[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Galvanic Cells Containing Potassium Triphenylmethyl

BY H. E. BENT AND E. S. GILFILLAN, JR.

One of the most interesting properties of organic free radicals is the reaction with an alkali metal to give a compound having many of the properties of a simple salt. Such a compound will react metathetically with an acid (*i. e.*, a methane),[1] will dissolve to give a solution which is an electrolytic conductor[2] and is formed with the liberation of an amount of energy not greatly different from that accompanying the formation of a typical inorganic salt.[3]

In spite of the salt-like character of these compounds we have been able to find no records of experiments in which solutions of them have been used as electrolytes in galvanic cells. Should they behave as normal salts in such experiments they would supply just the required properties for solving the problem of determining the standard electrode potential of cesium. The measurements would consist in determining the potential of a cell composed of electrodes of cesium and a dilute cesium amalgam and then the potential of another cell containing this same amalgam in contact with cesium ion in aqueous solution.[4]

In order to determine the suitability of these compounds for use in galvanic cells we have studied the behavior of cells in which the electrodes were potassium and potassium amalgam and of cells containing two electrodes of dilute amalgams. The electrolyte in these cells was a solution in diethyl ether of the potassium addition compound of triphenylmethyl or a closely related compound containing biphenyl or naphthyl groups.

Our experiments show that cells which have potassium amalgams for both electrodes give potentials which one would expect for a normal salt, *i. e.*, the same potential as is found when the electrolyte is potassium iodide dissolved in ethylamine or potassium hydroxide dissolved in water. However, cells containing one potassium amalgam electrode and one potassium electrode give very erratic potentials which are less than correspond to the transfer of one gram atom of potassium for each Faraday of current. A number of cells designed to determine the cause of this behavior show that it is not due to impurities in the electrodes or to surface effects but to some change in the electrolyte which takes place in the presence of potassium.

These observations indicate that these compounds are quite unsuited to the problem of determining the cesium electrode potential. They also

---

[1] Conant and Wheland, THIS JOURNAL, **54**, 1212 (1932).

[2] Schlenk and Marcus, *Ber.*, **47**, 1664 (1914); Ziegler and Wollschitt, *Ann.*, **479**, 123 (1930).

[3] Bent, THIS JOURNAL, **52**, 1498 (1930).

[4] Lewis and Kraus, *ibid.*, **32**, 1459 (1910).

suggest that a cell reaction cannot be taken for granted in determining potentials. Finally these results further justify the assumption that these compounds are simple salts except when undergoing a transformation in the presence of alkali metal.

Experimental

Eleven cells have been prepared and their potentials measured. A Wolff potentiometer and a Leeds and Northrup type HS galvanometer, which is sensitive to 10^{-11} ampere, were used. In general the technique consisted in evacuating the cell until the pressure was too small to be measured on a McLeod gage (less than 10^{-4} mm. of mercury), distilling the potassium into the cell, introducing the amalgam by means of a stopcock, and introducing the electrolyte by breaking the tip of a glass capsule with a magnetic hammer.

In order to test the materials and method of assembly, one cell was prepared as nearly as possible like the ones used by Lewis and Keyes in the determination of the standard electrode potential of potassium;[5] *i. e.*, potassium | potassium iodide in ethylamine | 0.2216 weight per cent. potassium amalgam. The e. m. f. obtained by Lewis and Keyes was 1.0481 volts. We obtained a value of 1.0487 ± 0.0002 volts using an amalgam containing 0.2216 weight per cent. potassium. This agreement indicates that the method of handling the materials is satisfactory.

The evidence that potassium addition compounds of free radicals behave in a perfectly normal manner in cells containing amalgam electrodes is furnished by the data from three cells. The first of these cells furnished the best evidence. It was constructed to give a very low resistance in order to give very high accuracy in the e. m. f. measurements. It consisted of a tube twenty centimeters long containing a ridge the length of the tube, formed by pushing in the glass with a copper tool. The amalgams extended the length of the tube but were kept separate by this ridge. The tube was then nearly filled with the ether solution of potassium triphenylmethyl. The e. m. f. could be measured to two one-hundredths of a millivolt and was found to be 0.12835 ± 0.0002. Amalgams from the same storage flask were then used in another cell of the type used by Richards and Conant,[6] using as electrolyte an aqueous solution of potassium hydroxide. The e. m. f. so obtained was 0.12835 ± 0.0001, in perfect agreement with the value previously obtained.

A second cell with amalgam electrodes was constructed to test the behavior of other organic free radicals and different methods of preparing the potassium addition compound. The electrolyte was prepared by treating a mixture of methyl diphenylbiphenylmethyl ether, methyl α-naphthyldiphenylmethyl ether and methyl-α-naphthylphenylbiphenyl methyl ether with metallic potassium. The observed e. m. f. was 0.0291 ± 0.0001. The value found for the same amalgams when using a solution of potassium iodide dissolved in ethylamine as the electrolyte was 0.0291 ± 0.0001. Here again the agreement is within the experimental error.

A third cell which was designed primarily for a different purpose gave still further proof that in such cells the electrolyte is behaving in a perfectly normal manner. The e. m. f. found was 0.0655 ± 0.0005. The value found with potassium iodide dissolved in ethylamine as the electrolyte was 0.0652 ± 0.0001.

Eight cells were constructed which contained one amalgam electrode and one electrode of potassium. With the exception of one cell which was doubtless defective[7]

---

[5] Lewis and Keyes, This Journal, **34**, 119 (1912).

[6] Richards and Conant, *ibid.*, **44**, 601 (1922).

[7] The defective cell gave very erratic potentials and soon exhibited so high a re-

the e. m. f. was always too low and was inconstant. Most of these cells could be measured with an experimental error of not more than 0.01%. However, the e. m. f. was from 0.5–0.95 of the correct value and usually decreased during a period of a week or two by 10–20% of its value.

The construction of these cells will not be discussed in detail. However, in their construction the following factors were considered as possibly related to their behavior: surface films on the potassium; mercury dissolved in the surface layer of potassium coming from the pump, amalgam or electrolyte; a change in the concentration of amalgam due to transfer of potassium; polarization; and the nature of the free radical. In addition cells were constructed which differed greatly in resistance. The concentration of the electrolyte was varied from a highly supersaturated solution to one whose mole fraction was 10^{-7}. This very high dilution was accomplished by decantations in a closed system and subsequent distillations of the ether back into the cell. The effect of time was studied by making measurements within a few seconds of the time of contact with the potassium and extending the measurements for a period of months. In order to avoid the possibility of traces of mercury from the solvent contaminating the potassium, the electrolyte was prepared in the absence of mercury. The usual way of making the electrolyte was to shake a solution of triphenylchloromethane with dilute potassium amalgam. In order to avoid the presence of mercury and vary the method of preparing the electrolyte, three ethers were prepared and then treated with metallic potassium. The reaction required five weeks for completion, the solution being shaken mechanically during this period. The resulting solution did not differ in appearance from solutions prepared from the chlorides. These ethers have apparently not been described in the literature. They were prepared by dissolving the chlorides in benzene, adding methyl alcohol and recrystallizing the products from dry ether. The three compounds were methyl diphenylbiphenylmethyl ether, m. p. 94–95°, methyl diphenyl-α-naphthylmethyl ether, m. p. 142°, and methyl-phenyl-α-naphthylbiphenyl ether, m. p. 190–191°.

The last cell which we constructed seems to shed the most light on the behavior of these cells. This cell contained three electrodes, two of dilute amalgams and one of potassium. The electrolyte was introduced in such a way as to come in contact with only the amalgams. The observed e. m. f. was 0.0655 ± 0.0005. The correct value is 0.0652 ± 0.0001. The cell was then tipped so that electrolyte came in contact with all three electrodes. As was to be expected, the value obtained using the potassium as one electrode was too small. However, the value obtained using the two amalgams was changed to 0.0605, a difference ten times the experimental error of measurement. Tipping the cell so as to remove the electrolyte from the potassium did not alter this value but after three weeks a value of 0.0599 was obtained. Further standing in contact with potassium resulted in a value of 0.0523. This cell indicates clearly that the electrolyte undergoes some slow irreversible reaction such that the cell reaction is no longer the transfer of one gram atom of potassium for each faraday of current passing through the cell.

Conclusions

1. Potassium triphenylmethyl and some related compounds function as normal electrolytes in galvanic cells containing amalgam electrodes.
2. Potassium triphenylmethyl and some related compounds undergo a slow irreversible reaction when in contact with potassium which precludes their use in galvanic cells containing potassium.

CAMBRIDGE, MASSACHUSETTS

RECEIVED AUGUST 4, 1932
PUBLISHED JANUARY 11, 1933

---

sistance that it could not be measured. We presume that the potassium pulled away from the connecting wire during solidification.