LXII.—*Decomposition of Chlorates. Part II. Lead Chlorate.*

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LEAD chlorate was prepared by adding carefully purified lead carbonate in excess to chloric acid, and on the following day slowly heating to the boiling point before filtering. The crystals obtained by concentrating the filtrate gave only a very faint opalescence with silver nitrate. They dissolve in about one-third of their weight of water at 19°, but do not deliquesce* unless the air is practically saturated with moisture. Commercial lead chlorate was found to contain barium which could not be removed by fractional crystallisation. It was noticed that mixed crystals were deposited when a saturated solution of barium chlorate was added to one of lead chlorate.

The crystallised lead chlorate was heated at about 140° under reduced pressure until apparently dehydrated, the mass was then finely powdered and heated at 130—140° under 3 mm. pressure for 50 minutes. The white, anhydrous product was neutral to methyl-orange; the minute trace of chloride had not increased.

Examination of the Products of Decomposition.

A standard solution was prepared by dissolving barium peroxide in excess of nitric acid and diluting until it exactly neutralised an equal volume of decinormal alkali; this solution kept fairly well in the dark and readily dissolved lead peroxide. The amount of oxide left, and consequently the amount of chlorine evolved, was ascertained by dissolving the residue in a known volume of this solution and titrating back with *N*/10 soda; methyl-orange worked well in the absence of unaltered chlorate, but the turbidity produced by a very slight excess of soda afforded an end reaction, which was preferred. The lead chloride was determined in the same portion by adding nitric acid and titrating with *N*/10 silver nitrate. The numerical results (including the weight of chlorate actually decomposed) given in this paper were calculated from analyses, but when practicable the gas was passed through potassium iodide solution; the latter did not become alkaline, and the amount of liberated iodine agreed with that of the oxide found in the residue, hence the gas must have been practically free from ozone and from oxides of chlorine.

* Wächter (*J. pr. Chem.*, 1843, **30**, 329) states that $\text{Pb}(\text{ClO}_3)_2 \cdot \text{H}_2\text{O}$ is not deliquescent, but this has been misquoted in more than one treatise.

In residues free from undecomposed chlorate, but not overheated, the amount of oxygen, found by difference, was practically that required to form peroxide; portions washed free from chloride were but little affected by boiling dilute nitric acid. A small quantity of lower oxide is apt to be formed by local overheating, owing to rapid decomposition.

The loss of weight during incomplete decomposition agreed fairly well with that calculated by subtracting the weights of peroxide and chloride, as found by titration, from the equivalent amount of lead chlorate; formation of perchlorate would have led to a smaller loss of weight, and so must have been very slight, as might be expected from the weakness of the base. Some residues free from chlorate were mixed together and portions reheated in oxygen until the 52.4 per cent. of peroxide had entirely decomposed, leaving a cream coloured mass; only minute traces of chlorine were evolved (requiring, for example, 0.2 c.c. *N*/100 thiosulphate per gram) and the redetermination of oxide indicated no increase, although the temperature had reached 450°. Other portions were heated in chlorine; 18.4 per cent. of the peroxide present was converted into chloride in 10 minutes at about 200°, but at about 240° the action was even more marked, 30.9 per cent. being converted in the same period. These are approximately the average temperatures employed in the decompositions under 760 mm. and 4 mm. pressure respectively, hence much of the chlorine evolved must be reabsorbed unless special precautions are taken.

It is thus seen that lead chlorate decomposes into lead chloride, oxygen, lead peroxide, and chlorine, the last two being the only products tending to react with each other under the conditions of a slow decomposition of the chlorate.

Slow Decomposition.

For studying slow decomposition under various pressures, the substance was placed in a soft glass tube closed at one end, 12—18 mm. bore, and about 20 cm. in length. By means of an india-rubber stopper, the tube was connected to a T-piece, one limb of which communicated with a vacuum gauge filled with strong sulphuric acid, the pressure under which the decomposition actually took place being shown on a scale in terms of mm. of mercury, whilst the other limb led to the absorption tubes containing either aqueous potassium iodide (for pressures greater than 15 mm.), or else undried granular soda-lime followed by glass beads covered with a solution of potassium iodide in glycerol as a test for unabsorbed chlorine. The last absorption tube was connected to a delivery tube, either directly or through a Fleuss pump, in order that the progress of the decomposition might be followed by noting the volume of the oxygen evolved. Some anhy-

drous lead chlorate (usually 1 gram) having been weighed into the tube, the lower end was covered with soot, and placed in a bath of fusible metal provided with a thermometer (readings corrected for exposed column). Before decomposition commenced, any trace of absorbed moisture was removed by heating under reduced pressure at about 160° for some time, dry air being admitted through a side branch, and then pumped out. At the conclusion of the experiment, the gaseous contents of the tube were removed by repeated exhaustion and admission of air, and the residue then weighed and analysed as already described. The substance did not fuse unless the decomposition chanced to become rapid; the tubes were not corroded, and remained fairly constant in weight. The experiments have been numbered in the order in which they were performed, and to facilitate comparisons, the chlorine has always been stated per 100 parts contained in the weight of chlorate actually decomposed. It will be seen from Table I that the proportion of chlorine remaining free varied greatly with the conditions. Six decompositions, namely, those numbered 70b and 70a; 71b and 71a; 73b and 73a, were performed in pairs as indicated, two tubes being placed together in the bath, the first of the pair being under atmospheric pressure, and the other under 20–25 mm.; in experiments 70b, 71b, and 73b, the gas in the tube remained in contact with the residue until the companion decomposition was complete; this permitted further reabsorption (p. 718), and these decompositions gave less chlorine (46.3 per cent.) than did experiment 77 (53.3 per cent.). The reabsorption was most marked towards the end of the decomposition, for the temperature had then been increased, and much peroxide was present; incomplete decomposition gave more free chlorine, amounting to 60.6 per cent. in experiment 92.

Reduction of pressure greatly decreased the reabsorption, especially when decomposition was not completed; the most successful experiments gave: At 4 mm., 79.1 per cent. of chlorine free and 20.9 per cent. as chloride; at 1 to 2 mm., 81.4 per cent. free and 18.6 per cent. as chloride. At pressures below 4 mm., some chlorine reached the pump, perhaps owing to the removal of moisture from the soda-lime.

Lead chlorate was intimately ground up with half a molecular proportion of lead chloride; the absorbed moisture caused the mixture to cake when re-dried before partially decomposing in the manner just described. Deducting the added chloride, the residue at 4 mm. contained 20.9 per cent. of the possible chloride, whilst at atmospheric pressure the percentage was 43.6; these are about the usual proportions, hence little or no chlorine was expelled from the chloride during the decomposition. Addition of chloride does not appear to influence the ease of decomposition.

As in the case of barium chlorate (Trans., 1900, 77, 139), the use

of a bath of constant temperature was impracticable; the range was about $190-210^{\circ}$ at atmospheric pressure, but a temperature of $225-260^{\circ}$ was required for the somewhat slower decompositions under 4 mm., although 225° soon caused violent decomposition under atmospheric pressure. In some experiments, a second thermometer was placed inside the decomposition tube, so that its bulb was completely surrounded by chlorate; the temperatures thus indicated during decomposition at atmospheric pressure were slightly above those of the bath, and about 30° lower than those at 4 mm.; toward the end of the decompositions, the difference was even greater. It is thus seen that the temperature of the substance must be increased in order to compensate for the *impeding* effect of reduction of pressure.

To prevent the reabsorption of chlorine, it is necessary to decrease the concentration without increasing the temperature; this was accomplished by employing a stream of dry nitrogen at atmospheric pressure, frequent titrations of the liberated iodine affording guidance in heating the bath.

In the first series (Nos. 120—134, Table II.), the nitrogen was passed through the chlorate by means of a narrow tube reaching nearly to the bottom of one of the decomposition tubes previously employed, to which a side tube had been added as an exit for the gases. In this series, the smallest proportion of chloride was 14.5 per cent. (hence free chlorine = 85.5 per cent.), using 1.8 litres of nitrogen for 1 gram of chlorate; a larger current blew a large channel through the mass, and the cooling effect on the surface necessitated overheating of the exterior portions. The simultaneous employment of reduced pressure failed from similar causes.

In the second series (Nos. 137—140), there was less surface cooling; two U-tubes, each of 7 mm. bore and containing 0.5 gram of chlorate, were placed side by side, deep in the bath, and connected in series so that the chlorine evolved from one portion was carried over the other. It will be seen from Table II that the residues in the two tubes approached each other in composition as the current of nitrogen was increased; thus, with 0.9, 1.2, 4 and 5 litres, the differences were 5.9, 5.5, 0.3 and 0.1 per cent. respectively. With the larger volumes of nitrogen, the chlorine from the first tube can have had practically no effect upon the contents of the second, hence it seems fair to conclude that the reabsorption of chlorine had been all but eliminated, and that about 12.5 per cent. of the possible chloride is formed directly in the decomposition, about 87.5 per cent. of the total chlorine being liberated,

Rapid Decomposition.

An attempt has been made to ascertain the amount of chlorine at first liberated when lead chlorate is rapidly heated, the mass then becoming incandescent in places and much of the peroxide being decomposed by the heat, which, of course, promotes reabsorption of chlorine. The rapid decompositions were conducted in much the same way as the first of the slow decompositions already described. In experiments 74 and 75 (Table I), the greater part of the substance decomposed in about three seconds on the bath reaching a temperature of about 225° , but the heating was continued until the last traces had been decomposed; in experiment 76, the residue was heated until converted into oxychloride. The amounts of chlorine remaining free were respectively 45.5, 47.3, and 32.9 per cent. of the total in the chlorate; the last result confirmed Wächter's statement (*J. pr. Chem.*, 1843, 30, 329) that the oxychloride has the composition $\text{PbO}, 2\text{PbCl}_2$.

In the subsequent experiments, the bath was rapidly heated and the decomposition semi-explosive, most of the gas being evolved in about one second. Experiments 95 and 96 (Table I) commenced at atmospheric pressure, and the free chlorine amounted to only 38.1 and 39.0 per cent. in these, although the gas was removed as soon as possible after the rush had taken place. The thermometer bulb had acquired a temperature of about 235° at the moment of decomposition. With semi-explosive decomposition under reduced pressure, the apparatus was several times modified in order to avoid a marked rise of pressure; the following arrangement was finally employed. The upper end of the decomposition tube, 18 mm. in diameter, was sheathed with india-rubber tubing and inserted in the neck of an inverted "Winchester quart" bottle, constriction being thus avoided; a short side branch was connected to a double T-piece leading to the manometer, a Fleuss pump, and a stoneware bottle of 20 litres capacity. The whole was exhausted to 6 mm., and, immediately the rush of gas had taken place, the bath was removed and dry air admitted through an inlet near the bottom of the decomposition tube in order to remove chlorine. Each improvement gave a lower maximum pressure and a larger proportion of free chlorine; in the last experiment, the maximum pressure in the tube could not have greatly exceeded the 16 mm. recorded; 58.7 per cent. of the chlorine remained free, but there was no real indication of a limit. The thermometer reading was about 270° at the moment of decomposition.

A current of nitrogen did not prove useful in the case of these rapid decompositions.

TABLE I.—*Lead chlorate decomposed under various pressures.*

No.	Duration.	Proportion decomposed (per cent.).	Pressure.	Chlorine (total in decomposed portion = 100).		Mols. chloride. Mols. oxide.
				Free.	As chloride.	
74	About 3 sec.	Nearly 100	1 atmosphere	45·5	54·5	1·21
75	" "	" "	"	47·3	52·7	1·11
76	" "	" "	"	32·9*	67·1	2·10
95	About 1 sec.	" "	"	38·1	61·9	1·62
96	" "	" "	"	39·0	61·0	1·56
100	" "	" "	6—>200 mm.	46·8	53·2	1·13
101	" "	" "	" "	48·4	51·6	1·06
102	" "	" "	6—170 "	54·5	45·5	0·837
103	" "	" "	" "	54·4	45·6	0·838
106	" "	" "	6—20 "	58·6	41·4	0·707
107	" "	" "	" "	58·4	41·6	0·712
118	" "	" "	" "	58·0	42·0	0·723
119	" "	" "	6—16 "	58·7	41·3	0·703
70b	35 min.	100	1 atmosphere	47·5†	52·5	1·10
71b	25 "	"	"	46·0†	54·0	1·18
73b	40 "	"	"	45·3†	54·7	1·21
77	65 "	"	"	53·3	46·7	0·88
85	15 "	28·1	"	59·4‡	40·6	0·684
92	27 "	61·6	"	60·6	39·4	0·650
70a	90 "	100	20—25 mm.	75·1	24·9	0·332
71a	80 "	"	" "	76·3	23·7	0·311
73a	110 "	"	" "	74·6	25·4	0·342
86	30 "	62·5	6 mm.	77·6	22·4	0·290
87	25 "	68·8	4 "	79·1	20·9	0·265
88	25 "	68·8	" "	78·8	21·2	0·269
89	23 "	65·4	" "	76·8	23·2	0·301
81	110 "	86·4	1—2 mm.	81·4	18·6	0·238

* Heating continued until all peroxide had decomposed.

† Gas remained in contact with residue for some time.

‡ 3 grams decomposed in narrow tube.

The average range of the temperature of the bath was about 190—210° in the slow decompositions at atmospheric pressure, and 225—260° in those at 4 mm.

TABLE II.—*Lead chlorate decomposed in a stream of nitrogen.*

No.	Duration. (minutes).	Proportion decomposed. (per cent.).	Litres of nitrogen. (N.T.P.)	Chlorine (total in decomposed portion=100).		Mols. chloride. Mols. oxide.
				Free.	As chloride.	
120	22	69.0	1.1	84.3	15.7	0.187
121	12	78.7	1.8	85.5	14.5	0.167
124	20	73.0	5.4	75.4	25.6	0.344
125	40	81.8	5.9	77.9	22.1	0.284
126	20	about 80	1.1	79.8	20.2	0.254
131	15	65.5	0.5	75.7	24.3	0.321
132	13	40.6	0.5	78.4	21.6	0.276
133	17	36.2	0.6	79.9	20.1	0.252
134	40	89.8	1.0*	80.6	19.6	0.243
127	25	88.2	0.8*	84.8	15.2	0.180
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137	50	{ a 73.9 } { b 94.1 }	0.9	{ 84.3 } { 78.4 }	15.7 21.6	0.187 0.276
138	50	{ a 61.2 } { b 73.0 }	1.2	{ 87.1 } { 81.6 }	12.9 18.4	0.148 0.225
139	85	{ a 44.2 } { b 86.5 }	5.0	{ 86.7 } { 86.6 }	13.3 13.4	0.154 0.155
140	76	{ a 58.4 } { b 75.8 }	4.0	{ 87.5 } { 87.2 }	12.5 12.8	0.143 0.147

* For 0.5 gram of chlorate.

In experiments 137—140, a=first U-tube, b=second U-tube; each contained 0.5 gram chlorate.

Conclusions.

Slow Decomposition.—The mode of discussion adopted in the case of barium chlorate (Trans., 1900, **77**, 147) is applicable to the results given in the present paper, and the latter appear to furnish an experimental confirmation of some of the reasoning employed in Part I, (*loc. cit.*). Lead chloride does not lose chlorine during the decomposition of lead chlorate mixed with it, or even when heated at 450° with lead peroxide in a stream of oxygen. These results show that chlorine and oxide must be direct products of decomposition and are not derived from lead chloride as supposed by H. Schulze (*J. pr. Chem.*, 1880, [ii], **21**, 424). Decomposition under reduced pressure requires the employment of a *higher* temperature and is hence not quite satisfactory as a means of eliminating the secondary reaction between chlorine and lead peroxide, as this is greatly accelerated by rise of temperature; thus, 81.4 per cent. of the total chlorine remained free

under 2 mm., as compared with 45·3 to 60·6 per cent. under atmospheric pressure, but the employment of a stream of dry nitrogen gave results indicating 87·5 per cent. as the limit when reabsorption of chlorine is completely eliminated. About 12·5 per cent. of the total possible chloride must therefore be formed directly; this excludes Spring and Prost's theory that the whole of the chloride is formed by the action of chlorine on the oxide (*Bull. Soc. Chim.*, 1889, [iii], 1, 340).

The numerical results for the first action of heat might be expressed by the equation: $8\text{Pb}(\text{ClO}_3)_2 = 7\text{PbO}_2 + \text{PbCl}_2 + 4\text{Cl}_2 + 17\text{O}_2$, but unless an equation is employed including the terms $\text{BaO} + 1500\text{BaCl}_2$ to express the decomposition of barium chlorate (*loc. cit.*) it seems better to regard the decomposition as consisting of two independent reactions, namely, $\text{Pb}(\text{ClO}_3)_2 = \text{PbCl}_2 + 3\text{O}_2$ and $\text{Pb}(\text{ClO}_3)_2 = \text{PbO}_2 + \text{Cl}_2 + 2\text{O}_2$, the latter proceeding at about seven times the rate of the former. In the case of this chlorate, there is a marked secondary reaction, $\text{PbO}_2 + \text{Cl}_2 = \text{PbCl}_2 + \text{O}_2$, occurring to an extent depending upon the conditions and sometimes involving most of the chlorine first liberated; Spring and Prost (*loc. cit.*), working with large quantities, obtained only 8 per cent. of the total chlorine instead of 87·5 per cent.

It is difficult to decide whether the peroxide is formed directly or by oxidation of the monoxide, but it seems probable that its occurrence may be intimately connected with the practical absence of perchlorate, as the tendency to form perchlorate would appear to be the cause of the reducing properties of heated potassium chlorate (Fowler and Grant, *Trans.*, 1890, 57, 282).

Rapid Decomposition.—If the substance is made to decompose in about one second, the high temperature, resulting from the reaction, causes the formation of oxychloride and prevents the successful elimination of the reabsorption of chlorine. At atmospheric pressure, 38·5 per cent.* of the total chlorine was obtained and this was increased step by step to 58·5 per cent. at 6—20 mm. without any indication of finality. The increase seems comparable with that similarly obtained in complete slow decomposition (53 per cent. at atmospheric pressure, and 75 per cent. at 20—25 mm.), so the results would not seem to prove that less chlorine was evolved during rapid decomposition. It seems probable that the decrease in the amount *remaining* free is due to the high temperature causing very active reabsorption rather than an alteration in the proportion first evolved. If the decomposition into peroxide, chlorine, and oxygen were endothermic, an increase of chlorine with rise of temperature would be expected, but the thermochemical aspect cannot well be discussed until the heat of formation

* Further decreased when the gas was not removed immediately (see expt. 76, Table I).

of lead chlorate has been determined, as the difference between chloride and peroxide is neither large enough nor small enough to warrant a conjecture.

It may be noted that this *decrease* in the proportion of chlorine remaining free appears to invalidate the mode of reasoning adopted by Spring and Prost (*loc. cit.*) in deducing their theory partly from the increase observed in the case of certain chlorates, but supports the author's criticism of their reasoning (Trans., 1900, 77, 147). Barium chlorate showed no reabsorption, but there was a marked increase of free chlorine with rapid decomposition, whilst lead chlorate showed marked reabsorption but no increase; in these cases, the supposed cause and effect do not occur together.

It seems probable that the conclusions deduced in the case of slow decomposition (p. 724) will apply to rapid decomposition with but little modification, the main difference being that in the latter case the high temperature decomposes some of the peroxide (giving oxy-chloride) and causes the reabsorption of chlorine to be more marked.

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