

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KANSAS.]

REACTIVITY AND CONDUCTANCE OF BENZENE SOLUTIONS.BY H. P. CADY AND E. J. BALDWIN.¹

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According to the accounts of certain investigations carried out by Kahlenberg² and associates, double decomposition reactions, with instantaneous precipitations, were found to take place in benzene solutions with no observed conductivity, hence, as interpreted, without previous ionization of the salts taking part in the reactions. Copper, cobalt and nickel oleates were the salts used. The solutions were dried over sodium and phosphoric anhydride. These solutions were found to show no conductivity and upon passing dry hydrogen chloride through them, a precipitate formed, with still no evidence of conductivity.

Similar work carried out by Allen³ and by Cady and Lichtenwalter⁴ gave results of a different nature. The latter used salts of both saturated and unsaturated acids, chiefly the copper, silver, and lead salts. These were prepared by adding a slight excess of sodium hydroxide solution to weighed quantities of the respective acids, forming the sodium salts, from which the salts used were prepared by treatment with solutions of the sulfates or acetates of the respective metals. Both benzene and toluene solutions were used, these being thoroughly dried by allowing them to stand for several weeks over a liquid alloy of sodium and potassium, or, in a few cases, by heating them over potassium on a water-bath using a reflux condenser. They found that all of the solutions gave a very noticeable conductivity, this being somewhat greater in the case of the unsaturated salts. Upon passing hydrogen chloride into the solutions, the unsaturated salts gave a marked increase in conductivity, followed by a precipitation and a great decrease in conductivity. By similar treatment the solutions of saturated salts showed an increase in conductance upon passing hydrogen chloride through them, but no precipitation occurred. The conclusion reached was that the conductivity recorded in each case was sufficient to show an accordance with the dissociation theory, especially if in the case of the precipitations which were not instantaneous, an intramolecular rearrangement might be considered to occur.

In a subsequent article by Alfred E. Koenig,⁵ the inference was made that the method used by Cady and Lichtenwalter in preparing the sodium salts used, *viz.*, the addition of a slight excess of alkali to the acid, caused the formation of basic salts, which would account for the observed con-

¹ Experimental work completed in 1916.

² Kahlenberg, *J. Phys. Chem.*, **6**, 1 (1902).

³ Allen, *Kansas Univ., Sci. Bulletin*, **1905**.

⁴ Cady and Lichtenwalter, *THIS JOURNAL*, **35**, 1434 (1913).

⁵ Koenig, *THIS JOURNAL*, **36**, 951 (1914).

ductivity upon the addition of hydrogen chloride. It was suggested in the article that the salts should be prepared by using a slight excess of the acid. It was partially with a view to investigating this suggestion that the following work was undertaken.

The apparatus used was similar to that used by Cady and Lichtenwalter. A cell of the Arrhenius resistance type was enclosed in an electrically heated upright jacket which was so arranged as not to interfere with observations. The electrodes were of platinum, placed about 2 mm. apart. Lead wires from these were sealed through the bottom of the cell and passed out through a split rubber stopper which closed the end of the heating jacket. This stopper was arranged to fit around the open end of the cell and served to hold it fairly rigid and out of contact with the heating jacket. Sulfur was used to insulate the wires from the rubber. The cell was fitted with a 3-hole rubber stopper through which glass tubes entered the cell. One of these tubes was drawn out at the end to a small diameter and served to introduce either hydrogen chloride or air into the cell. Another tube was used for introducing solutions into the cell, and another, which was connected with a calcium chloride tube in series with a phosphorus pentoxide tube, provided for the escape of the gases.

The hydrogen chloride was prepared in a Kipp generator using conc. sulfuric acid and ammonium chloride. From the generator the gas was led through 2 towers filled with alternate layers of pumice stone and phosphoric anhydride, and was thus thoroughly dried before reaching the cell.

A flask of liquid air was used to furnish air for drying the cell. It was connected in series with a sulfuric acid wash bottle and a phosphorus pentoxide tower. After passing through these drying agents, the air was led through an electrical resistance heater before reaching the cell. By heating the cell and passing hot dry air through it a thorough drying effect was obtained. The pressure of the air from the liquid air flask was also used for introducing the solutions into the cell. This was accomplished by placing the solution in a tube fitted with a 2-holed stopper which allowed the entrance of a tube carrying air from the last drying tower and an outlet tube leading to the cell. By means of a 2-way stopcock the air could be led into this container tube and the solution forced over into the cell.

When conductivity measurements were taken the cell was connected in series with a direct current generator of 110 volts, and with a sensitive galvanometer. Mention will be made whenever any other resistances were introduced into the circuit. The sensitivity of the galvanometer was determined and found to be 0.000022 milliamperes for one scale division. The resistance of the galvanometer was also determined and a value of 1225 ohms obtained. The entire system, including all instruments used, was placed upon blocks of sulfur. This was found to provide a very efficient means of insulation and sulfur was used for insulating at every point where there appeared to be the least chance for leakage.

Copper oleate, barium erucate, copper stearate, and silver melissinate were the salts used. These were prepared from the respective acids which were of the best quality obtainable. The sodium salts were prepared by adding *slightly less than the calculated amount* of sodium hydroxide solution to a weighed amount of the acid. The sodium hydroxide solution used was carefully prepared from metallic sodium. The flask containing the mixture was heated upon a water-bath for 10 hours using a reflux condenser. The contents of the flask were then poured through a cotton filter to remove the excess of acid.

Solutions of copper sulfate, lead acetate and barium chloride were used in preparing the various salts. The calculated amounts were added slowly to solutions of the sodium salts with constant stirring. The precipitates were then filtered off, washed,

placed in small Erlenmeyer flasks and dried by heating the flask and contents for several hours upon a water-bath, simultaneously passing a current of dry natural gas through the flask. By this method efficient drying was obtained without danger of oxidation of the unsaturated salts. The dried solvent was introduced directly into the flask containing the salt and heated when necessary to bring about solution. When there was an excess of the salt the saturated solution was decanted into another carefully dried Erlenmeyer flask. A small amount of an alloy of sodium and potassium containing about 20% of potassium was introduced into each flask, this alloy giving a melting point well below the boiling point of benzene, and the flask was fitted with a reflux condenser and heated upon a water-bath for several hours. The solutions were centrifuged whenever necessary to remove any suspended particles and then introduced into the cell as previously described.

The cell was first dried until the galvanometer showed a deflection of only a fraction of one scale division upon the application of 110 volts. The hydrogen chloride was passed through the cell and practically no increase was shown in the scale reading. This gas was swept out with a current of air before further use was made of the cell. The benzene, after being carefully dried, was placed in the cell and less than one scale division of deflection was shown by the galvanometer.

When a benzene solution of barium erucate was placed in the cell the conductivity was so great as to throw the galvanometer off the scale. A 40-ohm shunt was placed across the terminals of the instrument and the deflection was reduced to 30 scale divisions. Upon passing hydrogen chloride into the solution the conductivity quickly increased reaching a maximum of 31 scale divisions with a shunt of one ohm across the galvanometer. A fairly rapid precipitation occurred and the deflection gradually dropped to 7 scale divisions with no shunt.

A benzene solution of copper oleate was placed in the cell and the galvanometer needle was thrown off the scale. A shunt of 500 ohms was placed across the terminals of the instrument and the deflection dropped to 22 scale divisions. Upon passing in hydrogen chloride the galvanometer was again deflected off the scale. A precipitate formed and the conductivity gradually dropped to 3 scale divisions with no shunt.

A benzene solution of copper stearate gave a deflection of 26 scale divisions. Upon passing in hydrogen chloride this was considerably increased, giving a deflection of 14 scale divisions with a 200-ohm shunt across the terminals of the galvanometer. No precipitation occurred. Similar results were obtained for a solution of silver melissinate.

The above results seem to prove conclusively that the conductance previously observed by Cady and Lichtenwalter for similar solutions was not due to the manner of preparing the salts used, as was suggested in the article by Koenig.

Koenig's paper also described an experiment whereby a precipitate was obtained upon treating a benzene solution of copper stearate with a solution of stannic chloride in benzene. No mention was made of any

conductivity observations. This experiment was performed by the authors and the accompanying conductivity observed. The benzene solution of copper stearate used gave a conductance of 32 scale divisions. Upon passing into this a benzene solution of stannic chloride the conductivity was momentarily increased and then quickly dropped to 2 scale divisions, with a rapid precipitation. The stannic chloride used was prepared by passing chlorine over fused tin. It was redistilled, as far as possible out of contact with the air, and kept in a tightly stoppered flask inside a desiccator. The benzene used was carefully dried over sodium and potassium in the manner previously described. The benzene solution of stannic chloride used gave a conductivity reading of 1.5 scale divisions. This reading was increased only a fraction of a scale division upon passing hydrogen chloride into the solution. The dry benzene placed in the cell gave a reading of less than 0.5 of a scale division. Upon passing hydrogen chloride into it the reading was increased to a fraction over one scale division.

A solution of copper oleate in benzene was treated with a benzene solution of stannic chloride. The conductivity of the copper oleate solution was observed to be 28 scale divisions with a shunt of 500 ohms across the galvanometer. Upon passing into this a benzene solution of stannic chloride the conductivity first increased, then dropped to 18 scale divisions.

A benzene solution of oleic acid was next used. It was considered inadvisable to attempt to dry this by the method previously used for the other solutions. Instead, the solution, prepared from carefully dried benzene and pure oleic acid, was allowed to stand for several days over anhydrous copper sulfate and was frequently shaken. This solution gave no greater conductivity than the dry cell reading which was a fraction of one scale division. Upon passing a benzene solution of stannic chloride into this solution, the conductivity was so greatly increased that the galvanometer could not be brought back upon the scale, even by placing a one-ohm shunt across the terminals.

Another portion of the solution of oleic acid in benzene was placed in the cell and gave as before a deflection of only a fraction of one scale division. Hydrogen chloride was passed through the solution and the reading was increased to 4 scale divisions. Upon then passing into this solution in addition a benzene solution of stannic chloride the conductivity was increased to such an amount that no reading could be taken even with a one-ohm shunt across the terminals of the galvanometer.

Discussion.

The conductivity observed in connection with these reactions is sufficiently large to indicate a certain amount of ionization in the solutions; probably sufficient to account for their reactivity shown, on the basis of

the dissociation theory. The following table indicates the approximate conductance observed for the various solutions examined.

TABLE I.
Total conductance as milliamperes of current.

Benzene Solution of	For solution alone.	At moment of adding reagent.	After addition of reagent.
Barium erucate.	0.0208	+HCl 0.835	0.00015
Copper oleate.	0.0017	+HCl Large momentary increase.	0.000066
Copper stearate.	0.00057	+HCl 0.0022	0.0022
Silver melissinate.	0.00046	+HCl Large momentary increase.	0.00032
Oleic acid.	0.00012	+HCl 0.0001	0.0001
Copper stearate.	0.0007	+SnCl ₄ Slight momentary increase.	0.000088
Copper oleate.	0.0021	+SnCl ₄ Slight momentary increase.	0.00137
Oleic acid.	0.00012	+SnCl ₄ Too great to measure with instruments used.	Too great to measure with instruments used.

The great increase in conductivity observed upon the addition of stannic chloride to the benzene solution of oleic acid would certainly indicate the formation of ions there. This might be attributed to insufficient drying of the oleic acid solution, yet saturating the solution with hydrogen chloride increased its conductance only slightly which would seem to indicate the absence of any great amount of moisture.

Summary.

Experiments formerly carried out by Cady and Lichtenwalter were repeated, the salts used, however, being prepared by using an excess of acid instead of base. Carefully dried solutions of salts of organic acids in benzene were found to show a measurable conductivity which was increased when dry hydrogen chloride was passed through the solution. The hydrogen chloride caused the formation of a precipitate in the case of the unsaturated salts only. These results accorded with those previously obtained by Cady and Lichtenwalter.

The addition of a benzene solution of stannic chloride to a benzene solution of copper stearate caused a momentary increase in conductivity followed by a precipitation with an accompanying decrease in conductivity until the scale reading was very small. The benzene solution of stannic chloride used gave practically no evidence of conductivity. Its addition

to a benzene solution of copper oleate caused a momentary increase in the galvanometer reading followed by a decrease to somewhat less than the original reading.

A solution of oleic acid, in dry benzene, after drying over anhydrous copper sulfate, showed practically no conductivity. The addition of hydrogen chloride to this solution increased the reading only slightly. Upon treating it with a benzene solution of stannic chloride, however, the conductivity was increased to such an extent that no reading could be taken with the instruments used.

The conductivity shown in these cases is considered sufficient to account for the reactivity of the solutions on the basis of the dissociation theory.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

THE REACTION BETWEEN ACID HALIDES AND ALDEHYDES. II.

BY H. E. FRENCH WITH ROGER ADAMS.¹

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In an earlier paper from this laboratory,² the fact was brought out that many aromatic aldehydes and aromatic acid halides react readily to form halogenated benzyl benzoates and a study of a number of the reactions of these condensation products was made. In the present communication this work has been extended.

It has been shown that the reaction between aromatic acid halides and the aromatic aldehydes is very general. The previous work indicated that in a few instances perhaps, certain aromatic aldehydes would not condense with certain aromatic acid halides to give the expected derivatives. This conclusion resulted from the fact that solid products could not be isolated although from the nature of the substituents solid products might be expected. The oils which were produced always decomposed when vacuum distillation was attempted so that it was impossible to determine whether a definite substance existed or whether merely a mechanical mixture. By treating these oily reaction mixtures with pyridine, solid addition compounds of pyridine and the aldehyde-acid halide products were formed and easily purified. Thus it was shown that a reaction actually had taken place in these instances and the resulting products were oils. Moreover the aldehyde-acid halide condensation products which were solids but too unstable to purify and analyze could be isolated in the form of stable pyridine addition products. These same pyridine addition products could be made also by first treating pyridine with an acid-halide and then adding the aldehyde.

¹ This communication is an abstract of work carried out by H. E. French in partial fulfillment for the degree of Doctor of Philosophy at the University of Illinois.

² THIS JOURNAL, 40, 1732 (1918).