102 (1955).

⁽³⁾ G. G. Marvin and L. B. Woolaver, Ind. Eng. Chem., Anal. Ed., 17, 474 (1945).

⁽⁴⁾ F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., Ninth English Edition, 1942, pp. 383-384.

⁽⁵⁾ J. P. Simmons and C. D. L. Ropp, J. Am. Chem. Soc., 50, 1650 (1928).

⁽⁶⁾ D. Vorlaender and E. Kaascht, Ber., 56, 1157 (1923).

⁽⁷⁾ R. E. Gluyas, Ph.D., Thesis, Ohio State Univ., 1952.

⁽⁸⁾ A. Potilitzen, Chem. Centr., 61, I, 72 (1890); J. Russ. Phys. Chem. Soc., 19, 339 (1887); 20, 541 (1888).

⁽⁹⁾ T. W. Richards and H. H. Willard, J. Am. Chem. Soc., 32, 4 (1910).



The System LiClO₄-LiNO₃.—The salt mixtures indicated in Table I were subjected repeatedly to DTA with passage of nitrogen gas to minimize any effects due to water absorption By this means the eutectic data and part of the liquidus data of Table I were obtained. For samples numbered 6 through 12, the liquidus temperatures were determined by direct visual observation of the appearance and disappearance of the last traces of solid in the melt.¹¹ This was necessitated by the inadequate endothermal indications of the liquidus temperature on the DTA curves for samples so close to the eutectic composition. The complete data are incorporated in Fig. 1 from which it is seen that the system is of the simple eutectic type with the eutectic at about 172° and at a composition of 53.5 mole % LiClO₄, 46.5 mole % LiNO₃. None of the samples gave evidence of decomposition of the perchlorate as shown by the absence of chloride and chlorate in the melts upon analysis.

TABLE I

The System LiClO ₄ -LiNO ₃						
Sample no.	Mole % LiClO4	Mole % LiNO₃	Eutectic, cor., °C.	Liquidus, cor., °C.		
1	100.0	0.0		247		
2	91.5	8.5	158	234		
3	90.0	10.0	158	232		
4	80.0	20.0	172	224		
5	70.0	30.0	168	205		
6	65.0	35.0	171	194		
7	60.0	40.0	170	182		
8	55.0	45.0	166	173		
9	53.5	46.5	172	Eutectic		
10	50.0	50.0	170	178		
11	47.5	52.5	171	184		
12	45.0	55.0	171	188		
13	40.0	60.0	170	197		
14	30.0	70.0	172	216		
15	20.0	80.0	172	233		
16	10.0	90.0	166	246		
17	0.0	100.0	• •	257		

(11) S. T. Bowden, "The Phase Rule and Phase Reactions," The Macmillan Co., London, 1954, pp. 208-211.

Discussion

On the basis of thermogravimetric studies,⁸ the temperatures at which the perchlorates of lithium, sodium, and potassium start to undergo appreciable weight losses are about 420, 480 and 500° , respectively. From the present DTA study on anhydrous lithium perchlorate, the temperature interval between salt fusion and the onset of rapid decomposition is from 247 to about 502° or approximately 255° . Similar data² for the other anhydrous alkali metal perchlorates are given in Table II for purposes of comparison. The decomposition reactions correspond to the conversion of the alkali metal perchlorate to the chloride plus gaseous oxygen as indicated by an endothermic break on each of the DTA curves.

TABLE II

TEMPERATURE INTERVALS BETWEEN FUSION AND ONSET OF RAPID DECOMPOSITION FOR THE ANHYDROUS ALKALI

	WIETAL FE	RUNLORATES	
Compound	Fusion, °C.	Temp. of appreciable reaction rate, °C.	Δ <i>T</i> , °C.
LiClO ₄	247	502	255
NaClO₄	482	571	89
KClO ₄	588	608	20
$RbClO_4$	612	625	13
CsClO ₄	589	620	31

A number of points are clearly illustrated by the values given in Table II. Lithium perchlorate has the longest temperature interval between fusion and onset of rapid decomposition; accordingly, it has a true melting point. The other perchlorates cannot possess fixed points of fusion because of the corresponding short temperature intervals. For each perchlorate salt, under comparable experimental conditions, the DTA technique measures the temperature at which the rate of the decomposition reaction becomes appreciable; slow decomposition may, of course, ensue at lower temperatures as indicated by the thermogravimetric studies.³

The values of the decomposition temperatures as determined by DTA increase as the radius of the cation of the alkali metal perchlorate. This is an effect that has been noted previously for the alkali metal hydrogen phosphates by similar methods,¹² for various salts of oxy acids containing oxygen bridges such as pyrosulfates¹³ and dichromates¹⁴ by equilibrium measurements, and for the alkaline earth carbonates¹⁶ and alkali metal nitrates¹⁶ by vapor pressure measurements. The decrease in thermal stability with decrease in cation size must be related to the increasing polarizing power of the cation and to the increasing crystal energy of the decomposition products with decreasing cation size.¹⁵

Acknowledgment.—Thanks are extended for the encouragement given the performance of this work

(12) R. K. Osterheld and M. M. Markowitz, THIS JOURNAL, 60, 863 (1956).

(13) H. Flood and T. Foerland, Acta Chem. Scand., 1, 781 (1947).

(14) H. Flood and A. Muan, ibid., 4, 364 (1950).

(15) W. E. Van Arkel, "Molecules and Crystals in Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., First English Edition, 1949, p. 118.

(16) M. Centnerszwer, J. chim. phys., 27, 9 (1930).

by Dr. R. G. Verdieck, Manager of Chemicals Research, Research and Development Department, and by Dr. E. M. Kipp, Director of Research, Foote Mineral Company. Appreciation is also

expressed for the cooperation of Dr. Earl Feingold, Atlantic Refining Company, for the X-ray powder patterns of lithium perchlorate under anhydrous conditions.

THE STRUCTURE OF GAS-ADSORBENT CARBONS

BY W. F. WOLFF

Research Department, Standard Oil Company (Indiana), Whiting, Indiana Received February 26, 1958

Irregularly shaped and layer-type pore structures have both been proposed for gas-adsorbent carbons. In an attempt to distinguish between these structures, the penetration by liquids with different molecular shapes into the pore systems of these carbons has been studied. Conventional nitrogen-adsorption and analytical methods have been applied to the calcu-lation of structural dimensions. The evidence favors a layer-type structure, with a micropore system consisting of molecu-lar-size fissures between relatively large graphitic planes.

Introduction

Despite a long-standing interest in the properties and uses of active carbons,¹ their structure or structures remain obscure.² Recent studies in this Laboratory have been directed toward establishing the structure of active carbons used for gas and vapor adsorption. These gas-adsorbent carbons are commonly prepared by the high-temperature steam activation of such dense carbonaceous solids as charred nutshells. In common with other active carbons, they give X-ray patterns indicating graph-ite-like regions.³⁻⁵ Their adsorption characteristics appear to be associated with a system of remarkably small and uniform pores.⁶

The X-ray evidence is generally interpreted in terms of a structure with irregularly shaped pores, and a surface formed by the exteriors of small imperfect stacks of graphitic planes. Such "crystallites" are presumed to be interconnected by regions having a disordered cross-linked structure.^{2,3}

Adsorption studies, on the other hand, suggest a layer-type structure. According to this view, the pore structure is formed by fissures between graphitic planes, and the surface is provided by the graphitic walls of these pores.^{7,8}

In an attempt to distinguish between these structures, the molecular-sieve properties of two gas-adsorbent carbons have been investigated. The penetrations of various liquids into the pore structures of the carbons were measured by a nitrogen-desorption technique. By using liquids with suitable molecular shapes it was hoped to observe differences in penetration caused by the shape of the pores. To further define the structure, average pore dimensions, graphitic plane sizes and

(1) J. W. Hassler, "Active Carbon," Chemical Publishing Company, Brooklyn, N. Y., 1951, pp. 4-9.

(2) J. J. Kipling, Quirt. Revs., 10, 1 (1956).
(3) J. C. Arnell and W. M. Barss, Can. J. Research, 26A, 236 (1948)

(4) H. Richter, G. Breitling and F. Herre, Z. angew. Phys., 8, 433 (1956),

(5) H. L. Riley, Quart. Revs., 1, 59 (1947).

(6) S. Brunauer, "The Adsorption of Gases and Vapors. Vol. I. Physical Adsorption," Princeton Univ. Press, Princeton, N. J., 1943, pp. 159, 166, 345.

(7) P. H. Emmett, Chem. Revs., 43, 69 (1948).

(8) Reference 6, pp. 176, 207, 357.

the amounts of non-carbon constituents were also determined for several such carbons.

Experimental

Commercial active carbons were used without purifica-tion. The coconut charcoal was an 8- to 14-mesh product supplied by E. H. Sargent and Company. The coal-based carbon was a 20- to 50-mesh product from Pittsburgh Coke and Chemical Company. A 12- to 20-mesh active carbon from the Burrell Corporation, and other carbons designated either by type or source, also were used.

Liquids employed in the molecular-sieve studies included 2,2,4-trimethylpentane of 99+% purity from Phillips Petroleum Company, titanium tetrachloride of 99.5+%troleum Company, titanium tetraenforde of $99.3 + \%_0$ purity from Matheson, Coleman and Bell Company, *n*-dodecane from Humphrey-Wilkinson, and technical α -methylnaphthalene from the Eastman Kodak Company. These liquids were used without further purification. 96% α -Methylnaphthalene, from Reilly Tar and Chemical Corporation, was acid-treated, percolated and distilled to composition, was and thested, periodiced and distinct to give a product with a cryoscopic purity of 97 + %; the principal impurity, as determined from the infrared spec-trum, was the β -isomer. Reagent grade carbon tetrachlo-ride from Mallinekrodt Chemical Works was percolated through silica gel.

The liquids were used as nitrogen desorbents in studying the molecular-sieve properties of gas-adsorbent carbons. Fourteen grams of active carbon was weighed to 0.1 g. and heated to 320°, with stirring, under a stream of high-purity dry nitrogen. The dried carbon was cooled, under nitrogen, to room temperature. Twenty-five ml. of the desorbent liquid was then added to the carbon, and the volume of gas evolved during the first 18 hours was meas-ured by water displacement. The volume was corrected for the hydrostatic head and the vapor pressures of water and the desorbent.

Surface areas and micropore volumes of the active carbons were determined by conventional Brunauer-Emmett-Teller (B.E.T.) nitrogen-adsorption techniques.⁹ Micropore determinations were made at a relative pressure sufficient to obtain capillary condensation in all pores less than 600 Å. in diameter. The surface tensions of α -methylnaphthalene, *n*-dodecane and titanium tetrachloride were obtained by capillary rise. The surface tension of titanium tetrachloride was measured under a carbon dioxide atmosphere.

Carbon, hydrogen, sulfur and ash were determined by the classical procedures. Oxygen determinations were ob-tained by a modified Schütze method.¹⁰ A spectroscopic procedure¹¹ was used to determine metal contents.

Active carbons impregnated with sodium silicate and with silica were used to study the effect of ash on measured oxygen content. Sodium silicate on active carbon was

(9) Reference 6, pp. 285-299.

(10) I. J. Oita and H. S. Conway, Anal. Chem., 26, 600 (1954).

(11) A. J. Frisque, Anal. Chem., 29, 1277 (1957).