CXXV.—*The Hydrolysis of Platinum Salts. Part I. Potassium Platinichloride.*

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While carrying out a series of experiments on the solubility of potassium platinichloride (Archibald, Wilcox, and Buckley, *J. Amer. Chem. Soc.*, 1908, **30**, 747), it was noticed that this salt undergoes hydrolysis in aqueous solutions at the ordinary temperature. Some time later, while studying the conductivity of some platinum compounds (Archibald and Patrick, *ibid.*, 1912, **34**, 369), it was found that this hydrolytic decomposition proceeded much more rapidly when the solutions were exposed to the action of light. As the extent to which this reaction has taken place in any given time could be measured very accurately, whilst the rate at which it proceeded was sufficiently slow to allow of a number of measurements being made with any one solution—a condition that is satisfied by very few inorganic salts—it was thought worth while to make a somewhat extended study of the hydrolysis of this salt under different conditions as to (1) dilution; (2) the presence of other chlorides and neutral salts; (3) the reversibility of the reaction.

Previous Observations regarding this Hydrolysis.

The action of light on potassium platinichloride appears to have been first noted by Sonstadt (P., 1898, **14**, 25). He states that light has the same effect on very dilute solutions of the salt as heat. A solution containing 1 part of salt in 10,000 parts of water became turbid when heated for an hour or two. He observed no effect in the case of more concentrated solutions, and seems to have judged the extent of the reaction from the appearance of the solution and the formation of a sediment, considered to be platinum monochloride.

It is of interest here to refer to a letter of Sir John Herschel to Dr. Daubeny, written in 1832 (*Phil. Mag.*, 1832, [iii], **1**, 58). This letter states that if a solution of platinum in nitromuriatic acid, in which the excess of acid has been neutralised by the addition of lime, this being followed by filtration, is mixed with water in the dark, no precipitation takes place for a very long while, but if the mixture is exposed to sunlight it instantly becomes milky and a copious precipitate forms. The writer of the letter further showed that this effect was confined to the violet end of the spectrum, no action taking place when tubes containing the platinum solutions were immersed in red- or yellow-coloured solutions and then exposed to the sunlight.

That light greatly accelerates the hydrolytic decomposition of platinum tetrachloride seems to have been generally recognised. Kohlrausch found that the conductivity of aqueous solutions of this compound increased much more rapidly when under the influence of light than when kept in the dark. The presence of the platinum electrodes also increased the velocity of the reaction. Solutions of chloroplatinic acid more concentrated than $N/10$ were apparently not affected by light.

EXPERIMENTAL.

Preparation of Materials.

Hydrochloric Acid.—The hydrochloric acid used was prepared by heating concentrated hydrochloric acid and passing the liberated gas into distilled water, the first and last parts of the distillate being rejected.

Potassium Chloride.—Commercial potassium chloride was recrystallised several times from water saturated with hydrogen chloride, finally from pure water. Portions so obtained were washed free of mother liquor and dried at a high temperature.

Potassium Platinichloride.—In preparing the chloroplatinic acid from which the platinichloride was obtained, platinum scrap was freed of surface impurities, then boiled for some time in concentrated hydrochloric acid. The platinum was then dissolved in aqua regia and the solution evaporated almost to dryness, after adding concentrated hydrochloric acid. After again adding hydrochloric acid and evaporating a second time, the residue was dissolved in water containing hydrochloric acid, and the platinum precipitated from this by adding a solution of ammonium chloride. The resulting ammonium platinichloride was collected in a Gooch filter, washed with alcohol and water, and dried in an air-bath at a low temperature. The dry salt was then reduced by heating in a current of hydrogen, and the platinum-black formed was well washed in water.

In order to ensure the absence of any nitric acid from the final preparation, the platinum-black was dissolved according to the method suggested by Weber (*J. Amer. Chem. Soc.*, 1908, **30**, 29) and modified by the author (*Zeitsch. anorg. Chem.*, 1910, **66**, 169). According to this method, the platinum-black is made the anode in the lower part of a glass tube, about 2 cm. in diameter, containing concentrated hydrochloric acid as electrolyte. At the anode the chlorine attacks the platinum, forming platinum chloride, and the resulting chloroplatinic acid falls to the bottom and can be drawn off through a siphon sealed to the bottom of the main tube. The solution prepared in this way is somewhat diluted, and the platinum then precipitated by adding slowly a solution of a portion of the purified potassium chloride. The precipitated platinichloride, after being washed and dried, is ready for use.

Apparatus.

The graduations on the pipettes and burettes were tested by weighing the water delivered, allowance being made for air-displacement and the temperature of the water. In the case of the flasks, a graduation mark was made at that point on the stem at which the flask contained water sufficient to balance brass weights equal to the apparent weight of a kilogram or 100 grams, as the case might be, of water weighed in air at 20°.

The weights were corrected by the method suggested by Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144).

Method of Measuring the Extent of the Hydrolytic Action.

As hydrochloric acid is formed as the hydrolysis proceeds, the rate at which the reaction takes place and the extent to which it has proceeded at any given time can be measured by titrating a known volume of the solution with a standard solution of an alkali, such as barium hydroxide. Among several indicators tried, such as methyl-red, methyl-orange, cochineal, and phenolphthalein, none appeared superior to phenolphthalein. The colour reaction with this substance was distinct and delicate. With the burettes employed in this work, the error in reading the volume delivered did not exceed 0·02 c.c., and this, with the strength of solution employed as standard, corresponded with 0·0000078 gram of hydrogen chloride.

The solutions first studied contained $\frac{K_2PtCl_6}{100}=4{\cdot}864$ grams, $\frac{K_2PtCl_6}{200}=2{\cdot}432$ grams, $\frac{K_2PtCl_6}{400}=1{\cdot}216$ grams, and $\frac{K_2PtCl_6}{800}=0{\cdot}6080$ gram of potassium platinichloride in a litre of solution. In terms of equivalent gram-molecules of platinum chloride they were, respectively, *N*/25, *N*/50, *N*/100, and *N*/200. These solutions were prepared by weighing the required amount of salt in each case; the necessary water was added in the dark, and the solution carefully protected from the light until everything was in readiness to begin a series of measurements. The velocity of the hydrolytic reaction was so low, even for the most concentrated solution studied, that the time required to dissolve the platinum salt need not be considered in any of the measurements. The initial acidity was now measured—this was seldom equivalent to more than 0·05 c.c. of the standard for a 10·0 c.c. portion of the platinum solution. The vessels containing the solutions were then immersed in water-baths contained in glass tanks, and here exposed, at a certain distance, to the radiations from a 300-watt lamp. The temperature of the bath was maintained constant within 0·5° by means of a system of tubes, through which water circulated. An ammeter reading to 0·001 ampere was placed in series with the lamp, and by means of a voltmeter the energy being used was measured at frequent intervals. From time to time, 10 c.c. portions of the platinum solutions were withdrawn by means of a pipette, and the acidity was titrated against the standard alkali. The results obtained for the above four solutions are given below.

The figures in the first column indicate the time, in minutes, during which the solution has been exposed to the light. The second column shows the number of c.c. of alkali necessary to neutralise a 10 c.c. portion of the platinum solution. The third column contains the weight, in grams, of hydrogen chloride formed in 100 c.c. of solution.

Table I.

N/200-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
5	0·04	0·00015
20	0·10	0·00039
40	0·14	0·00054
65	0·20	0·00073
125	0·32	0·00125
215	0·54	0·00210
265	0·64	0·00249
400	1·08	0·00421
580	1·72	0·00671
945	2·34	0·00913
1736	3·06	0·01193
2200	3·30	0·01287
2900	3·35	0·01365

N/100-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
40	0·20	0·00078
125	0·40	0·00156
265	0·74	0·00288
410	1·34	0·00495
580	1·92	0·00749
955	3·00	0·01174
1455	3·96	0·01544
1810	4·14	0·01615
1900	4·20	0·01638
2150	4·24	0·01653
2750	4·29	0·01673

N/50-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
40	0·27	0·00105
60	0·32	0·00125
125	0·51	0·00199
240	0·84	0·00328
430	1·53	0·00597
1035	4·04	0·0158
1630	5·24	0·0204
1910	5·68	0·0222
2050	5·86	0·0229
2400	6·36	0·0248
2700	6·45	0·0252

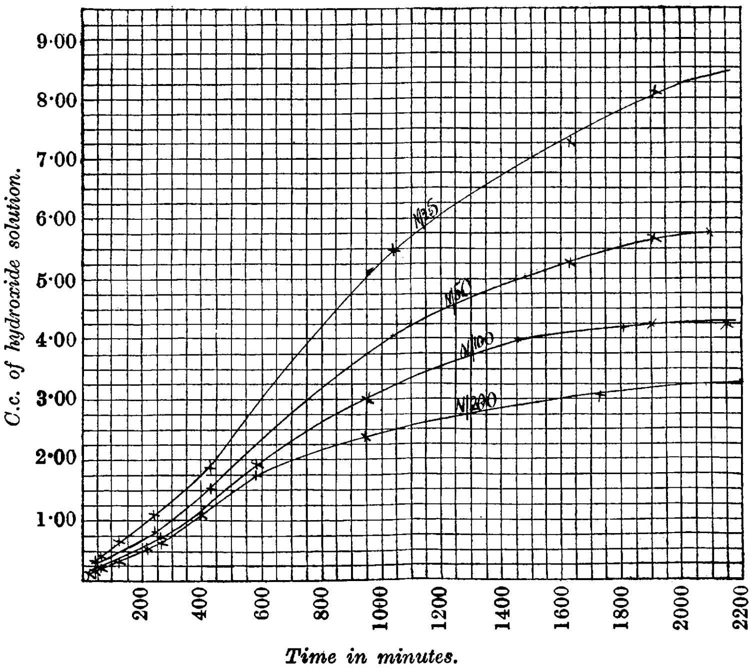
N/25-K_2PtCl_6 *Solution.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
40	0·32	0·00125
60	0·42	0·00164
125	0·68	0·00265
240	1·10	0·00429
430	1·88	0·00733
1035	5·46	0·0213
1630	7·24	0·0282
1910	8·12	0·0317
2280	8·56	0·0334
2600	8·70	0·0339

These results show that the different solutions reach a condition of equilibrium in almost the same time. The $N/200$-solution attains a condition of maximum acidity some two or three hours after the most concentrated one.

If we calculate the percentage of chlorine that has been set free from the platinum salt when equilibrium has been reached, we find that for the four solutions the values are, beginning with the most dilute solution, 74·7, 45·8, 35·2, and 23·2 per cent. of the chlorine present as platinic chloride.

FIG. 1.



The relationship between the time and the progress of the reaction is better shown by the curves of Fig. 1, where times are plotted as abscissæ against volumes of barium hydroxide solution used for the titration.

The first part of the curve shows nearly a straight line, that is, during the period that the first three-fifths of the reaction is taking place, indicating that the hydrolysis goes on at an almost constant rate for a considerable period of time. A velocity-constant for this part of the reaction may then be calculated by dividing the amount of hydrogen chloride formed by the time and multiplying by the dilution.

There is an indication in the case of the two weaker solutions of what Goodwin (*Zeitsch. physikal. Chem.*, 1896, **21**, 1) has termed an induction period, during which the reaction proceeds very slowly. This would suggest that some substance may be forming—a product of the reaction—that catalyses the reaction during its later stages. This point can be discussed to better advantage when considering the reaction that takes place in the dark.

In order to show that the rate of the reaction is proportional to the intensity of the light for a given source of light, the following measurements were made for $N/100$- and $N/200$-solutions placed at a distance of 40 cm. from the source. The temperature and other factors were maintained the same as in the previous measurements.

N/200-*Solution at* 40 *cm.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.
220	0·14
405	0·28
585	0·48
950	0·76
1741	1·44
2472	2·24
3195	2·56
4010	2·70
5135	2·84

N/100-*Solution at* 40 *cm.*

Time, minutes.	$Ba(OH)_2$ solution, c.c.
125	0·16
265	0·24
410	0·40
580	0·64
955	0·94
1455	1·68
1810	2·12
2370	2·92
3165	3·48

For the sake of comparison, we may set down opposite the volume of hydroxide solution necessary for the titration the time during which the solution was exposed; the corresponding time for the solutions exposed at 20 cm. distance is also shown in the table, these values being taken from the curves of Fig. 1.

TABLE III.

	Time of exposure for solution $N/200$, minutes.			Time of exposure for solution $N/100$, minutes.	
$Ba(OH)_2$ solution, c.c.	At 20 cm.	At 40 cm.	$Ba(CH)_2$ solution, c.c.	At 20 cm.	At 40 cm.
0·14	40	220	0·16	35	125
0·28	100	405	0·24	50	265
0·48	188	585	0·40	125	410
0·76	300	950	0·64	205	580
1·44	510	1741	0·94	315	955
2·24	870	2472	1·68	515	1455
2·56	1125	3195	2·12	640	1810
2·70	1280	4010	2·92	925	2370
2·84	1460	5135	3·48	1175	3165
2·92	1555	5665	4·00	1500	4105
			4·16	1860	6685

These results show that at the beginning of the hydrolysis the rate of the reaction is approximately proportional to the intensity of the light. However, after the reaction has proceeded a certain distance—when about one-tenth of the total amount of hydrogen chloride has been formed—the rate of the reaction for the solution at the greater distance is more rapid than the intensity law would predict. This is perhaps to be expected if the later stages of the reaction are influenced by a product formed during the hydrolysis. It is worth noting that this change in rate occurs when practically the same amount of hydrogen chloride has been formed in each solution. The final equilibrium point is apparently not affected by a change in the intensity of the light, as the titration is almost identical in the two cases.

It will be of interest to record at this point the behaviour of solutions of the platinichloride when made up and kept in the dark. The solutions were protected from the light by wrapping the container in black paper and then enclosing it in a thick wooden box, blackened within and without. The following tables will show the results of these observations. In the preparation of the *N*/25-solution the water had been very carefully distilled, and boiled again just before using. The salt had been kept in the dark for several days before making up the solutions, and every precaution was taken to exclude light, both while preparing the solutions and after.

The volumes of solution and weights of hydrogen chloride are expressed in the units used before.

TABLE IV.

N/25-K_2PtCl_6 *in Darkness.*

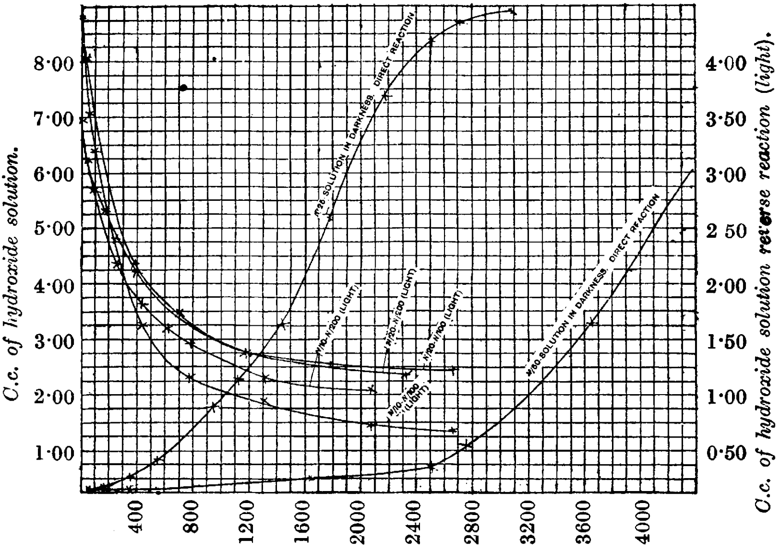
Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Grams.
68·3	0·06	0·00023
162·0	0·12	0·00047
354·0	0·28	0·00110
546·0	0·60	0·00236
937·0	1·52	0·00592
1120·0	2·04	0·00796
1440·0	3·04	0·01185
1775·0	4·94	0·01927
2177·0	7·14	0·02785
2515·0	8·13	0·0317
2735·0	8·46	0·0330
3090·0	8·65	0·0337

N/50-K_2PtCl_6 *in Darkness.*

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
68·3	0·04	0·00016
162·0	0·04	0·00016
354·0	0·04	0·00016
546·0	0·04	0·00016
1625·0	0·28	0·00110
2455·0	0·44	0·00173
2755·0	0·84	0·00330
3662·0	1·54	0·01177
4850·0	6·04	0·02355

In the case of the *N*/100- and *N*/200-solutions, there was no indication that hydrolysis had even started after they had been in the dark for six months. For the *N*/25- and *N*/50-solutions, the results were as indicated. In the latter case, the hydrolysis had not proceeded far enough to be measured until approximately thirty days had elapsed. For the $N/25$-solution, the reaction had proceeded to such an extent that it could be detected at the end of five days. The curves of Fig. 2, obtained by plotting the results of table IV, show much more distinctly the character of the "induction" period. This period becomes more extended and exaggerated as the solution becomes more dilute, until, for a solution as dilute as $N/100$, no hydrolytic decomposition whatever takes place over as extended a period as six months. It appears strange, perhaps, that the more dilute solutions are the more stable. The concentration of the hydrogen and hydroxyl ions has evidently little to do with the progress of the reaction, although it might be argued that these factors are practically constant for the different solutions, the proportion of water to salt being so large for all concentrations studied.

FIG. 2.



Time in minutes for reaction in light, in hours for reaction in dark.

The time required for the $N/25$-solution to reach an equilibrium point in darkness is approximately one hundred times as long as when exposed to the radiations of the 300-watt lamp. For the $N/50$-solutions, the difference in time is somewhat greater.

It seems possible that for the more concentrated solutions a sufficient, although perhaps an exceedingly small, amount of some substance—perhaps an hydroxy-salt—is produced when the salt is first dissolved to catalyse the hydrolytic reaction, and, in the case of the *N*/25-solution, to give the reaction an appreciable velocity almost at the beginning. The shape of the curves of Fig. 2 is then more easily understood. The steep parts show the accelerating effect of the catalyst, in the absence of any effective radiations, in a very striking way. For the more dilute solutions, this catalyst is not produced in concentrations high enough to affect the progress of the reaction.

The Reverse Reaction.

On testing the solutions to determine whether the reaction could be driven in the opposite direction, it was found that when potassium chloride, sodium chloride, or hydrochloric acid was added to a hydrolysed solution, the reaction proceeded in the opposite direction, either in the dark or in the light, the extent to which the reverse reaction took place depending, in the case of any one solution, on the amount of chloride that had been added. The rate at which the reverse reaction proceeded was very much slower in the dark than in the light, as measurements given below will show. The effect of platinum-black on the reaction was also studied, as set forth in the tables. For this purpose, a strip of platinum foil was covered electrolytically with platinum-black, and this strip, after being thoroughly washed, was immersed in the solution to be studied.

TABLE V.

Reverse Reactions in Light: $N/100$-K_2PtCl_6 Solution.

$N/10$-KCl.			$N/20$-KCl.		
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	Time, minute.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167	Initial	4·29	0·0167
65	3·40	0·0133	20	3·90	0·0152
95	3·08	0·0120	245	2·56	0·00998
255	2·28	0·0089	385	2·06	0·0080
430	1·50	0·0059	700	1·62	0·0063
620	1·16	0·00452	1175	1·26	0·0049
775	1·04	0·00436	1775	1·16	0·0045
1305	0·82	0·00320	2665	1·10	0·0043
2070	0·60	0·00234			
2660	0·56	0·00218			

TABLE V. (*continued*).

$N/200$-K_2PtCl_6 Solution.

$N/10$-KCl.			$N/20$-KCl.		
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131	Initial	3·35	0·0131
65	2·86	0·0112	35	3·00	0·0117
95	2·74	0·0107	185	2·54	0·0099
255	2·06	0·0080	385	1·98	0·0077
430	1·70	0·0066	810	1·46	0·0057
620	1·48	0·0058	1205	1·24	0·0052
775	1·34	0·0052	1775	1·12	0·0044
1305	1·04	0·00405	2323	1·06	0·0041
2070	0·92	0·00359	4850	0·86	0·00335
4850	0·59	0·00230	5600	0·70	0·00273
5600	0·52	0·00203			

The reverse reaction is seen to take place at a comparatively rapid rate at the beginning, the amount of change being greater here, in a given time, than for the direct reaction. This is no doubt because the added salt has so greatly increased the concentration of the chlorine ion. Towards the end, however, the progress becomes very slow, with the result that the time required for the reverse action to go to completion is much greater than the time necessary for the hydrolysis to take place. In the case of the $N/200$-platinum solutions, the time required for the reverse reaction is much greater than for the $N/100$-solutions.

The latter stage of the reaction for the $N/100$-potassium platinichloride–$N/10$-potassium chloride solution is complicated by the fact that, as the potassium platinichloride is regenerated, the solution becomes supersaturated with respect to this compound, and it crystallises out to a slight extent. This probably explains the crossing of the curves for the $N/10$-potassium chloride solutions, as shown in Fig. 2. This also goes to show that the hydrolysed salt is slightly more soluble in potassium chloride solutions than the normal compound.

If the rate of the reverse reaction is expressed according to the usual formula, using the results of the measurements, say, for the $N/200$-potassium platinichloride–$N/10$-potassium chloride solution, a constant is not obtained. The expression for a unimolecular reaction gives a value which continually diminishes, whilst the bimolecular formula yields a continually increasing number.

The results of measurements made on solutions reacting in the reverse direction in the dark are shown below in table VI. The effect of the addition of sodium chloride to the hydrolysed solution is also shown.

TABLE VI.

Reverse Reactions in Darkness.

Potassium Chloride Added.

N/50-K_2PtCl_6. *N*/20-KCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	6·60	0·0257
1·50	5·32	0·0208
19·58	4·98	0·0194
73·50	4·32	0·0169
260·50	3·34	0·0130
601·50	2·80	0·0109
1101·5	2·38	0·0093
1657·0	2·10	0·0082
2540·0	1·84	0·0072
3096·0	1·80	0·0070

N/200-K_2PtCl_6. *N*/10-KCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
4·25	3·22	0·0126
49·25	2·60	0·0102
317·0	1·98	0·0077
1973·0	1·10	0·0043
3797·0	0·90	0·00351
5957·0	0·72	0·00281
8693·0	0·52	0·00203

N/200-K_2PtCl_6. *N*/20-KCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
49·25	2·78	0·0108
317·0	2·22	0·0087
1973·0	1·32	0·00515
3797·0	1·12	0·00437
5957·0	0·92	0·00359
8693·0	0·74	0·00289

Sodium Chloride Added.

N/200-K_2PtCl_6. *N*/10-NaCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
48	2·62	0·0102
75	2·42	0·0094
1732	1·34	0·0052
3556	1·10	0·00429
5716	0·86	0·00335
8452	0·50	0·00195
12300	0·29	0·00109

N/200-K_2PtCl_6. *N*/20-NaCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	3·35	0·0131
48	2·94	0·0115
76	2·82	0·0110
—	—	—
3556	2·16	0·0084
5716	1·80	0·0070
8452	1·72	0·0067
16828	1·50	0·0059
20476	1·20	0·0047

N/100-K_2PtCl_6. *N*/10-NaCl.

Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167
29	3·98	0·0155
219	3·42	0·0133
1296	2·52	0·0098
2376	2·16	0·0084
4488	1·68	0·00655

These results show that the reverse reaction, brought about by the addition of a soluble chloride to the hydrolysed solution, continues in the absence of light until, for the more concentrated solutions, much the same equilibrium point is reached as in the case of the same reaction taking place in the light. For the more dilute solutions, the latter equilibrium point is past, the reaction continuing for approximately two years, by which time the hydrolysis has almost disappeared.

The catalytic effect of platinum-black on the reverse reaction is shown by the results set forth below. In the first case, the solutions were exposed to the radiations from the 300-watt lamp, whilst the second series of results refers to the reaction taking place in the absence of light. In each case, these reactions were studied simultaneously with solutions kept under exactly the same conditions, except that no platinum-black was present.

TABLE VII.

Reverse Reactions with and without Platinum-black.

In Light.

$N/100$-K_2PtCl_6. $N/20$-KCl.

	With Platinum-black.		Without Platinum-black.	
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167	4·29	0·0167
20	3·90	0·0152	3·90	0·0152
245	2·56	0·0100	2·56	0·0100
385	2·06	0·0080	2·06	0·0080
700	1·62	0·0062	1·62	0·0063
1175	1·26	0·0049	1·26	0·0049
1775	1·16	0·0045	1·16	0·0045
2665	1·10	0·0043	1·10	0·0043

In Darkness.

$N/100$-K_2PtCl_6. $N/20$-KCl.

	With Platinum-black.		Without Platinum-black.	
Time, hours.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	4·29	0·0167	4·29	0·0167
28·75	3·72	0·0145	3·88	0·0151
219·7	2·84	0·0111	3·52	0·0137
1296·0	1·80	0·0070	2·36	0·0092
2376·0	1·36	0·0053	2·02	0·0079
4488·0	1·14	0·0045	1·54	0·0060
8376·0	1·02	0·0040	1·30	0·0051

It is apparent that the effect of the platinum-black is not great enough to show when the reaction is taking place at a relatively rapid rate before the lamp, but it is quite noticeable when the reaction is proceeding slowly in the dark.

A few results will show the effect of the presence of a neutral salt, such as potassium nitrate, in the solution undergoing hydrolysis. The values from measurements of two solutions are given.

TABLE VIII.

Direct Reaction with Potassium Nitrate.

$N/200$-K_2PtCl_6. $N/20$-KNO_3.			$N/200$-K_2PtCl. $N/10$-KNO_3.		
Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.	Time, minutes.	$Ba(OH)_2$ solution, c.c.	HCl. Gram.
Initial	0·00	—	Initial	0·00	0·0000
100	0·20	0·00078	100	0·22	0·00086
175	0·40	0·00156	190	0·46	0·00179
350	0·78	0·00304	225	0·58	0·00226
465	1·00	0·00390	315	0·84	0·00328
665	1·44	0·00562	605	1·52	0·00592
850	1·86	0·00725	800	1·91	0·00745
1380	2·66	0·0104	1215	2·40	0·00936
1775	2·92	0·0114	1775	2·90	0·0113
2020	3·04	0·0119	2020	3·08	0·0120
2650	3·28	0·0128	2650	3·26	0·0127
3000	3·44	0·0134	3000	3·40	0·0133

These results show that whilst the potassium nitrate has a retarding effect at the beginning of the reaction, the acidity of the solution finally reaches just as high a value as in the absence of the neutral salt. The total time required for the reaction to reach an equilibrium point is but slightly greater when the potassium nitrate is present. In agreement with the retarding effect of the nitrate is the fact that the solution which contains the greater amount of neutral salt lags slightly behind the other.

As stated above, it appears from the results in table I that a substance may be formed from the hydrolysis which acts as a catalyst of the reaction, increasing the speed very perceptibly during the first half of the decomposition. This point was further tested, as follows. Two solutions were prepared in the same manner, of equal concentration as regards platinum salt, whilst one contained 1 c.c. of dilute hydrochloric acid. They were then exposed at the same temperature and at the same time to the radiations from the lamp, at equal distances from the source. Measurements of the acidity of the solutions were then made at frequent intervals. The results failed to show any accelerating influence whatever on the part of the hydrochloric acid. The reaction necessarily did not proceed so far in the solution containing the added chlorine ions, but this was the only effect noticed.

Another experiment with the same object in view was made, as follows. Two solution of the platinum salt were prepared, one *N*/100, the other *N*/400. These were exposed to the light until partly hydrolysed, then placed in the dark. The acidity of the more concentrated solution was measured after twenty days, and the measurement showed that the hydrolytic reaction had continued until the usual equilibrium point had been reached. In the case of the *N*/400-solution, a measurement was made after thirty days, but the rise in acidity, if any, was so small that it could not be detected with certainty. After thirty-eight days more, the result of another measurement indicated that the hydrolysis was proceeding, but very slowly. A 10 c.c. portion, which neutralised 0·88 c.c. of alkaline solution when first placed in the dark, now required 0·98 c.c. The next two months brought no perceptible change in this solution, and sixteen months after it had been placed in the dark a 10 c.c. portion required only 1·10 c.c. of hydroxide solution. Another *N*/400-solution, made up at the same time as this one, but never exposed to the light, showed no indication of any hydrolytic action after sixteen months. It would seem as if a certain concentration of the catalytic reagent was necessary before the hydrolysis will proceed. In the case of the *N*/400-solution that had been exposed to the light, this concentration had apparently just been reached before the solution was placed in the dark.

It was not expected that the accelerating influence of platinum-black would be sufficiently great to be noticed in a solution undergoing hydrolysis before the light. It was thought worth while, however, to measure this effect on solutions reacting in the dark. Accordingly, two solutions were carefully prepared, each *N*/25. In one was placed 0·05 gram of platinum-black. Both solutions were placed in the dark and measured from day to day. After three days, 10 c.c. of one solution neutralised 0·06 of alkali solution, whilst the same volume of the one containing the platinum-black required 0·25 c.c. After five days, the corresponding volumes of alkali solution were 0·06 c.c. and 0·45 c.c. The effect of the platinum-black was very evident both in starting the hydrolysis and in accelerating the reaction.

Another experiment, almost identical with this one, was made by adding 5 c.c. of an *N*/25-solution completely hydrolysed to a newly prepared *N*/100-solution, and placing this in the dark. The reading for a 10 c.c. portion of this solution was now 0·98 c.c. of alkali; after two months, the volume of alkali required for a 10 c.c. portion was 2·32 c.c., showing that a sufficient amount of the accelerating substance had been added to cause the hydrolysis to take place.

The effect of the temperature on the rate of the reaction and the extent of the hydrolysis received some attention. It was first ascertained whether a solution which would not undergo hydrolysis in the dark at the ordinary temperature would hydrolyse if kept at 80°. An *N*/100-solution was tested in this way. The titration for a 10 c.c. portion of this solution was 0·04 c.c. at 20°. After being kept in the dark at 80° for three hours, the corresponding titration was 0·16 c.c. On cooling to 20°, still in the dark, the titration fell to 0·08 c.c. After being kept in the dark at 80° for another period of three hours, a 10·0 c.c. portion again required 0·16 c.c. of alkali. In the absence of light, the temperature has little, if any, influence on the hydrolysis. The same conclusion is drawn from a comparison of the rate of the reaction taking place at 25° with that at 35°. The variation here is only manifest toward the end of the reaction, when the difference in the equilibrium point—a greater degree of hydrolysis at the higher temperature—is sufficient to show in the final readings.

For the purpose of ascertaining to what extent the hydrolysis would be increased by a rise in temperature, three solutions were exposed to the radiations of the 300-watt lamp at a distance of 20 cm., the water-bath being maintained at the temperature shown below. From time to time, 10 c.c. portions of the platinum solutions were withdrawn and titrated, the light being continued at any one temperature until equilibrium had been attained.

TABLE IX.

Effect of Temperature on the Hydrolysis.

	N/100-K_2PtCl_6.		*N*/50-K_2PtCl_6.		*N*/25-K_2PtCl_6.	
Temperature.	$Ba(OH)_2$ solution, c.c.	HCl (100 c.c.). Gram.	$Ba(OH)_2$ solution, c.c.	HCl (100 c.c.). Gram.	$Ba(OH)_2$ solution, c.c.	HCl (100 c.c.). Gram.
20°	4·29	+0·0167	6·45	+0·0252	8·70	+0·0339
50	5·24	+0·0204	7·45	+0·0291	10·16	+0·0396
80	5·90	+0·0230	8·20	+0·0319	11·06	+0·0431

If we express the increase in the acidity of these solutions as percentages of the values at 20° we obtain the following coefficients for temperatures between 20° and 80°: *N*/100 0·62, *N*/50 0·45, *N*/25 0·45 per cent.

These coefficients are not very different for the several concentrations studied. From the amount of hydrogen chloride formed at 80°, we find that for the *N*/100-solution 63 per cent. of the chlorine present as platinic chloride has been used to form hydrogen chloride.

If we represent by chemical equations the several stages of the hydrolytic decomposition of the platinum salt, we find that for the $N/25$-solution the equation

$$K_2PtCl_6 + H_2O = 2K^{\cdot} + PtCl_5(OH)'' + H^{\cdot} + Cl'$$

indicates pretty closely the extent to which the hydrolysis has taken place, whilst for the $N/50$-solution the expression

$$2K_2PtCl_6 + 3H_2O = 4K^{\cdot} + PtCl_5(OH)'' + PtCl_4(OH)'' + 3H^{\cdot} + 3Cl$$

would represent more nearly the condition of the solution. When the solutions are as dilute as $N/100$ or $N/200$, the respective equations would be

$$K_2PtCl_6 + 2H_2O = 2K^{\cdot} + PtCl_4(OH)_2'' + 2H^{\cdot} + 2Cl^{\cdot}$$

and

$$K_2PtCl_6 + 3H_2O = 2K^{\cdot} + PtCl_3(OH)_3'' + 3H^{\cdot} + 3Cl'.$$

The above equations correspond with a temperature of 20°. At higher temperatures, the decomposition of the salt is more nearly complete, which is in agreement with the fact that when a dilute solution of the platinichloride is boiled in the light, an insoluble substance is deposited.

Obviously the possibilities of this hydrolytic action should be kept in mind when making a determination of potassium by means of this salt; if a solution of the platinichloride is being evaporated, a sufficient amount of hydrochloric acid must be present to prevent the hydrolysis taking place, whilst if the salt is being precipitated, hydrochloric acid must again be present to ensure the formation of the normal compound.

Potassium platinibromide shows some interesting features not noticeable in the case of the platinichloride, and it is hoped to submit soon a communication dealing with this compound.

Summary.

It has been shown that solutions of potassium platinichloride undergo hydrolysis when exposed to the action of light.

If the solution is as concentrated as $N/50$, this hydrolysis will begin and will be completed in the dark; for a $N/100$-solution or one more dilute, no decomposition takes place when light is excluded.

A substance is formed by the hydrolysis which catalyses the reaction, and will initiate the decomposition in a newly prepared solution.

The addition of a soluble chloride to the hydrolysed solution

causes a complete reversal of the reaction, showing that the substances formed during the direct reaction are soluble.

The reverse reaction is influenced by light in much the same way as the direct. The complete reversal of a solution as dilute as $N/200$ requires nearly two years.

A neutral salt has a slight retarding effect on the direct reaction, but does not influence the equilibrium point.

The accelerating influence of platinum-black on both the direct and reverse reactions is quite noticeable when these reactions are taking place in the dark, but is not measurable when light is acting on the solutions.

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