[CONTRIBUTION FROM THE CHEMICAL LABORATORY AT BROWN UNIVERSITY]

The Electrolysis of Liquid Ammonia Solutions of Sodium Triphenylgermanide

BY LAURENCE S. FOSTER AND GILMAN S. HOOPER

Sodium triphenylgermanide, $NaGe(C_6H_5)_3$, is very soluble in liquid ammonia[1] and in solution is highly ionized into sodium ions and negatively charged triphenylgermanyl groups.[2] Upon electrolyzing a solution of this salt in ammonia, the sodium liberated is dissolved in the pool of mercury serving as a cathode and uncharged triphenylgermanyl groups are freed at the anode. If the viewpoint of Goldschmidt and Nagel[3] is correct, the triphenylgermanyl groups, since they are not capable of independent existence, would be expected to react in one of four ways: they might react with each other to form a dimer; they could attack the solvent with the formation of a hydride and, ultimately, gaseous nitrogen, through further reaction of the liberated amino groups; they might react with the metal electrode; and finally if other active molecules are present in the solution, a reaction between them and the liberated triphenylgermanyl groups could occur. Under the conditions of the experiments reported here, only the first two reactions are observed.

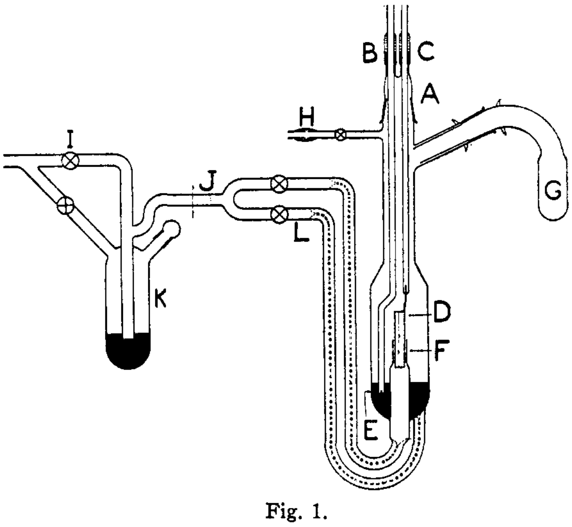

Fig. 1.

The solid product contains hexaphenyldigermane, $[Ge(C_6H_5)_3]_2$, in amounts varying from 10 to 35%, resulting from the association of two triphenylgermanyl groups. The rest of the solid product is triphenylgermane, $Ge(C_6H_5)_3H$, which is precipitated when ammonia molecules are attacked. The nature of anode metal does seem, however, to have an influence on the secondary reactions which result in the formation of nitrogen from the residual amino groups of the ammonia molecules. With a platinum anode the volume of nitrogen is roughly equivalent to, and never less than, the amount of triphenylgermane collected, but with a mercury anode, less than an equivalent quantity of nitrogen is evolved. It appears likely that in the presence of platinum the disproportioning of the hydrogens of the freed amino groups, as illustrated by equation I, occurs without difficulty, but with the substitution of mercury for the platinum, this disproportioning occurs to a much smaller extent.

$$6NH_2 \longrightarrow N_2 + 4NH_3 \qquad \text{(I)}$$

With the limited data obtained it is not possible at present to offer an explanation for this striking difference in behavior. It is certain, nevertheless, that the reactions which are observed when using a platinum anode, and to a limited extent with a mercury anode, are those represented by equations II and III.

$$2Ge(C_6H_5)_3^- \longrightarrow [Ge(C_6H_5)_3]_2 + 2e \qquad \text{(II)}$$

$$6Ge(C_6H_5)_3^- + 2NH_3 \longrightarrow 6Ge(C_6H_5)_3H + N_2 + 6e \qquad \text{(III)}$$

I. Electrolysis between a Mercury Cathode and a Platinum Anode

Apparatus.—The apparatus was of the type commonly used in liquid ammonia work.[4] The cell, pictured in Fig 1, was provided with platinum electrodes which could be raised above the surface of the solution during the preparation of the sodium triphenylgermanide. Tube K[5] was provided to make it possible to introduce and remove the mercury which, after electrode E had been lowered, served as the cathode. In all of the experiments, the cell was immersed in a bath of liquid ammonia at its normal boiling point.

The electrical circuit included a copper coulometer, an ammeter, a voltmeter and a resistance coil. The direct current was supplied by a motor generator capable of variation from fifteen to one hundred and fifty volts.

The Preparation of Sodium Triphenylgermanide.—The solution of sodium triphenylgermanide was prepared in the cell by the reaction of sodium on hexaphenyldigermane, in accordance with the directions of Kraus and Foster.[1] A

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(1) Kraus and Foster, THIS JOURNAL, **49**, 462 (1927).

(2) Kraus and Kahler, *ibid.*, **55**, 3537 (1933).

(3) Goldschmidt and Nagel, *Ber.*, **64**, 1745 (1931).

(4) Johnson and Fernelius, *J. Chem. Ed.*, **6**, 445 (1929).

(5) The tube was constructed by G. K. Teal, and described in his Thesis, Brown University, 1931, page 45.

slight excess of sodium was used to ensure complete reaction of the hexaphenyldigermane. To remove the excess sodium, the mercury in apparatus K was transferred, by means of ammonia pressure, through tubes J and L into the bottom of the cell. By forcing gaseous ammonia through the mercury layer, the solution was agitated and the excess sodium dissolved in the mercury, leaving a clear yellow solution of sodium triphenylgermanide.

Electrolysis of the Solution.—Tubes D and E were lowered into the position shown in Fig. 1 and filled with mercury to make external electrical connections to the sealed-in platinum wires. The rubber joints B and C were made gas tight by means of shellac and tightly wound wire. The current was turned on at a voltage low enough to give a convenient rate of reaction. Immediately the evolution of nitrogen began and simultaneously a white precipitate appeared, which adhered tenaciously to the platinum anode. The rubber joint C was constructed so as to permit a vertical motion of electrode D against the edge of tube F which effectively detached the solid material. Electrolysis was continued, with frequent adjustment of the voltage to higher values, until the color of the solution had disappeared and the current flow had diminished to a very small value. As soon as the current had been turned off, the mercury layer was removed from the cell, back through tube L, as it was found that, on coming to room temperature, the sodium amalgam produced at the cathode reacted with the anode products. The solution was then allowed to evaporate, the ammonia being dissolved in the water over which the nitrogen, evolved during the reaction, was collected. The product left in the cell was first extracted with low boiling petroleum ether, in which hexaphenyldigermane is not soluble, but in which triphenylgermane dissolves readily. The material remaining in the cell was washed out with benzene, in which hexaphenyldigermane is soluble. The evaporation of the solution in each case was carried out in a weighed Erlenmeyer flask so that a fairly accurate estimate of the quantity of each of the products could be made. The products were identified as hexaphenyldigermane and triphenylgermane, respectively, by their melting points and other physical properties. Since triphenylgermane in solution is converted slowly into triphenylgermanium oxide by the action of the atmosphere, the oxide occasionally found was considered to have been derived from the hydride.

The nitrogen evolved was collected over distilled water, previously saturated with nitrogen. It was passed through tubes containing moist phosphorus pentoxide to remove residual ammonia, and after it had been dried, the density was determined. The density was usually very close to that of pure nitrogen, but occasionally it was much too low, and analyses showed the presence of hydrogen which had resulted from the extended electrolysis of the solution. Experiments in which hydrogen was found were discarded.

It is evident that the collecting of the evolved gases over water is not to be recommended. The solubility of gases like hydrogen and nitrogen in water is appreciable and while saturating the water previously may reduce the error due to the solubility, it is not easy to predict how much of the gas is driven out of the water again as the latter becomes saturated with ammonia. It is possible that the high values for the volume of nitrogen obtained in some cases may be ascribed to this phenomenon.

The results of three runs are shown in Table I. The results are typical of those obtained in many more. The data are presented in terms of equivalent weights and have been recalculated on the basis of one equivalent weight of sodium triphenylgermanide.

TABLE I

ELECTROLYSES WITH A PLATINUM ANODE

Experiment no.	I	II	III
Approx. concn. of soln., N	0.095	0.076	0.192
Equiv. of $NaGe(C_6H_5)_3$ used	1.000	1.000	1.000
Equiv. $[Ge(C_6H_5)_3]_2$ obtained	0.109	0.222	0.353
Equiv. $Ge(C_6H_5)_3H$ obtained	.884	0.750	0.656
Equiv. N_2 evolved	1.27	.915	.724
Molecular wt.	30	27.4	26
Faradays of electricity passed	0.98	0.93	0.98
Duration of electrolysis, hrs.	10.5	9	28

II. Electrolyses between Two Mercury Electrodes

Apparatus.—The apparatus used was the same as in the previous experiments with the exception of the cell. This was constructed with a small cup sealed in the bottom so that two concentric pools of mercury could be used as electrodes. It was possible to force ammonia vapor through each pool of mercury independently to break up amalgam crusts.

Preparation of the Solution and its Electrolysis.—The sodium triphenylgermanide was prepared as before by adding sodium to a suspension of hexaphenyldigermane in about 50 cc. of liquid ammonia. The excess of sodium used was removed as described above by means of the mercury used for the electrodes. The passage of current was accompanied by the appearance of a precipitate and the collection of a *very small* amount of nitrogen. The electrolyses were carried out until the amount of current passed was only slightly in excess of the amount necessary to decompose the salt, and the volume of nitrogen evolved was very much smaller than that expected on the basis of equation III. If, however, the duration of electrolysis was greatly extended, further quantities of gas were collected; the gas was found, however, to be a mixture of hydrogen and nitrogen resulting presumably from the decomposition of the ammonia in the presence of traces of conducting substances other than the original sodium salt.

Table II gives the results of three typical runs. The data in this table are much more self-consistent than those in Table I, due to improvements in technique made during

TABLE II

ELECTROLYSES WITH A MERCURY ANODE

Experiment no.	I	II	III
Approx. concn. of soln., N	0.134	0.141	0.135
Equiv. $NaGe(C_6H_5)_3$ used	1.000	1.000	1.000
Equiv. $[Ge(C_6H_5)_3]_2$ obtained	0.141	0.141	0.106
Equiv. $Ge(C_6H_5)_3H$ obtained	.858	.860	.893
Equiv. N_2 evolved	.142	.118	.115
Molecular wt.	27.9	...	...
Faradays of electricity passed	1.24	1.12	0.98
Duration of electrolysis, hrs.	15	18	17

the course of the work. The apparent agreement between the amount of nitrogen and the amount of hexaphenyldigermane, however, has no significance. It results from the fact that the concentrations of the starting solutions were about the same. With more concentrated solution, in general, more hexaphenyldigermane results. The results have been recalulated to a basis of one equivalent weight of sodium triphenylgermanide.

Summary

1. When a solution of sodium triphenylgermanide in liquid ammonia is electrolyzed, the products are hexaphenyldigermane, triphenylgermane and nitrogen.

2. When a platinum anode is used, the quantity of nitrogen corresponds roughly to the amount of triphenylgermane obtained, but when a mercury anode is used, the quantity of nitrogen is markedly smaller than the predicted value. No explanation of this striking difference in behavior can be made at present.

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The Apparent Molal Isochoric Heat Capacity of Electrolytes[1]

BY FRANK T. GUCKER, JR., AND T. RICHARD RUBIN

Recent studies of the thermal properties of solutions have shown that the apparent molal heat capacity of electrolytes is a linear function of the square root of the concentration over a remarkably wide range, but that individual salts of the same valence type differ considerably both in their slopes and in the limiting values to which they appear to extrapolate at infinite dilution. These facts recently have been summarized and discussed in an article[2] which contains references to the experimental work. All of this was carried out in the usual constant pressure calorimeter, and the apparent molal isopiestic heat capacities alone have been considered. We undertook the present investigation to find out how much the isochoric values differed from the isopiestic ones and to see whether they exhibited any greater regularity among salts of the same valence type.

The difference between the two heat capacities *for 1 cc. of any substance* can be calculated from the well-known thermodynamic equation[3]

$$c_p - c_v = \alpha^2 T/\beta \qquad (1)$$

$$\text{where } \alpha = \frac{1}{V_0}\left(\frac{\partial V}{\partial T}\right)_P \text{ and } \beta = -\frac{1}{V_0}\left(\frac{\partial V}{\partial P}\right)_T$$

are the coefficients of thermal expansibility and of compressibility and T the absolute temperature. V_0 is the volume of the substance under consideration *at atmospheric pressure.* The apparent molal isopiestic and isochoric heat capacities may be defined by the equations

$$\Phi(C_{p2}) = c_p V - c_{p1} V_1 \qquad (2)$$

$$\Phi(C_{v2}) = c_v V - c_{v1} V_1 \qquad (3)$$

where c_p and c_{p_1}, c_v and c_{v_1} are the respective heat capacities *per cubic centimeter* (*not per gram*) of solution and of solvent; V is the volume of solution which contains a mole of solute and V_1 the volume of solvent in which the solute is dissolved. Combination of (1), (2) and (3) gives us the difference between the two apparent molal heat capacities, namely

$$\Delta\Phi(C_2) = \Phi(C_{p2}) - \Phi(C_{v2}) = (\alpha^2 VT)/\beta - (\alpha_1{}^2 V_1 T)/\beta_1 \qquad (4)$$

Calculation of β at 1 Atmosphere.—The calculation of the difference requires a knowledge of the coefficients of expansibility and compressibility at 25° and under one atmosphere pressure. The series of compressibility measurements by Lanman and Mair[4] upon which we based our calculations were made at 25°, but over the pressure range 100 to 300 bars.[5] Our first problem was to reduce these values to atmospheric pressure, and our method was that recently applied by Gibson[6] in his treatment of the properties of solutions under pressure.

It is well known that the compressibility of water decreases as the pressure is increased. The behavior of 1 g. of water can be expressed very satisfactorily by means of a differential equation which Tait suggested in 1888

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[1] Presented at the Cleveland Meeting of the American Chemical Society, September 12, 1934.

[2] Gucker, *Chem. Rev.*, **13**, 111 (1933).

[3] *Cf.* Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923, p. 136, for the corresponding equation for 1 *mole* of the substance.

[4] Lanman and Mair, THIS JOURNAL, **56**, 390 (1934).

[5] 1 bar = 10^6 dyne/sq. cm. = 0.9869 atmosphere.

[6] Gibson, THIS JOURNAL, **56**, 4 (1934).