explained if the primary reaction is assumed to be a dissociation into an excited oxygen atom and an oxygen molecule. It must, however, be emphasized that further experiments in this region would be of great use in order to elucidate the details of chain formation.

The author is greatly indebted to Dr. G. B. Kistiakowsky for permission to use his unpublished experiments. Thanks are also due Dr. O. R. Wulf of Washington, who kindly communicated the results of his investigations of the spectrum of ozone, and Dr. E. O. Wiig for translating the paper into English.

Summary

1. A critical survey of the experimental data involving the photochemical decomposition of ozone has been given.

2. The kinetics of the reaction have been explained on the assumption that the ozone spectrum shows predissociation and that the primary process is therefore $O_3 + h\nu \longrightarrow O_2 + O$. In red light a normal oxygen atom is assumed to be formed and in the ultraviolet an excited atom.

3. The probability of the occurrence of the reaction $O + O_3 \longrightarrow 2O_2$ has been calculated to be 5×10^{-4} if the oxygen atom is normal and it is assumed that the reaction $O + O_2 \longrightarrow O_3$ occurs only in a three-body collision.

4. The influence of temperature and of foreign gases has been discussed. The effect of gases which do not react with ozone can be interpreted by their specific influence on the three-body reaction $O + O_2 + M \longrightarrow O_3 + M$.

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PREPARATION AND PROPERTIES OF LEAD PERCHLORATE

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Introduction

Lead perchlorate was first prepared by Serullas[2] by heating lead oxide with perchloric acid. It was also prepared by Marignac[3] and Roscoe[4] by adding lead carbonate to perchloric acid and evaporating to a sirupy liquid. Roscoe was the first to point out the fact that lead perchlorate is extremely deliquescent. The formula of the salt which he obtained was $Pb(ClO_4)_2\cdot$-

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[1] From a dissertation submitted by J. L. Kassner to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry.

[2] Serullas, *Ann. chim. phys.*, **46**, 297 (1831).

[3] Marignac, "Oeuvres Complètes," Vol. I. p. 401 (1840–60); *Compt. rend.*, **42**, 288 (1856); *Mem. Soc. Phys. Genève*, **14**, 260 (1855); *Arch. Phys. Nat.*, **31**, 170 (1856).

[4] Roscoe, *Proc. Roy. Soc.* (London), **11**, 493 (1861); *Ann.*, **121**, 346 (1862); *J. Chem. Soc.*, **16**, 82 (1863).

$3H_2O$. There is no record of any other hydrate of lead perchlorate, although Hoffmann[5] interpreted Roscoe's figures as corresponding to the formula, $Pb(ClO_4)_2 \cdot 1.5H_2O$.

Two forms of basic lead perchlorate have been described by Marignac,[3] Weinland[6] and Weinland and Stroh.[7] Marignac prepared the basic salts by boiling a concentrated solution of normal perchlorate with a slight excess of lead carbonate and evaporating the filtrate. The formula of his salt was $PbO.Pb(ClO_4)_2.2H_2O$. Rammelsberg[8] also prepared this same salt. Weinland[6,7] prepared basic lead perchlorates to which he ascribed the formulas, $Pb_2(ClO_4)_2(OH)_2 \cdot 1.5H_2O$ and $Pb_3(OH)_4(ClO_4)_2$. He prepared the first by treating lead oxide with more than one and less than two equivalents of perchloric acid. The latter was prepared by treating three moles of lead oxide with two moles of perchloric acid and crystallized in two forms as described by Marignac.[3]

Experimental

Preparation of Normal Lead Perchlorate.—Lead perchlorate was prepared by adding to lead nitrate about 1% excess over the calculated amount of perchloric acid and evaporating to remove all nitric acid. Lead nitrate of C. P. grade was twice recrystallized with centrifugal drainage and washing. Perchloric acid (72%) of a high degree of purity was further purified by fractional distillation in a vacuum. It was diluted with a little water, added to the lead nitrate and the solution evaporated until fumes of perchloric acid were given off. The lead nitrate did not entirely dissolve in the acid at first but gradually went into solution as the evaporation progressed. The solution was tested for nitrate from time to time by adding a drop of it to a solution of diphenylamine in concd. sulfuric acid, and the fuming was continued until no test for nitrate was obtained.

Removal of Excess Perchloric Acid.—Owing to the great solubility of the salt, it was found impossible to remove the excess of perchloric acid even by two recrystallizations. It could not be volatilized by heating because anhydrous lead perchlorate, stable up to 200°, begins to decompose above that temperature into lead chloride and lead oxide, evolving both oxygen and chlorine, and also because the last traces of acid, becoming anhydrous, readily decompose into chlorine and oxygen, contaminating the salt with chloride. Moreover, the salt containing excess of perchloric acid was decomposed slightly when dehydrated in a vacuum in the presence of phosphorus pentoxide.

The obvious method of neutralizing the excess of acid by the addition of lead oxide or carbonate is not readily applicable in this case, because these substances are readily soluble in a solution of lead perchlorate, forming soluble basic salts and there is no way of knowing when just the proper amount has been added except by making rather troublesome analyses of the solution.

Because perchloric acid dihydrate, unlike the anhydrous acid, is very stable, it seemed probable that the excess of acid could be removed by passing a stream of moist air over the fused salt, as was done by Richards and Willard[9] with lithium perchlorate.

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[5] Hoffmann, "Lexicon der anorg. Verbindungen," **1915**, Vol. I, p. 699.

[6] Weinland, *Z. angew. Chem.*, **34**, 354 (1921).

[7] Weinland and Stroh, *Ber.*, **55**, 2706 (1922).

[8] Rammelsberg, *Handb. kryst. phys. Chem.*, **1**, 318 (1881).

[9] Richards and Willard, THIS JOURNAL, **32**, 4 (1910).

This was found to be satisfactory and because it is the most effective method for many perchlorates, it will be described in some detail.

A heater was constructed from a 20 × 30 cm. beaker which was wrapped with damp sheet asbestos and wound with seventy turns of chromel ribbon, 0.2 × 1.6 mm. The heating unit for the bottom of the beaker was made by coiling together chromel ribbon and a strip of asbestos 1 cm. wide to form a disk of suitable size which, while damp, was pressed against the bottom of the beaker. The two heating units could be connected either in series or in parallel. The beaker was insulated by asbestos wool, held in place by sheet asbestos, and the whole supported on a base of asbestos board. The beaker was covered with a quartz plate. Air purified by passing it through a solution of silver nitrate and a soda-lime tower was passed through water at about 100° by bubbling it through a three-necked Woulff bottle, electrically heated by a winding of No. 28 chromel wire, and supplied with water from a large stock bottle. The moist air passed through a delivery tube extending to within 5 cm. of the bottom of the large beaker.

The lead perchlorate solution, free from nitrate, was evaporated below 125° until it contained only a little more water than was required to form the trihydrate. This solution was then placed in the heater described above, on a support 10 cm. high, and steamed for three hours at about 160°. At the end of this time the salt was free from acid and a nephelometric test[10] showed that it contained only a few thousandths of one per cent. of chloride.

If more than 1% excess of acid is used in preparing lead perchlorate, longer steaming will be necessary. The vapor pressure of water in the air passing through the heater must be high enough to prevent complete dehydration of the salt; otherwise considerable chloride will be formed.

In order to determine accurately the amount of free acid, a sample of 3 to 4 g. of the salt was dissolved in about 7 cc. of water free from carbon dioxide. The lead was precipitated as sulfate by the addition of excess of neutral sodium sulfate, and removed by filtration. The acid in the filtrate was determined colorimetrically by using brom thymol blue as indicator and 0.001 *N* hydrochloric acid and sodium hydroxide as standard solutions.

Crystallization of Lead Perchlorate.—Lead perchlorate is extremely soluble in water and the trihydrate melts at 83–84°. In order to obtain a satisfactory yield of crystals the amount of water present must be carefully regulated. It was found best to start with a known weight of lead nitrate and for every 500 g. of lead perchlorate trihydrate, to allow 8 to 10 g. excess of water. A semi-fluid mass was then obtained on cooling to 0°. The crystals were drained centrifugally in platinum cups and a yield of 58% was obtained. The trace of chloride originally present could not be detected nephelometrically after crystallization. The yield decreased rapidly as the amount of water increased beyond that required to form the trihydrate. For example, in the above case, 555 g. of the salt was present, and if 25 g. of water instead of 10 g. was present, no crystals appeared on cooling to 0°.

Preparation of Anhydrous Lead Perchlorate.—Lead perchlorate trihydrate, dried at room temperature with phosphorus pentoxide in a vacuum for nine months, was not completely dehydrated. To increase the rate of dehydration by drying in a vacuum at a higher temperature the following apparatus was devised. A flanged pyrex cylinder[11] 60 cm. long by 12.5 cm. inside diameter and 0.5 cm. thick, was provided with covers to which were fused glass stopcocks. The flanges and covers were so carefully ground that, using only a trace of grease, the cylinder maintained a vacuum. This cylinder was placed in an electric oven 25 × 30 × 28 cm., made of "transite" asbestos board. The

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[10] Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904).

[11] Specially made by the Corning Glass Works.

oven was wired in two units, the sides and bottom with twenty turns of No. 28 chromel wire and the top with twenty-two turns. There was a mica window on top and another on one side. The advantage of this apparatus was that the central portion of the cylinder, containing the salt to be dehydrated, could be heated to the desired temperature, while the ends, containing the desiccant, phosphorus pentoxide, were relatively cool.

Because anhydrous lead perchlorate takes up moisture with such extraordinary rapidity, it was necessary to handle it only in very dry air. A large tight box was constructed of wood with a plate glass top and large enough to manipulate three ordinary desiccators. It was provided with a door, made air tight by means of a soft rubber gasket. There were two "manipulating arm-holes" in which long-sleeved rubber gloves were fastened air tight. A sulfuric acid manometer was provided for observing the pressure. Air, dried successively by calcium chloride and phosphorus pentoxide, was passed into the box for a few hours before and during use.

Lead perchlorate trihydrate was placed in an evaporating dish supported in the center of the cylindrical pyrex desiccator described above. Phosphorus pentoxide placed in the cool ends of the cylinder served to remove the moisture. The oven was adjusted to maintain a temperature of 65°. It was evacuated to a pressure of 35 mm. and the drying continued for nineteen hours. The salt was then removed and weighed on a platform balance in the manipulating box. When the hydrated salt had lost about one-third of its water of hydration, the temperature was raised to 100° for eight hours and then to 120° for fourteen hours. Analysis of the salt at this time showed 50.73% of lead compared with a theoretical value of 51.02% for the anhydrous salt. The heating was continued at 120° for twenty-four hours and at the end of this time the salt contained 51.02% lead.

Analysis of Anhydrous Lead Perchlorate.—While still hot, the salt was removed from the vacuum desiccator and placed in an ordinary desiccator containing phosphorus pentoxide. This was then placed in the manipulating box along with a similar desiccator containing two tared weighing bottles with carefully ground stoppers. After flushing out the box with dry air, a sample was transferred to the weighing bottle, and replaced in the desiccator. The stoppers were so well ground that there was no gain in weight during the process of weighing.

The amount of lead in the salt was determined by precipitating it as lead sulfate and weighing on a Gooch crucible. Duplicate analyses gave 51.016 and 51.020% of lead as compared to a theoretical value of 51.02%.

Anhydrous lead perchlorate is white and when exposed to air takes up moisture with amazing rapidity, forming the monohydrate and trihydrate. It is stable at 200° but begins to decompose at about 250° into lead chloride and lead oxide, evolving both oxygen and chlorine. It fuses at 270–275°, and above this completely decomposes.

Preparation of Lead Perchlorate Monohydrate.—Lead perchlorate trihydrate was partially dried at room temperature in a vacuum desiccator with phosphorus pentoxide. It then contained a little more water than corresponded to the monohydrate (6.77% instead of 4.25%, calculated from a determination of lead). The pentoxide was then replaced by a large excess of anhydrous lead perchlorate and the desiccator evacuated. The salt was allowed to remain in this desiccator for fifteen months and then analyzed for lead and perchlorate.

To obtain samples without exposure to atmospheric moisture, the manipulating box was used as before. Lead was determined as sulfate and the perchlorate by precipitation with "nitron" as described by Storm[12] and also by removing the lead electrolytically and then titrating the acid with standard alkali using methyl red as indicator. The results were as follows. Calcd.: Pb, 48.85%; ClO_4, 46.90%. Found: Pb, 48.85,

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[12] Storm, U. S. Bur. of Mines, Bull. 96, **1916**, p. 65.

48.85; ClO_4, 47.06 (nitron), 46.67 (acid titration). A test of the methods of determining perchlorate showed that the nitron method, using twice the theoretical amount of reagent, was excellent and that no correction for solubility loss was necessary if the precipitate was transferred by means of the filtrate and washed with 10 cc. of ice water, added in 1–2 cc. portions, using slight suction. The removal of lead electrolytically tended to give slightly low results, perhaps due to slight loss by spraying. Precipitation of the lead by means of hydrogen sulfide and removal of the latter by boiling gave good results. No matter what method is used, the determination of perchlorate is less accurate than that of lead.

The melting point of $Pb(ClO_4)_2 \cdot H_2O$ was found to be 153–155°. The above data prove the existence of this hydrate, which has not previously been obtained, and indicate that there is no lower hydrate.

Preparation of Lead Perchlorate Trihydrate.—A sample of lead perchlorate which had just been recrystallized was used. It contained 12.10% water as compared with 11.74% for the trihydrate. It was placed in a vacuum desiccator over a large excess of the monohydrate and the desiccator evacuated. It was allowed to stand for twelve months and then analyzed. Calcd.: Pb, 45.03; ClO_4, 43.73. Found: Pb, 45.17, 45.15; ClO_4 (nitron), 43.55, (acid titration), 43.20. The melting point of the trihydrate was 83–84°. The above data show the existence of the trihydrate and that another hydrate does not exist between the tri- and monohydrate.

Preparation of Basic Lead Perchlorate, $Pb_3(OH)_4(ClO_4)_2$.—This salt was prepared by saturating a hot solution of perchloric acid with lead oxide. The excess lead oxide was filtered out of the hot solution using a hot water funnel. On cooling, the basic salt crystallized in large irregular crystals. It was centrifuged in platinum cups and washed twice on the centrifuge with hot water. The salt was then crystallized from carbon dioxide-free water, centrifuged and washed. Weinland and Stroh[7] state that this salt may be prepared by treating three moles of lead oxide with two moles of perchloric acid. When attempting to prepare other basic lead salts than those described by Weinland, it was discovered that this same salt could also be prepared by using lead oxide and perchloric acid in the molecular ratio of four to three. When the ratio of lead oxide to perchloric acid was less than 4 to 3 and greater than 2 to 3, a mixture of the above basic salt and another, described later, was obtained. This shows that the limits of the ratio for this basic salt are between 4 of oxide to 3 of acid and the saturation point of hot perchloric acid with lead oxide. The results of analysis are as follows. Calcd.: Pb, 69.96; ClO_4, 22.39; OH, 7.65. Found: Pb, 70.05, 70.00; ClO_4, 22.38, 23.36; OH, 7.65, 7.60.

The direct determination of hydroxyl was carried out as follows. The salt was dissolved in a slight excess of $N/10$ nitric acid. The solution was diluted and the lead precipitated as lead sulfate by adding excess of neutral sodium sulfate. After warming for a time it was cooled in ice and filtered. The excess acid was titrated with $N/10$ sodium hydroxide using phenolphthalein as indicator. It was observed that if the salt was dissolved in water, a turbidity appeared, probably due to a trace of carbonate, and if $N/10$ nitric acid was added slowly to the hot solution, the disappearance of the turbidity could almost be used as the end-point of the titration. It disappeared a trifle too soon, the difference being about 0.07 cc. of $N/10$ acid. Neither Marignac nor Weinland reported a determination of the hydroxyl group.

Preparation of $Pb_2(OH)_2(ClO_4)_2 \cdot 1.5H_2O$.—Weinland and Stroh[7] state that this salt may be prepared from a solution of lead oxide in the calculated quantity of perchloric acid. An attempt was made to prepare this salt by his method, and also by varying the ratio of lead oxide to perchloric acid. Although the analysis indicated the existence of a salt of the above composition, it was not conclusive. The variation in the results seemed to indicate a mixture rather than a salt of definite composition.

The Solubility of Lead Perchlorate.—A slight excess of lead perchlorate trihydrate was added to water in a glass tube, which was sealed up and rotated for several days in a thermostat at 25 ±0.005°. After settling for several days, some of the clear liquid was transferred to a pycnometer with a carefully ground stopper consisting of a tube with a capillary bore. The capacity of the pycnometer at 25° was found to be 9.9783 g. of water, or 10.0180 cc. The weight of lead perchlorate solution required to fill it was 27.7950 g., or 27.8029 g. corrected to vacuum. The calculated density is 2.7753. The solution was transferred to a beaker, precipitated as lead sulfate, filtered and weighed on a Gooch crucible after heating at 600°. The corrected weight of $PbSO_4$ was 16.9111 g., equivalent to 22.6464 g. of $Pb(ClO_4)_2$ or 25.6603 g. of $Pb(ClO_4)_2 \cdot 3H_2O$. The following table shows the solubility calculated from these figures.

TABLE I

SOLUBILITY OF LEAD PERCHLORATE IN WATER AT 25°

Density, 25°/4°, 2.7753

	G. per 100 cc. of soln.	G. per 100 g. of soln.	Mole per 100 cc. of soln.	Mole per 100 g. of soln.
$Pb(ClO_4)_2$	226.103	81.472	0.55676	0.20061
$Pb(ClO_4)_2 \cdot 3H_2O$	256.200	92.315		

Thiel and Stoll[13] called attention to the high density of the saturated solution and suggested its use as a heavy liquid for determining the specific gravity of organic substances. They stated that a solution saturated at 15° had a density of about 2.6 and contained 78% of lead perchlorate.

Anhydrous lead perchlorate is readily soluble in many organic solvents but work along this line was discontinued after the violent explosion of an almost saturated solution of this salt in anhydrous methyl alcohol. This solution was prepared by adding the perchlorate in small amounts to the alcohol, cooling after each addition because considerable heat was given off during this process. The solution was cooled in ice to see if crystals would form. This did not occur, and the solution was allowed to warm up to room temperature. A little more of the salt was added and when the flask was disturbed the contents exploded.

Summary

1. Anhydrous lead perchlorate, the mono- and trihydrates, have been prepared in a high degree of purity and their properties studied.

2. One basic lead perchlorate, $Pb_3(OH)_4(ClO_4)_2$, was prepared.

3. A method of determining the hydroxyl group in the basic salt is described.

4. The solubility of lead perchlorate in water at 25° is 81.472 g. per 100 g. of solution and the density is 2.7753.

5. A solution of anhydrous lead perchlorate in anhydrous methyl alcohol is explosive.

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[13] Thiel and Stoll, *Ber.*, **53**, 2003 (1920).