rivalent platinum which is not converted into an aquo compound even by concentrated hydrochloric acid.

Summary

1. A new complex compound of quadrivalent manganese has been prepared which has the composition $K_2[Mn(C_2O_4)_2(OH)_2]\cdot 2H_2O$. The barium and chloropentamminecobalti salts were also isolated.

2. The absorption spectrum was measured in the visible region.

BUFFALO, NEW YORK RECEIVED JUNE 19, 1936

NOTES

Sodium Fluorenone as a Dehydrating Agent[1]

BY H. E. BENT AND H. M. IRWIN, JR.

The most rapid method of drying an organic liquid is to dissolve in it some compound which reacts rapidly with water. For this purpose sodium benzophenone has been widely used although this involves using an alkali metal, sodium–potassium alloy or some other material which introduces considerable hazard into such work. Fluorenone has the advantage over benzophenone that it will react readily with dilute sodium amalgam to form an addition compound which has a deep green color and therefore like benzophenone gives a definite indication by its color of the absence of water. Dry solvent is then obtained by distilling from this solution.

The object of this investigation is to compare the efficiency of sodium fluorenone with the customary drying agents, magnesium perchlorate and activated alumina. Since the compound formed by the addition of sodium to fluorenone is more stable than that formed with benzophenone, it is important to be sure that the ketyl is still sufficiently reactive to be an effective drying agent.

A dilute solution of sodium fluorenone was prepared for this work by introducing 0.025 g. of fluorenone and evacuating with a mercury pump for one hour. Three to five cubic centimeters of a saturated amalgam (about 1%) was then added *in vacuo* and 50 cc. of dry ether. Shaking produced a solution which was sufficiently concentrated to react with at least one hundred times as much water as is retained by the glass on its surface.[2] A tube, connected to the reaction flask by a capillary capable of being broken and thereby opened by a magnetic hammer, carried four side-tubes. The first two were empty and used as a check on the method. The third and fourth contained activated alumina and magnesium perchlorate, respectively. The samples of alumina and magnesium perchlorate were prepared by exposing them in a thermostat to one liter of air saturated with water vapor at 25°. The quantity of water absorbed by the sample was at least one hundred times as much as was necessary to destroy the sodium fluorenone with which it came in contact, while still being small enough to give the very low vapor pressure characteristic of the dehydrating agent. The tubes containing the solid dehydrating agents were evacuated for a short time before sealing the apparatus, and immediately the capillary was broken in order to prevent diffusion from one solid to the other. The fluorenone was decolorized in the first empty tube on account of moisture on the glass and in the vapor state. In the second tube the solution retained its color. In the third and fourth tubes the solution was immediately decolorized by the alumina and by the magnesium perchlorate, indicating that the vapor pressure of water was sufficiently high to be removed by the ether solution of sodium fluorenone. A duplicate run verified the conclusion from this experiment.

The vapor pressure of water is given as 0.003 mm. for alumina and the water is given as unweighable in 210 liters for magnesium perchlorate.[3] If unweighable means less than 1 mg. this would give a vapor pressure of less than 0.005 mm. If we assume that in the presence of a small amount of water the ketyl is converted to fluorenone and fluorenole,[4] then we can estimate a mini-

---

[1] This problem was studied as a reading period assignment in the first course in physical chemistry at Harvard University.

[2] Bent and Lesnick, THIS JOURNAL, **57**, 1246 (1935).

[3] Yoe, *Chem. News*, **130**, 340 (1935).

[4] Bachman, THIS JOURNAL, **55**, 1179 (1933).

mum value for the equilibrium constant for the reaction

$$NaR + H_2O = NaOH + {}^1/_2R + {}^1/_2RH_2$$

Since the sodium hydroxide is present as a solid we may express the equilibrium constant by the equation

$$K = (R)^{1/2}(RH_2)^{1/2}/(NaR)(H_2O)$$

If we assume, as a consequence of the complete destruction of the green color of the solution, that the reaction goes at least 99.9% to completion, then we obtain

$$K = 0.5 \times 999 \times 23/0.003 = 3.8 \times 10^6$$

referring the vapor pressure of water to that of pure liquid water as the standard state. This gives a value for ΔF of -9.0 kcal. These figures represent the minimum efficiency of sodium fluorenone as a drying agent. In any normal procedure a large excess of the drying agent would be used which would result in the removal of water until the pressure is at least as low as 10^{-7} mm.

CONTRIBUTION FROM THE
CHEMICAL LABORATORY
HARVARD UNIVERSITY
CAMBRIDGE, MASS.

RECEIVED JULY 30, 1936

The Vapor Density of Hexaphenylethane

BY H. E. BENT AND E. S. EBERS

In a recent publication the statement is made that hexaphenylethane probably does not dissociate in the vapor state.[1] In order to verify this statement an attempt was made to measure directly the vapor density of hexaphenylethane. This measurement combined with the previous data on the vapor pressure would give the molecular weight in the vapor state.

Since the vapor pressure of hexaphenylethane at 120° is only 0.004 mm. a very large volume would be necessary in order to produce a weighable amount of compound. For this purpose a ten-liter flask was attached to the fiber gage used in the previous research and to a capsule of hexaphenylethane. Ground joints controlled by electromagnets were so arranged as first to saturate the ten-liter flask with the ethane and then, closing the ethane capsule, condense the vapor in a small ampoule. The flask could then be saturated again and the vapor a second time condensed and in this way any desired amount of material obtained.

The method was checked by determining the vapor density and the molecular weight of triphenylmethane. The result was high by about 20% which we assume to be due to adsorption. As it was expected that difficulty would be encountered with hexaphenylethane on account of decomposition a procedure was adopted with triphenylmethane which would avoid this difficulty as far as possible. The ground joint to the pump was opened just enough to reduce the pressure to about three-fourths of the saturation pressure. After the pressure had become constant the valves to the pump and to the capsule of sample were closed simultaneously and the valve to the receiver opened for a time sufficiently long to condense about half of the total amount of material in the ten-liter flask. The valve to the receiver was then closed and the pressure again measured, the difference between the initial and the final pressure giving a measure of the amount of material condensed. This process was repeated about ten times and the flask then cooled and the receiver cracked off. The amount of material was determined by weight, both by difference and by evaporation of the solution of the compound to dryness in a crucible. This method of operating between three-fourths and three-eighths saturation would also be effective in avoiding condensation in the ten-liter flask or in removing adsorbed material from the surface of the glass during condensation.

When the method was applied to hexaphenylethane it was found that decomposition was too rapid to permit even an approximate determination of the vapor density. In a flask of such a large size decomposition was so great that even with the pump operating the pressure remained several times that of hexaphenylethane for a space of three hours at 120° (the valve to the solid remaining open). By this time apparently all of the ethane had decomposed for the pressure gradually decreased. However, the material in the flask was no longer hexaphenylethane but a decomposition product for on closing off the flask the pressure remained perfectly constant. Under these conditions hexaphenylethane decomposes rapidly enough to be measured easily. We concluded, therefore, that it is not possible to meas-

---

[1] G. R. Cuthbertson and H. E. Bent, THIS JOURNAL, 58, 2000 (1936).