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CHEMICAL REACTIONS AND ELECTRICAL CONDUCTIVITY OF NON-AQUEOUS SOLUTIONS.

BY H. P. CADY AND H. O. LICHTENWALTER.

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During recent years, Kahlenberg[1] and others have published several papers in which they set forth reasons for not accepting the dissociation theory. For instance, Kahlenberg[2] conducted double decompositions in non-aqueous solutions and states that some instantaneous reactions occur without any conductivity, hence no ionization. It is with a view of studying similar double decompositions that this investigation has been undertaken. Kahlenberg chose benzene as a solvent and copper, nickel and cobalt oleates as the solutes. After drying the benzene very care-

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[1] Kahlenberg, *J. Phys. Chem.*, **6**, 1 (1902); Sammis, *Ibid.*, **10**, 593 (1906); Gates, *Ibid.*, **15**, 97 (1911).

[2] *Loc. cit.*

fully, he found the conductivity to be practically negligible. After drying the oleates over phosphoric anhydride and sodium, their solutions in benzene also were found to be non-conductors. He then passed dry hydrochloric acid into this solution and observes that a large precipitate formed and still no conductivity was observed. From this he drew the conclusion that instantaneous double decomposition occurred without the presence of ions.

Since the above work was done, Professor H. C. Allen,[1] of this University, has repeated the experiments and also found that the dry benzene is practically a non-conductor. However, when he introduced the dry oleates into the benzene, a marked increase was observed in the conductivity and when hydrogen chloride was passed into this solution, a precipitate formed, but by no means instantaneously. From the moment the hydrogen chloride was added, the conductivity increased until it reached a maximum at the instant the precipitate appeared, when it was so great as to deflect the galvanometer needles off the scale. As the precipitation became complete, this deflection grew much smaller. The apparatus used was similar to that described by Kahlenberg in the above reference and corresponds in most respects to the description, which will follow, of the apparatus used in this investigation.

In addition to the above knowledge concerning the solutions of salts of unsaturated acids, it was thought desirable to learn whether salts of the saturated acids would give similar reactions, and also to study salts of unsaturated acids with two double bonds as well as others with one double bond besides the oleates.

One of the first difficulties encountered was in finding salts which are soluble in hydrocarbons. It was found that benzene, toluene and petroleum ether can equally well be used as solvent, being almost perfect insulators. The following salts were found to be soluble in one or more of the above: silver melissate,[2] copper melissate,[3] lead stearate, barium linoleate,[4] lead erucate and copper oleate.[5]

These salts were prepared from the respective acids obtained from Kahlbaum or Schuchardt. A slight excess of sodium hydroxide was added to the acids forming the sodium salts. The calculated amounts of sulfates or acetates of the respective metals were then added to these sodium salts giving the desired products. These precipitates were carefully washed with water and dried in a water oven for several days. They were then dissolved in benzene or toluene and placed in bottles with a

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[1] "Instantaneous Chemical Reactions in Benzene and Toluene," *Kans. Univ. Sci. Bulletin*, **1905**.

[2] *Archiv. Pharm.*, **246**, 170.

[3] *Ann.*, **183**, 354.

[4] Lewkowitsch, p. 112.

[5] *Ann.*, **244**, 266 (1888).

liquid alloy of metallic potassium and sodium, and left there for several weeks until perfectly dry. It was found that this alloy of potassium and sodium serves very well to dehydrate the solutions. In order to obtain an alloy liquid at ordinary temperatures, the metals were heated together in proportions of at least 50% potassium.[1] Such a liquid continually keeps a clean metallic surface exposed to the solution.

The hydrogen chloride was prepared in a Kipp generator by concentrated sulfuric acid and ammonium chloride. The generator was connected to a gas washing bottle, containing concentrated sulfuric acid. After passing through this, the hydrochloric acid was conducted through two towers about 40 cm. in height. These towers were filled with alternate layers of pumice stone and phosphoric anhydride. From the tower the hydrochloric acid was led through an electric resistance heater and into the cell used to measure the conductivity.

The cell was enclosed in a larger jacket in which phosphorus pentoxide was placed to keep the outer portion of the cell perfectly dry. It was one of the same type as the Arrhenius resistance cell. The electrodes were of platinum and placed about 1 mm. apart. They were connected. by platinum wires sealed through the bottom of the cell, to lead wires connected to the galvanometer and current. These lead wires passed through openings in the rubber stopper which closed the casing around the cell. Sulfur was used to insulate the wires from the rubber. In the top of the cell was placed a three-holed rubber stopper through which three glass tubes entered the cell. Through one of these tubes was admitted the hydrochloric acid. One was used to carry in the air, which served to dry the cell, also to introduce the solution. The third was connected with a phosphorus pentoxide tube in series with a calcium chloride tube. The escaping gases from the cell passed out through this last tube. When conductivity measurements were taken, the cell was connected in series with a direct current generator of 110 volts and with a sensitive galvanometer. No other resistance—except that of the lead wires and of the galvanometer—was introduced except in instances that will be mentioned later. The sensitiveness of the galvanometer was determined by connecting it with a potentiometer and measuring the deflection when the electromotive force was varied, but always at known value. It was found that when an electromotive force of one volt was applied, it would require 8,654,700 ohms resistance in order that the galvanometer would show a deflection of 1 division (cm.). The resistance of the galvanometer coil was found to be 1243 ohms. The galvanometer cell and entire system were insulated by placing them on sulfur. This proved to be the best insulator that was available. It was used to insulate every place where there was a chance for leakage of current. Hard rubber and other sub-

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[1] Landolt-Börnstein, p. 304.

stances were tried, but in every case where they were used the instrument showed marked effects of leakage.

Before making conductivity measurements, dry air was passed through the cell until the deflection of the galvanometer was negligible. A flask of liquid air was connected in series with a wash bottle filled with sulfuric acid and a tower filled with pumice stone and phosphorus pentoxide similar to the one mentioned above. From this tower the air was led through the electric resistance heater, then through the cell. Thus, the cell was thoroughly dried by passing this hot air through each time before use. The tower connected with the hydrochloric acid generator and the one through which the air was passed connected to the same glass tube by a two-way stopcock, thus enabling the operator to pass in either hydrochloric acid or air at will.

The solutions used were centrifuged whenever necessary in order to settle out any particles. They were then placed in a tube fitted with a two-holed rubber stopper. These connected with a tube passing to the conductivity cell and one connected with the drying tower through which the air passed. By means of a two-way stopcock the air could be passed through the tube thus forcing the solution into the cell.

Before taking readings of the conductivity of the solution, the cell was, in each instance, dried so thoroughly that when the 110 volts was applied the galvanometer would show a deflection of only about one division or less. The toluene and benzene, dried over sodium-potassium alloys, the same as were the solutions, were placed in the cell and showed scarcely any deflection—a small part of a scale division. The hydrochloric acid was also tested and conducted scarcely any better than the air. This was again swept out by air before using the cell further.

When a toluene solution of copper oleate was introduced, the conductivity was so great that the galvanometer needle was thrown off the scale (40 divisions). A shunt of 200 ohms was placed across the galvanometer, thus carrying approximately one-seventh of the current through the instrument—and the reading was found to be about 9 divisions. Hydrogen chloride was then admitted and the deflection was so large as to again pass off the scale, with only this portion of the current. A rather rapid precipitation of copper chloride occurred. The deflection soon began to decrease and finally became negligible. The shunt was then disconnected from the galvanometer and still the deflection was less than a division after the precipitate had settled. Instead of drying the copper oleate used here by the method described above, it was placed in the toluene with potassium, then heated in an Erlenmeyer flask fitted with a condenser tube. This was found to dry the solution in a short time when heated to boiling. This method was used because it was found when dried by the slower process nearly all the copper was thrown out of solution forming a dark layer just above the sodium-potassium.

With a benzene solution of lead erucate the deflection was again so great as to throw the galvanometer off the scale. When a shunt of 40 ohms was placed across the instrument, the deflection was 14 divisions. When introducing hydrogen chloride, it went off the scale but gradually lowered to a negligible deflection. In this case, also, a precipitate was observed. Another sample gave similar results.

The first of the saturated salts used were the melissates. The copper salt was dried in same way as the copper oleate for the same reason. The silver salt was kept in a dark place while drying. When a benzene solution of the copper melissate was used the deflection was again great enough so that it was necessary to put in a shunt of 300 ohms. It now read 34 divisions. When hydrogen chloride was passed, the deflection at first was too great to read on the scale, but soon came down to a few divisions. No precipitate was observed. The silver melissate gave similar results, except that the conductivity was less. A toluene solution of lead stearate was used and it gave a deflection of about 13 divisions. On passing hydrogen chloride, this was increased to 17 divisions. No precipitate formed.

Barium linoleate was then tried in a benzene solution. This salt was used because it contains two double bonds. When dried in the air, as mentioned above, the solution was found to give a deflection of about 7 divisions, which increased to 21 divisions when hydrochloric acid was introduced. However, no precipitate was formed. This salt was again prepared but instead of drying in the air before final dehydration over sodium and potassium, it was dried as well as possible between filter paper and immediately placed in solution over sodium and potassium and heated as the above salts. When introducing this solution into the cell the deflection was so great that it was necessary to insert a shunt of 200 ohms across galvanometer. The reading on the scale was then 7 divisions. When hydrogen chloride was admitted, the deflection was too large to read at first. A large precipitate rapidly formed and after this settled the deflection decreased to 3 divisions. The difference in the results obtained with this salt suggest that, when dried in air, it becomes saturated—the two double bonds becoming satisfied by oxidation—and under these conditions one would expect results as above, which were similar to those with the saturated salts.

It is seen from the above that in no instance did precipitation occur between the hydrogen chloride and the salts of saturated acids—melissates and stearates. However, their benzene and toluene solutions showed some conductivity which increased when hydrogen chloride was passed through the solution. The salts with one double bond—oleates and erucates—precipitated in every instance and showed considerable conductivity. Likewise, with the linoleate where we have two double bonds.

An increase in conductivity was observed in each solution when hydrogen chloride was added, showing ionization to some extent at least. After saturating the solution with hydrogen chloride, it was partly swept out by passing air through the cell. By thus decreasing the concentration, the deflection increased for some time, then decreased, thus showing maximum conductivity when not completely saturated with the acid.

In no instance was the reaction found to be instantaneous, although rather rapid, especially with the linoleate.

The decrease in the conductivity soon after the solutions were introduced suggested that the polarization was quite appreciable. In order to test for this, we passed the current of 110 volts through the cell containing the solution for a short time. Then, by means of a specially constructed switch set in sulfur, the current was broken and at the same time, the cell was connected to a condenser with a capacity of one microfarad, thus charging the latter. The condenser was also connected—through a condenser key—to the galvanometer. By this condenser key the condenser was discharged through the instrument. It gave a considerable deflection. On comparing this deflection with that given by the charge stored in the condenser by a standard Weston cell, it was found that the solutions gave rise to a black electromotive force of a large fraction of a volt. This polarization again shows that the solutions have electrical properties similar to those of any ordinary electrolyte.

Kahlenberg states that reactions like the above cannot be explained by the dissociation theory. While the conductivity with the above unsaturated salts is perhaps insufficient to account for the rapid reactions, it is great enough to indicate that the reactions may be due to ionization. Another explanation may be offered which would seem very reasonable from the results obtained. This explanation assumes that the reactions with the salts of the unsaturated acids take place in two steps. First, the salt combines with the hydrogen chloride and forms addition products. Second, intramolecular rearrangement occurs with the precipitation of the chloride and the formation of the acid. If such addition products are formed with salts of unsaturated acids, we would expect results such as were obtained, since they would not be formed in saturated salts. If this is true, we would then conclude that ionization in the latter was insufficient to cause precipitation, while, in the unsaturated, the precipitation did occur due to the combined effects of ionization and the formation of addition products.

In view of the appreciable conductivity observed with each solution that gave a precipitate, every one of the above reactions is in accord with the dissociation theory, especially if, in addition, the explanation, which has just been mentioned, is accepted.

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VALENCE AND TAUTOMERISM.

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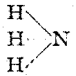
CONTENTS.—1. Two Valence Numbers, Polar and Total. 2. A Method of Classifying Tautomeric Changes.

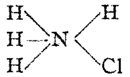
So much has been written on valence and tautomerism that we are making, with some hesitation, an attempt to state certain ideas in simple language, and in a way which we hope will be acceptable to organic, inorganic and theoretical chemists. In the present brief paper we shall not attempt to trace the historical development and we cannot hope properly to assign credit for the various ideas. We wish, however, to mention that these subjects have often been discussed in the colloquiums at the Massachusetts Institute of Technology and at the University of California, and that we are indebted in particular to Professor G. N. Lewis for his suggestions and criticisms.

Polar Number and Total Valence Number.—In the first place, it is necessary to differentiate the two ideas embodied in the term valence number, each of which is frequently emphasized to the exclusion of the other. We suggest that these be distinguished by the names *polar* number and *total* valence number. The latter, alone, is met with in elementary organic chemistry; and the former is becoming more and more popular in elementary inorganic chemistry.

The difference between the two ideas may be illustrated by means of ammonia and ammonium chloride. Many organic chemists insist that the valence numbers of the nitrogen in these compounds are 3 and 5 respectively, and thus emphasize the total number of valence bonds of the nitrogen, as illustrated by the following structural formulas:



and



On the other hand, many inorganic chemists consider that it is more important to emphasize the relationship between ammonia and ammonium chloride, and insist that the valence number of the nitrogen is —3 in both cases. From this point of view the valence number of hydrogen in its compounds is in general +1, that of chloride chlorine is —1, and that of nitrogen is —3 in ammonia, ammonium ion, or any ammonium salt.

Many of the misunderstandings which have arisen in this matter seem to us to be due to the failure to recognize that two separate ideas are in-