

Instantaneous Chemical Reactions in Benzene and Toluene

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June 7th, 1905

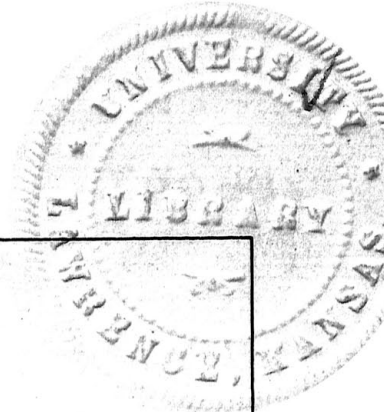
Submitted to the Department of Chemistry of the University of Kansas in partial fulfillment of the requirements for the Degree of Master of Arts

Master Thesis

Chemistry

Allen, H.C. 1905

"Instantaneous reactions
(chemical) in benzene and
toluene".



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Until quite recently the study of chemical reactions in solutions had been confined almost exclusively to those in which water was used as a solvent, and the phenomena exhibited have led to the advancement of many and varied theories by different men.

Most conspicuous among these phenomena are the differences in the conductivities of different solutions, and variations in the conductivity of the same solution with varying dilution; and abnormal variations in the vapor pressure with change of concentration as shown by the abnormal depression of the freezing point, rise in the boiling point or change in the osmotic pressure; also the fact that the heat of neutralization of the strong acids and strong bases is a constant in dilute solutions.

Shortly after the epoch making discoveries of Galvani and Volta(1) Davy(2) began his experiments with the electric pile which finally resulted in the separation of the alkali metals from their oxides. The result of his studies is the electro-chemical theory that bears his name. This theory, however, never gained much prominence but soon gave place to the theory of Berzelius which differed from it fundamentally in that, while Davy believed that the atoms as such are electrically zero, and become charged positive or negative by contact with other atoms, that take a charge of the opposite sign; Berzelius(3) claimed that every atom is charged with both kinds of electricity. These exist upon the atom in polar arrangement, and the electrical and chemical

1. Phil. Trans., 1798, I, p. 10. Gress. Journ. d. Phys. 3, 479 (1798)
2. Nicholson's Journ., 4, 275, 326. Gilb. Ann. 7, 114, (1801); 28, 1, 161 (1808).
E. Gilb. Ann. 27, 270, (1807).

nature of the atom depends upon which kind of electricity is present in excess.

The theory of Grotthuss(1) to account for the electrolytic decomposition of water was very satisfactory for a time. Grotthuss brought forward the view that the molecules of an electrolyte arrange themselves polarly so as to form a chain: according to this hypothesis, which was believed for some time, and even yet finds a place in many text books, all the dissolved molecules in a solution take up such a position that their positively charged sides are towards the negative electrode, and the negatively charged ones towards the positive electrode. During the electrolysis the positive atom next the negative electrode, and the negative one next the positive electrode, are separated. The negative atom of the first molecule now combines with the positive atom of the molecule next it, and this new molecule now turns round so as to take up a position similar to that of the original molecule.

A step in the right direction was made by Williamson(2) who discarded these theories; called statical because each atom was supposed to be attached to a particular atom of opposite sign in the solution; and believed "that in an aggregate of the molecules of every ~~substance~~ compound, a constant interchange between the elements contained in them is taking place," or that there is movement among the atoms.

Clausius, however, did not think it necessary to go as far as Williamson but also recognised that the theory of Grotthuss was deficient. Accordingly he proposed what might be called a compromise, which supposed that under ordinary circumstances only a portion of the molecules of an electrolyte were broken down. Under the influence of an electric current these part-

1. Ann. de Chim. (1), 58, 54 (1806).
2. Lieb. Ann. 77, 37 (1851).
3. Pogg. Ann. 101, 338 (1857).

molecules will be attracted to the electrode of opposite sign.

This assumption of a partial breaking down of the molecules before the passage of a current accounted very satisfactory for the fact that a very weak current could effect the decomposition of water containing a little acid. This will be recognized at once as containing the fundamental proposition of the 'Dissociation Theory' as proposed by Arrhenius in 1884.

According to this theory the solute is partially; pr in dilute solutions entirely; broken down into a cation and an anion, carrying a positive and a negative charge of electricity. Upon the passage of an electric current through a solution containing these ions they will move towards the electrode of opposite sign. The conductivity of the solution will depend upon the extent to which this dissociation takes place. So far as the effect upon the vapor pressure of the solvent is concerned, each of these ions will act the same as a molecule and consequently will produce abnormal results when measured by either the depression of the freezing point, rise in the boiling point or variations in the osmotic pressure.

The electrical conductivity and the variation in the vapor pressure furnish two distinct and independent methods for measuring the degree of dissociation of a substance in solution. These have been determined for a great many substances and in nearly every case found to agree within the limits of the experimental error.

Another fact, also, that had long been observed but never before satisfactorily accounted for is that the heat of neutralization of a strong acid with a ~~weak~~^{strong} base in dilute solutions is a constant. This is necessary according to this theory, as in any case the only change taking place is the combining of the hydrogen of the acid with the hydroxyl of the base to form water while the remaining ions remain in their original condition.

It might also be added that this theory proposes that most chemical reactions, and especially instantaneous ones, are reactions between these ions.

These facts along with many other ones, have led chemists in general to accept this explanation as the one that approaches nearest to the condition of a salt that is in solution; and while it is recognized as being, not the widest generalisation, it is at least believed to be an approximation.

Kahlenberg has collected data and published papers at various times setting forth his reasons for not accepting this theory, and it is in a line suggested by one of these papers(1) that the present work has been done.

He chooses a hydrocarbon, benzene, as the solvent and finds that its electrical conductivity is practically nothing, when thoroughly dry. Then a solution of copper, nickel or cobalt oleate is made and dried over sodium and the conductivity found to be no better than the benzene. These salts are chosen as they are practically the only salts of the heavy metals that are soluble in benzene. Next perfectly dry hydrochloric acid is passed into the solution and immediately there is formed a heavy, brown precipitate of the chloride of the metal.

Here, then is a case where we have no ionization as shown by the electrical conductivity method but upon passing in the hydrochloric acid a heavy precipitate is formed, which shows that there must be ions present according to the same theory, and this is the discrepancy shown

~~in the paper which we will attempt to account for.~~

Our chief work was done with and our conclusions drawn from substances mentioned in the paper mentioned above: the solvents used being benzene and toluene while the solutes were copper and cobalt oleate.

The salts were made substantially as described in the paper, the sodium salt being made first from sodium hydroxid and then the sodium was replaced by the copper or cobalt by adding a slight excess of a solution of the sulfate of the heavy metal. The sodium hydroxid was made by allowing clean metallic sodium, placed under a bell-jar to react with water vapor from a dish of water placed under the same jar. The precipitates; thick, tarry substances with the characteristic color of the copper and cobalt salts, were then obtained by filtering off the liquids. They were then thoroughly washed and dried in an air bath heated to 100° , through which air was drawn.

These salts were then dissolved in benzene and toluene and further dried by allowing to stand for several weeks over metallic sodium. We observed, however, that the sodium soon became coated over with a very thin layer of what was probably sodium oleate and would not act upon the water even when it was added to the solution. This protective layer was very thin and the sodium had the appearance of a freshly cut metallic surface. On account of the difficulty experienced in obtaining anhydrous solutions in this way we tried another which seemed to give us better satisfaction and by means of which the solutions could be thoroughly dried in less than an hour.

This method was to boil the solutions, using a reflux condenser, over metallic sodium or potassium (The toluene over sodium and the benzene solution over potassium). The metals are fused at this temperature and by agitation new, bright metallic surfaces will be exposed at all times.

We sought to obtain the same condition by using the fluid sodium-potassium alloy but found this less satisfactory.

The solutions when dried in this manner, become dark brown in color and considerable quantities of a dark brown substance, which is probably of the nature of a lake, are formed. This mixture was then 'centrifuged' and within an hour after commencing to dry the solution was ready for the conductivity determination and precipitation.

Our hydrochloric acid was first generated as described by Kahlenberg but later we found it more convenient ~~and~~ and as reliable to generate it by means of an ordinary Kipp apparatus charged with ammonium chloride and sulfuric acid. This showed a decided tendency to get through our drying apparatus and retain traces of moisture and so we passed it through sulfuric acid and then through two drying towers in series. These towers were 40 centimeters in height and about 6 in diameter and were filled with alternate layers of pumice stone and phosphorus pent-oxid.

The hydrogen used in displacing the air was also generated in a Kipp and dried in a train similar to the above, except that only a single tower was used. This tower was connected to the last one of the hydrochloric acid train by means of the double arm of a two way stop cock while the single arm went to the cell used for measuring the conductivity of the solutions. In all cases the hydrogen and hydrochloric acid were passed slowly in order to allow ample time in the towers for thorough drying. We had some trouble at first with a single tower for drying the hydrochloric acid and this led to the use of the two towers.

The cell was what practically amounted to an Arrhenius resistance

cell with the electrodes less than a millimeter apart and with an area of 3.2 sq.cm. The lead wires were fused into the bottom of the cell. Each time before using, the cell was cleaned with sulfuric acid and washed with ~~distilled~~ water, alcohol and ether. It was then placed in position and strongly heated while dry hydrogen was passed through it. It contained a three hole, rubber stopper; one hole being used for introducing the solution, another the hydrogen and HCl while the third was an exit and connected with a phosphorus pentoxid tube to keep the interior of the cell dry. The exterior was kept dry by a casing, larger than the cell and containing P_2O_5 and the lead wires were passed out through the top and insulated by means of sulfur. The conductivity of this cell may be judged from the fact that the double deflection of a galvanometer with a sensibility of 300 megohms, with a difference of potential of 110 volts, only amounted to from 0.2 to 0.5 of a small (mm) scale division when the cell contained air and would remain practically constant for a period of twenty four hours.

Our solutions were introduced by placing the small Erlenmeyer in which the drying and centrifuging had been done upon a two hole rubber stopper that had been previously thoroughly cleaned and dried. One of the holes connected to the hydrogen drying tower, while the other contained a glass tube that dipped below the surface of the solution and connected with the cell. By turning on the hydrogen the solution could be forced into the cell without its being removed or any of the connections being broken. In fact nothing was removed from the measurement of the conductivity of the empty cell till the close of the experiment.

The resistance of the galvanometer was 1300 ohms and it was connected in series with the cell and a reversing key and Ayrton shunt

No other resistance was in the circuit except the slight resistance of the lead wires and it was subjected to the full 110 volts. It was insulated from the possible leakage effects by being mounted upon a stand insulated by means of sulfur, which proved to be the best insulator for the purpose that we could find.

Invariably before measuring the conductivity of a solution the conductivity of the empty cell was taken and brought down by repeated heating to a double deflection of less than a small scale division. No attempt was made to measure this conductivity exactly as it was not considered necessary.

At the moment of introducing the solution with connections made we noticed a slight movement of the galvanometer which soon subsided and the conductivity returned to practically the conductivity of the empty cell though slightly better. Thinking to test whether the conduction was a well defined phenomena or only the result of accident we used a galvanometer about ten times as sensitive as the former and found that the solution showed decided conductivity. With the dilute solutions with which we were working this would sometimes throw the galvanometer off the scale.

The fact that the conductivity quickly diminished after introducing the solution led us to suspect polarization and we accordingly set about to measure it. For this purpose we used quite concentrated solutions to increase the effect and measured the polarization by charging a condenser and then discharging through the more sensitive galvanometer. The calibration was made by means of both standard Clark and Weston cells. When measured in this way a concentrated solution of copper oleate in benzene gave a back E.M.F. of 1.9 volts, showing polarization to that

extent. In the toluene solutions the polarization was not so great but this may have been due to the fact that the solutions were not so concentrated. In regard to the conductivity of these concentrated solutions they would frequently throw the mirror off the scale, even when shunted down till only one thousandth of the current was passing through the instrument. This would diminish very appreciably after a few minutes and would usually remain on the scale with all the current acting. In addition to the back E.M.F. we believe that there is a resistant film formed that increases the resistance but have not had time to investigate as yet.

Upon passing through the HCl the conductivity was again increased which might be due to the breaking down of the film mentioned above; however at the moment of precipitation the conductivity decreased and so markedly that the person at the telescope could tell to a nicety the moment the precipitate was formed by the movements of the galvanometer. It must be remarked that the formation of the precipitate; while quite rapid was by no means instantaneous, and it eventually collected between the electrodes of the cell and increased the conductivity.

The solutions of copper and cobalt oleate in benzene and toluene are conductors of the second class because during conduction they exhibit the phenomena of polarization. Hence in these solutions ionization to an easily appreciable extent exists and the reaction between the HCl and the oleate is exactly what would be expected from the standpoint of the DISSOCIATION THEORY.

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