method, as carried out by myself, gives 0.01998 gram sulphur trioxide equivalent to 0.00851 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.35 cc. of which equals twenty cc. of the $\frac{N}{4}$ sulphuric acid) is equivalent to 0.003396 gram ammonia by the barium chloride method and by the ammonium sulphate method as carried out by myself 0.003380 gram ammonia.

Another solution of $\frac{N}{4}$ sulphuric acid was tested by the two methods.

In one cc. of the solution there was found by the barium chloride method 0.01977 gram sulphur trioxide equivalent to 0.008421 gram ammonia.

The ammonium sulphate method, as carried out by myself, gives 0.019895 gram sulphur trioxide equivalent to 0.008474 gram ammonia. Therefore, one cc. of the sodium hydroxide solution (50.25 cc. of which equals twenty cc. of the $\frac{N}{4}$ sulphuric acid) is equivalent to 0.003351 gram ammonia by the barium chloride method, and 0.003372 gram ammonia by the ammonium sulphate method, as carried out by myself. I think that as a method of standardization the ammonium sulphate method will be found very simple and accurate and for these reasons should commend itself to those analysts who make use of sulphuric acid as their standard acid.

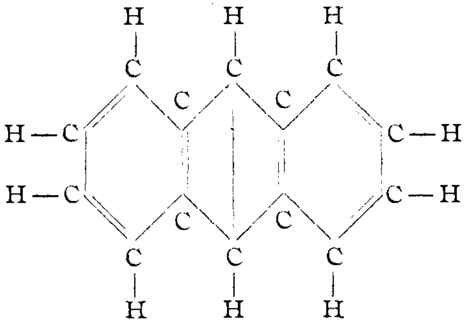
February 11, 1895.

ON SOME EXPERIMENTS IN THE ANTHRACENE SERIES.

BY C. E. LINEBARGER.

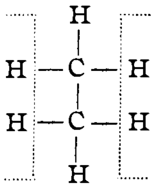
Received March 4, 1895.

TO anthracene is generally assigned the formula:

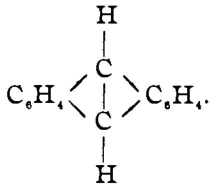


;

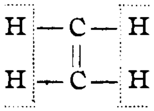
it may also be thought of as ethane, in which four of the hydrogen atoms have been replaced by the two bivalent radicals, phenylene:



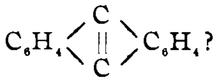
$$\begin{array}{ccc} & H & \\ & | & \\ H- & C & -H \\ & | & \\ H- & C & -H \\ & | & \\ & H & \end{array}$$



In both the formulas, the two middle atoms of carbon are bound directly together, and the hydrogen atoms in immediate union with them—in the so-called γ-position,—exhibit a characteristic behavior. The question arises, can not the γ-carbon atoms become bound together doubly, so as to form a hydrocarbon, which may be regarded as derived from ethylene,

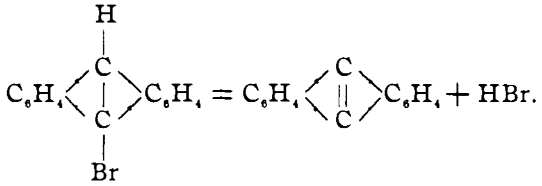


$$\begin{array}{ccc} H- & C & -H \\ & \| & \\ H- & C & -H \end{array}$$



The question appeared to possess enough importance to merit investigation, and in what follows an account is given of the experiments carried out in seeking an answer to it.

The first attempt to prepare such a compound as the above was made by a study of the action of heat upon mono-brom-anthracene. It seemed likely that through the application of heat hydrobromic acid would be formed by the combination of the hydrogen and bromine in the γ-position, and the bonds of carbon thus set free would unite with each other, as shown in this equation:

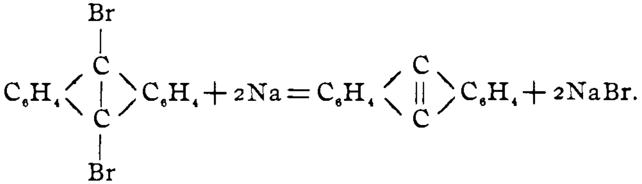


Ten grams of pure mono-brom-anthracene were heated in a small round-bottomed flask provided with a delivery-tube. The flask was set upon a sand-bath, and its upper part protected from the direct action of the heat by means of a shield of asbestos board. A thermometer was inserted through the cork, reaching almost to the bottom of the flask, so that its bulb was completely immersed in the heated substance. Heat was applied slowly, and it was found that hydrobromic acid gas commenced to pass off at 250° C., and the evolution became quite brisk at 280° to 300°. The temperature was not, however, allowed to rise higher than 300°, and when the evolution of gas had nearly ceased, the heating was discontinued. The neck of the flask was full of yellowish crystals, while in its bottom there remained a black resinous mass from which no crystalline substance could be obtained. The crystals were dissolved in hot benzene, and the solution, on cooling, became filled with tablets resembling those of anthracene. These, by a second crystallization from a mixture of alcohol and benzene, were obtained in a state of purity. Their melting-point was found to be 210° to 212°, which is that of anthracene; they were also, like anthracene, soluble with dark green color in concentrated sulphuric acid; there is no doubt, therefore, that the product of the reaction, that is, as far as anything crystallizable is concerned, is anthracene. The hydrogen necessary for its formation must have been taken from the resinous mass.

Experiments were now carried out on the action of alcoholic potash on the brominated compound of anthracene. Three grams of mono-brom-anthracene were heated with twenty grams of alcoholic caustic potash in sealed tubes at temperatures varying from 100° to 250°. No reaction seemed to occur at temperatures below 150°; the products obtained at higher temperatures were always about the same. When the tubes, which were always filled with crystals, were opened, considerable quantities of inflammable gases escaped; the crystals, when washed free from caustic potash and purified by crystallizations from alcohol, melted at 207° to 211°. This point of fusion together with the appearance of the crystals—small glistening tablets possessing fluorescence—and the characteristic green coloration with strong sulphuric acid is sufficient evidence that the product is merely anthracene.

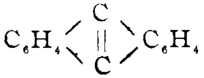
The action of solid caustic potash in like circumstances gave also nothing but anthracene.

An investigation was now made of the action of metallic sodium on di-brom-anthracene dissolved in different liquids. It was thought that, perhaps, the sodium would abstract the halogen from the anthracene compound, and that union would then occur between the two γ-carbon atoms, thus:



A molecule of di-brom-anthracene, together with nearly enough benzene to dissolve it, was sealed up in a tube with somewhat more than four molecules of sodium, and heated at 100° for eight hours; no reaction took place. When heated, however, for the same length of time at 125°, the contents of the tube had turned black. The tube was opened, and the dark-colored crystals purified by repeated crystallizations from mixtures of benzene and alcohol. The crystallizable product finally obtained was nothing else than di-brom-anthracene; the reaction which had supervened had evidently not effected the desired synthesis.

The reaction was now tried with xylene as solvent. Ten grams of di-brom-anthracene were dissolved in sixty grams of xylene—which had been distilled over sodium—and an excess of sodium added. The solution was kept vigorously boiling for twenty hours, an inverted condenser being used. The dark colored products of the reaction were filtered off hot, and the crystals, that soon separated out from the filtrate, repeatedly crystallized out of benzene until a pure product was obtained. This showed itself, by its melting-point (207° to 210°), fluorescence, and coloration with concentrated sulphuric acid, to be anthracene. The sodium did, indeed, remove the bromine, but so unstable a molecule was formed that a portion of the product was destroyed in order to yield hydrogen for the formation of anthracene.

The above are the simplest and most direct methods for realizing the proposed synthesis. Whether others will succeed where these have failed is an open question; at any rate the theoretical importance to be attached to the possibility of existence of such a hydrocarbon as  $C_6H_4{<}\overset{C}{\underset{C}{\|}}{>}C_6H_4$ makes it desirable that all the methods be tried.

CHICAGO, March 1, 1895.

ON THE REACTION BETWEEN ZINC SULPHATE AND POTASSIUM HYDROXIDE.[1]

BY C. E. LINEBARGER.

Received March 4, 1895.

It is customary in books on analytical chemistry to represent the precipitation of zinc hydroxide from solutions of its sulphate by means of potassium hydroxide, and its redissolution by the action of an excess of the alkali by these two equations:

$$(1)\ ZnSO_4 + 2KOH = Zn(OH)_2 + K_2SO_4.$$
$$(2)\ Zn(OH)_2 + 2KOH = ZnO_2K_2 + 2H_2O.$$

These equations are, however, far from corresponding to actuality, and it seems really deplorable that chemists in their desire to formulate compounds and balance equations should, by symbolical representations on paper, give the impression of having duly explained such a reaction as the above, which even a superficial examination shows to vary considerably with the temperature, dilution, and relative masses of the components.

The general scheme followed out in this preliminary study of the reaction of the two salts in question consisted in the addition to a constant quantity of zinc sulphate, varying quantities of potassium hydroxide, the total volume and temperature of the

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[1] This investigation was begun in 1888 in the chemical laboratory of the Northwestern University at the suggestion and under the guidance of Prof. A. V. E. Young. It had been the intention to study the reaction between zinc sulphate and potassium hydroxide in a manner analogous to that in which Prof. Young had made "A Thermochemical Analysis of the Reaction between Alum and Potassium Hydrate," published in the Proceedings of the American Academy of Sciences and Arts, June 10, 1885. Only certain preliminary experiments, however, had been performed when I left the University, and the research has not received further attention at the hands of Prof. Young or myself. While these preliminary experiments can be said to be but a small part of the work necessary for the elucidation of the problem of the chemical equilibria presented by the system of zinc sulphate, caustic potash, and water, yet they possess a certain interest, especially for analytical chemistry, which may warrant their being made known.