A resemblance between the absorption spectra of dimethylpyrone (and its salts) and 1,2,6-trimethylpyridone, a compound in which only the ketone structure is possible, and between those of xanthone and of xanthene and xanthydrol has been observed. On the other hand, it has been noted that the spectrum of dimethylpyrone differs greatly from that of 4-methoxy-2,6-dimethylpyridine, an analogous compound which has the benzenoid type of structure. From these observations the conclusion has been drawn that the structure of the pyrone and pyroxonium ring is best represented by a ketonic formula.

It has been pointed out that formulation of the salts of xanthydrol and of trimethylpyroxonium perchlorate as compounds of an oxonium type is open to question.

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ELECTROLYSIS OF GRIGNARD SOLUTIONS[1]

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In a previous article[2] there is described a series of experiments on the electrolysis of certain Grignard compounds in ether solutions, using platinum electrodes. The purpose of that investigation was to determine the quantity of a Grignard compound which is decomposed by one equivalent of electricity, and to determine the products resulting from that decomposition.

The present paper describes some experiments on the electrolysis of Grignard solutions using anodes of various metals with platinum cathodes.

Apparatus and Procedure

The electrolytic cells were made of glass tubing, and were approximately 200 × 40 mm. in size. These were closed with tight fitting cork stoppers through which the two electrodes were suspended close to the stoppers by copper wires. These electrodes were held parallel to each other and about 3 cm. apart by means of bent glass rods. Short-circuiting between the electrodes through the formation of bushy deposits of magnesium on the cathode was prevented by placing on the bottom of each cell a long glass rod with which such deposits were broken off by occasionally tilting the cell.

A glass tube of 1 cm. diameter was inserted through the center of each of the stoppers which closed the cells, and extended about 1 cm. beyond the inner faces of the stoppers. Through these tubes the cells were filled and emptied.

For anode materials the following metals were used, either in the form of the foil or as long narrow flat pieces of the metal: aluminum, tin, cadmium, zinc, bismuth, gold, silver and nickel. The areas of the anodes were approximately 20 sq. cm., while those of the platinum cathodes were about 10 sq. cm. In order to eliminate the magnesium

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[1] This paper is an abstract of the thesis submitted by Mary Drane in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Gaddum and French, THIS JOURNAL, **49**, 1295 (1927).

halide etherates as factors in the electrolyses, isoamylmagnesium chloride was chosen for these experiments, the magnesium chloride etherate being but slightly soluble in the ether.

The currents through the solutions varied from 24 to 100 milliamperes, under a potential of 110 volts. Since this caused the solutions to boil vigorously, the currents were adjusted to 10 milliamperes for the first fifty hours and to 20 milliamperes for the remaining one hundred and fifty hours, by the introduction of resistances. In every case a light, bushy deposit of magnesium began to form on the cathode within a few minutes after starting the electrolysis.

When the electrolysis was complete, the solutions were drawn from the cells by suction and filtered, and both the filtrates and the residues were analyzed for the anode material. The concentration of the Grignard compound was also determined, before and after the electrolysis. The results are summarized in Table I.

Of the various anodes, only the aluminum, zinc and cadmium were attacked during the course of the electrolysis. Of these metals, only the aluminum was found in the ether solution, presumably in the form of the aluminum alkyl. In this cell the conductance was apparently due to the magnesium compound alone, since all of the aluminum was found in the solution, and was approximately equivalent to the quantity of electricity passing through the cell. The appearance of the zinc and cadmium anodes in the earlier experiments led us to suspect that small pieces might have broken off and fallen to the bottom of the cells. Those results were therefore discarded, and the experiments were repeated using paper extraction thimbles around the anodes.

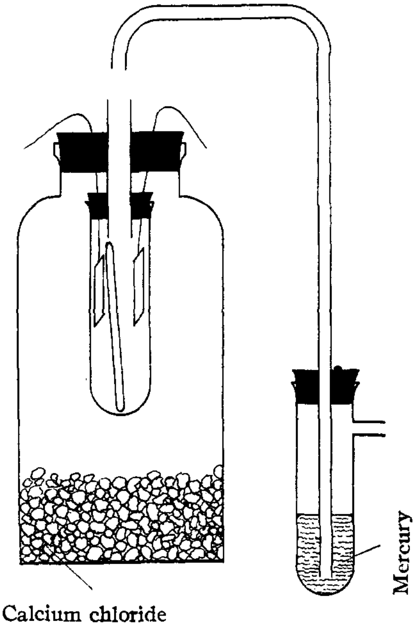

Fig. 1.

TABLE I

SUMMARY OF ELECTROLYSIS EXPERIMENTS

Cell	Anode material	Molar concn. of Grignard compound	Equiv. of Grignard compound in the cell At start	At end	Change	Equiv. of anode material found In soln.	In residue	Coulometer reading in equiv.
1	Aluminum	2.231	0.383	0.104	0.279	0.074	0.000	0.082
2	Bismuth	1.692	.338	.286	.052	.000	.000	.052
3	Gold	1.692	.321	.260	.060	.000	.000	.063
4	Nickel	2.231	.629	.490	.138	.000	.000	.104
5	Silver	2.231	.334	.218	.116	.000	.000	.117
6	Tin	2.231	.334	.254	.079	.000	.000	.099
7	Zinc	1.647	.288	.211	.077	.000	.044	.071
8	Cadmium	1.647	.288	.254	.034	.000	.022	.031

In both of these cases anode material dissolved off and was found later in the residue in the bottom of the cell, while the ether solutions contained none of that material. In neither case was the amount of anode material which was recovered equivalent to the amount of current passing through the solution. Presumably, in these two cells, the anode materials formed metallic alkyls as the result of electrolytic action and were then decomposed by the electric current simultaneously with the Grignard compound. Cadmium alkyls, however, have been reported as being decomposed by the action of light, with the deposition of metallic cadmium[3] and it is possible that the cadmium obtained in these experiments was formed, in part at least, by such action.

In Cells 2, 3 and 5 the amount of isoamylmagnesium chloride decomposed was equivalent, within experimental error, to the quantity of current passing through the solutions. In Cells 1, 4, 7 and 8 the amount of chemical change was greater than can be accounted for by the quantity of current carried. This failure of the analytical results to check is readily explained by the fact that in these cells a certain amount of hydrolysis took place with the formation of a precipitate of basic magnesium chloride. In cell No. 6, however, the amount of chemical change was less than would have been expected on the basis of the quantity of electricity carried through the cell. It is possible that this was due to a short circuit between the electrodes formed by a deposit of magnesium along the glass rod used to hold the electrodes in place. Such a deposit might have escaped observation, since the solution was dark colored.

Summary

1. Ether solutions of isoamylmagnesium chloride were subjected to electrolysis using anodes of various metals and cathodes of platinum.

2. Anodes of aluminum, zinc and cadmium were dissolved off as the result of electrolytic action. Those of bismuth, gold, nickel, silver and tin were not attacked. The amount of aluminum which went into solution was approximately equivalent to the quantity of current passing through the cell.

3. In several cases where the anode was not attacked, an amount of isoamylmagnesium chloride equivalent to the amount of current passing through the cell was decomposed.

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[3] J. Newton Friend, "Textbook of Inorganic Chemistry," Vol. XI, p. 27.