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ACTION OF HALOGENS ON PYRROLE TO GIVE COLORED SOLUTIONS

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In an attempt to prepare derivatives of pyrrole which might dissociate into odd molecules, the authors were led to study the action of halogens on metallic compounds of this substance.

Various halogen derivatives of pyrrole have been obtained by other investigators. Thus Ciamician and Dennstedt[1] prepared tetra-iodo-pyrrole by the action of iodine on potassium pyrrole or pyrrole in an alkaline medium; Caminetti and Silber[2] obtained the bromo- and chloro-maleinimides when an alkaline solution of sodium hypobromite or sodium hypochlorite was treated with pyrrole, and Hess and Wissing[3] isolated chloro- and bromopyrroles from the products resulting from the action of chlorine and bromine on pyrrolemagnesium compounds. However, products of quite a different character have also been obtained by very similar means. Thus Agraz[4] obtained a blue ethereal solution by treating pyrrole in ether with potassium hydroxide in water, and iodine in aqueous potassium iodide, a method which, with the exception of dissolving the pyrrole in ether, can be used successfully in the preparation of tetra-iodo-pyrrole. Also, Angelli and Pieroni[5] obtained a blue solution by treating ethylmagnesium bromide with pyrrole and then exposing it to the air, which treatment finally gave a black powder. It was found by the authors and Mr. Groening that a great many colored solutions can be obtained by treating pyrrole with halogens under a variety of experimental conditions. Since attempts to obtain these substances in a pure state were unsuccessful owing to their instability, a typical case was investigated by an indirect method.

In the first part of the paper an account of the preparation and properties of a few of these highly colored substances is given. This is followed by a description of quantitative experiments devised to give some insight into the nature of the reaction which gives one of these colored solutions.

Methods of Preparation and Properties

When potassium pyrrole suspended in absolute ether is treated with a solution of iodine in ether, or when a mixture of alcohol, sodium ethylate and pyrrole is treated with an alcoholic solution of iodine, the iodine is

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[1] Ciamician and Dennstedt, *Ber.*, **15**, 2502 (1882).

[2] Caminetti and Silber, *Ber.*, **17**, 1745 (1884).

[3] Hess and Wissing, *Ber.*, **48**, 1884 (1915).

[4] Agraz, *Mem. Rev. Soc. Cien "Antonio Alzate,"* **32**, 77 (1913); *C. A.*, **8**, 308 (1914).

[5] Angelli and Pieroni *Gazz. chim. ital.*, **49**, 154 (1919).

immediately decolorized, and a colorless solution of tetra-iodo-pyrrole is formed. However, when the iodine is introduced into either of these mixtures in the solid state a blue solution is obtained.[6] Of course in both cases some tetra-iodo-pyrrole appears as well.

The chief characteristic of these solutions is the ease with which they give black powders on evaporation, exposure to air, acidifying, or even, though more slowly, on standing in an atmosphere of hydrogen.[7] The solutions are rapidly decolorized when they are exposed to an atmosphere of nitric oxide. On very careful treatment with acid, or on washing thoroughly with water, or if all traces of alkali are removed by cooling in a mixture of carbon dioxide and ether and precipitating with petroleum ether, the color changes to purple; and if the solution, without further standing, is rendered alkaline the blue color is restored. On pouring the alcoholic solution into water a black precipitate is obtained which partially redissolves when immediately shaken with ether. This was the nearest approach to isolating the compound. These blue solutions appear to be identical with that described by Agraz.[4] It is apparent that this is a surface reaction, since the conditions for obtaining it are similar to those in which nothing but tetra-iodo-pyrrole is produced, except in the introduction of a solid iodine-solution or ether-water interface.

Ethereal solutions similar to the above in being highly colored and easily decomposed to give black powders can be obtained by the action of iodine and bromine on pyrrolemagnesium iodide, or on a mercuric pyrrole compound obtained by treating pyrrolemagnesium iodide with mercuric chloride; also by the action of an aqueous alkaline solution of sodium hypobromite on pyrrole. In this last case a purple solid, which dissolves to give a purple solution in ether, a blue in carbon disulfide and a green in acetone, was isolated in an impure state and in small quantities.

When a solution of pyrrole in moist ether in which mercuric iodide is suspended is treated with an ethereal solution of iodine (nearly an atom of iodine per molecule of pyrrole) a green solution is obtained and the mercuric iodide is dissolved. Further addition of iodine causes the rapid precipitation of a black solid, but if a little sodium ethylate is added at this stage, two or three more equivalents of iodine may be made to react. The solution obtained when a small amount of iodine is used gives a blue ethereal layer on the addition of aqueous ammonia, whereas when several equivalents have been added the green solution turns pink under similar treatment. In both cases the ethereal layer becomes green on re-acidify-

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[6] The alcoholic solution, when added to ether and the latter sparingly washed with water, gives a solution apparently identical with that obtained when the reaction is carried out in ether.

[7] An ethereal solution may still have a strong blue color after standing for two hours in an atmosphere of hydrogen.

ing. These two green solutions are more stable than the blue obtained by the action of iodine on pyrrole dissolved in an alcoholic solution of sodium ethylate, the more stable being that which gives a pink color with ammonia. The decomposition of the green solutions, which is facilitated by air, yields a black powder rich in mercury and in iodine. If small quantities of the one which yields a pink color with ammonia are rapidly evaporated, the substance is evidently not entirely decomposed, for after washing out the excess of mercuric iodide a small fraction of the resulting black powder redissolves in ether giving a blue solution which turns red with alkali.

Quantitative Study of Reactions

The compounds described above are too unstable to permit an investigation of their structure by direct methods. An attempt was made, however, to follow the course of the reaction between solid iodine and pyrrole in the presence of sodium ethylate by finding out what happens to the iodine. It was first necessary to make sure that in the formation of tetra-iodo-pyrrole under similar conditions nothing but iodination occurs. The results of the following experiments prove this.

To known quantities (about 0.5 g.) of pyrrole dissolved in measured volumes of a standardized solution of sodium ethylate in alcohol (about 1 *N*) a standard alcohol solution of iodine was added.[8] The resulting mixture was added to an excess of ether, and the sodium iodide extracted with water. This aqueous extract was then neutralized with dil. sulfuric acid, washed with ether, and the dissolved ether removed by blowing a stream of air against the surface. The solution was then analyzed for iodide ion by titration with standard silver nitrate solution.

It was found that when tetra-iodo-pyrrole is produced, the ratio of iodine used to iodide ion formed is unity (1.01, 1.03, 1.00), and hence when in an experiment the blue compound is also produced, any variation of this ratio must be ascribed to the reaction by which the latter substance is formed.

It was necessary then to devise a method for estimating tetra-iodo-pyrrole in alkaline alcoholic solution, since by so doing it would be possible to determine what proportion of the iodine was used to form the blue compound. The following method was found to be practically quantitative.

A solution of tetra-iodo-pyrrole and sodium ethylate in alcohol is poured into water and evaporated to a small bulk by blowing air on the surface. It is then neutralized to methyl orange, allowed to stand until the precipitate settles and is filtered through a Gooch crucible, previously dried to constant weight in a vacuum over sulfuric acid. The crucible is then re-dried to constant weight under the same conditions. The difference of the two weighings gives the amount of tetra-iodo-pyrrole.

As it was found that the blue compound is completely precipitated as a black powder from an alkaline alcoholic solution by adding less water

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[8] None of the blue compound was formed in these experiments.

than would precipitate tetra-iodo-pyrrole from a similar solution, the following method was adopted to estimate the quantities of iodine, tetra-iodo-pyrrole and iodide ion involved in experiments in which both the blue substance and tetra-iodo-pyrrole were formed.

A weighed quantity of iodine was added to an excess of pyrrole and sodium ethylate dissolved in alcohol (0.5 cc. of pyrrole and 4 cc. of 1.6 *N* sodium ethylate in alcohol); after the iodine had all reacted the resulting blue solution was poured into 30–40 cc. of water, and the mixture filtered after being allowed to stand for a short time. The precipitate was washed with mixtures of alcohol, alkali and water (about 4 cc. of 1.6 *N* sodium ethylate in alcohol to 20 cc. of water), containing enough alcohol and alkali to dissolve tetra-iodo-pyrrole easily and enough water to keep the black powder as a filterable precipitate, and finally with water. The filtrate and washings were then analyzed for tetra-iodo-pyrrole by the method given above, and after its removal the filtrate was titrated for iodide ion with standard silver nitrate. By subtracting the amount of iodine necessary for the formation of the tetra-iodo-pyrrole from the total amount of iodine used, the quantity of that element necessary to form the blue compound was found; and the amount of iodide ion produced at the same time was estimated by taking the difference between the total amount of iodide ion and that corresponding to the formation of the tetra-iodo-pyrrole. The ratio in moles of iodide ion formed to iodine used up in the reaction giving the blue substance was found in three experiments to be 3:2.03, 3:2.01 and 3:2.05.

It is apparent that three atoms of hydrogen are removed for every atom of iodine that enters or, in other words, there have been two units of oxidation for every unit of substitution. From the ratio between nitrogen and iodine in the black powder obtained under the conditions of this experiment it is possible to express the amount of oxidation per mole of pyrrole.[9]

The black powder for analysis was prepared by a method similar to that described in the experiments outlined above except that larger quantities were used and centrifuging was substituted for filtration when the precipitate was washed.

The iodine was determined by the method of Carius and the nitrogen by that of Kjeldahl.

Anal. Calc. for $C_8H_7N_2O_2I$: N, 9.6; I, 43.8. Found: N, 9.74; I, 43.15, 42.77.

This corresponds to two nitrogen atoms to one iodine, that is, one unit of oxidation per atom of nitrogen or per mole of pyrrole. This is not enough oxidation to permit of the removal of any carbon from the pyrrole nucleus and consequently it is justifiable to assume that the four carbons of the pyrrole nucleus are still there. But eight carbon,

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[9] It may be noted that, strictly speaking, these experiments directly elucidate the nature of the formation of the black decomposition product of the blue solution. However, it seems very probable that we are justified in assuming, as we have done here, that they equally show the course of the reaction which gives the blue substance, for we could find no signs that iodate ion, iodide ion, iodine or pyrrole is formed when the blue solution decomposes under varying conditions. Further, Mr. de Bussiere prepared the black powder by passing air through a blue solution made by the action of solid iodine on potassium pyrrole in anhydrous ether, analyzed it for iodine and obtained results similar to ours: I = 42.6% and 43.4%; calc. for $C_8H_7O_2N_2I$, I, 43.8.

two nitrogen, one iodine and seven hydrogen gram atoms are equivalent to 258 g., whereas the analysis corresponds to about 295 g. per gram atom of iodine. There is, therefore, also an addition of two atoms, carbon or oxygen, per atom of iodine. Presumably this is oxygen absorbed from the air, because when the black powder is prepared under conditions in which the only sources of oxygen and carbon are ether and air, it gives the same analysis. This point was verified by measuring the ratio of oxygen absorbed to oxidation (as distinguished from iodination) by iodine, by performing the reaction in a glass bulb inverted over mercury and in contact with a known volume of oxygen; the iodine used, the iodide ion formed and the oxygen absorbed being measured. If the number of moles of iodine (I_2) used is subtracted from the number of moles of iodide formed, and the result multiplied by two, the number of units of oxidations is obtained.

In three such experiments 0.89, 0.94 and 0.83 gram-atoms of oxygen were absorbed per unit of oxidation. Since it was found that under the times and conditions of these experiments there was a slight formation of iodide ion by the action of the sodium ethylate on the black powder, these results are probably low; hence this ratio may be regarded as unity and the amount of oxygen absorbed, being two atoms for every atom of iodine in the black powder, is sufficient to account for the percentages of iodine and nitrogen in that compound.

Discussion

The following equations for the formation of the blue compound and the black powder, respectively, are in agreement with all of the quantitative data, and probably represent the reactions,

$$2nC_4H_5N + 2nI_2 = C_{8n}H_{7n}N_{2n}I_n + 3nI^- + 3nH^+ \qquad (1)$$

$$C_{8n}H_{7n}N_{2n}I_n + nO_2 = C_{8n}H_{7n}O_{2n}N_{2n}I_n \qquad (2)$$

The evaluation of n in these formulas has so far proved to be an insoluble problem. It is of course impossible to determine the value of n by a direct measurement of the molecular weight. Indirect methods dependent on the change of number of moles during the reaction, although possible on paper, are not feasible in practise in this case, owing to the great instability of the substance and the fact that the problem is complicated by the occurrence of a by-reaction. The properties of the blue solution are very similar to those of free radicals. For example, it has a bright color, is very unstable and adds oxygen.[10] This would rather suggest that the value of n for the blue compound is 2, but the authors believe that the real value is some large number, for in ethereal solution the washing-out of a very small trace of alkali causes an abrupt change in the color, which would indicate that a great many pyrrole nuclei were associated with one sodium hydroxide group, and although this might still be spoken of as an adsorption of many small molecules around a sodium hydroxide molecule, it would seem rather metaphysical to distinguish between such a condition and the polymerization of the pyrrole nuclei into a large molecule. Again, the reactions to form the blue substance seem only to take place on some interface, which would

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[10] Apparently it also absorbs nitric oxide as it is almost immediately decolorized in ethereal solution by an atmosphere of that gas.

seem to suggest the necessity for the bringing together of many molecules of pyrrole by adsorption, and consequently that the *n* in the above equations is large.

The formula $C_{8n}H_{7n}N_{2n}I_n$ suggests that the pyrrole nuclei are linked together by single bonds formed by the removal of hydrogen. But many pyrrole nuclei cannot be joined in this way without the loss of more than one hydrogen per molecule of pyrrole, so that if the surmise that *n* is large is correct, then the pyrrole nuclei must have an auxiliary linkage not involving the removal of any atoms. This would probably be through their double bonds as in the current formula for tripyrrole. The resulting complex arrangement of unstable rings must produce a condition of great strain which would find relief in the breaking of some of the bonds, thus forming atoms with anomalous valences. To these atoms may be ascribed the close similarity of the properties of the blue substance to those of free radicals.

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Summary

Reactions which yield highly colored unstable substances when iodine or bromine reacts with pyrrole in the presence of other reagents and in a variety of solvents were investigated.

After deducting the amount of iodine necessary to form tetra-iodopyrrole, a by-product, and the resulting iodide ion, it was found that three molecules of iodide ion were produced for every two molecules of iodine used in forming the blue substance made by treating pyrrole in alcoholic sodium ethylate solution with solid iodine.

The blue compound absorbed oxygen, giving a black powder containing two atoms of nitrogen for every atom of iodine. The amount of oxygen absorbed was measured and found to be one atom for every atom of nitrogen.

From these experiments the empirical formula of the blue substance was deduced as $C_{8n}H_{7n}N_{2n}I_n$.

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