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ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASIUM FERRI-CYANIDE AND CAUSTIC POTASH.

W. A. NOYES.

[Read December, 1882.]

INTRODUCTION.

During several years past a series of investigations on the oxidizing action of a mixture of potassium bichromate, sulphuric acid and water upon benzene derivatives has been carried on by Professor Remsen and students at work in his laboratory.[1] As a result of this work and that of many other chemists, a law, first proposed by Remsen,[2] has been pretty thoroughly established. This law is, that when in a benzene derivative a hydrocarbon residue is protected from oxidation with the mixture mentioned above, by the presence of a "negative" atom or group (such as Cl, Bi, I. NO_2, SO_2OH, SO_2NH_2), such atom or group is always situated in the ortho position with regard to the protected group; on the contrary, a hydrocarbon residue situated in the meta or para position with regard to a "negative" group is oxidized just as though that group were not present.

At present there are more than twenty-five cases on record where an ortho methyl group is protected from oxidation by the presence of a negative atom or group.

The action of other oxidizing agents has not been made the

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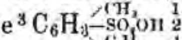
[1] Amer. Chem. Jour. 1879-82 inclusive.

[2] Ib. 1879, p. 36.

subject of such exhaustive study, but many facts of interest bearing on the question are already known.

It seems that when only one methyl group is present an ortho negative group does not prevent its oxidation by nitric acid;[1] but, when two methyl groups are present, the one which is meta or para to the negative group seems to be oxidized by preference.

Fusion with caustic potash oxidizes by preference a methyl group which is ortho and hydroxyl.[2]

A methyl group which is ortho to a negative atom or group is readily oxidized by potassium permanganate in alkaline solution. A meta or para group is also readily oxidized by the same agent, at least in some cases; though in one case at least (that of sulphocymene[3]  $C_6H_3\begin{array}{l}\diagup CH_3 \quad 1.\\ -SO_2OH \quad 2.\\ \diagdown C_3H_7 \quad 4.\end{array}$), the ortho methyl seems to be oxidized by preference.

A consideration of the facts briefly sketched above leads to the question: Is the different action of these oxidizing agents due to the character of the particular agents in themselves, or is it due to their more general character as acid or alkaline? It was for the purpose of throwing more light on this question that a series of experiments, of which those described in this paper are the first, were undertaken. They consist in a study of the action of another alkaline oxidizing agent, potassium ferricyanide. So far as I know this has never been used for the oxidation of benzene derivatives of the character considered here.

I. OXIDATION OF THE NITRO-TOLUENES.

The first substance chosen for study was ortho-nitro-toluene. A sample of this substance was procured from Kahlbaum in Berlin. It boiled at 221°-229° (corrected), and, as will be seen later, contained some para-nitro-toluene. The proportions used in the oxidation were: 2 grains of the nitro-toluene, 50 grains of

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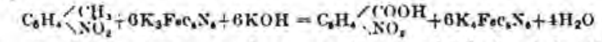
[1] Kekule, Berichte der Deut. Chem., Gesellschaft VII., 1007, and Zincke, VII., 1502.
[2] Jacobsen, Ib. XI., 375, 572.
[3] R. Meyer and A. Baue, Bll. XIII., 1195.

potassium ferricyanide, 23 grains of caustic potash and 200 grains of water. Some other proportions were tried, but these were found the most satisfactory. The main reaction which takes place is:



$$C_6H_4\left\langle\begin{matrix}CH_3\\NO_2\end{matrix}\right.+6K_3FeC_6N_6+6KOH=C_6H_4\left\langle\begin{matrix}COOH\\NO_2\end{matrix}\right.+6K_4FeC_6N_6+4H_2O$$

There are also some secondary reactions which lead to the formation of considerable quantities of ferric oxide and potassium carbonate. These were on one side of the main purpose and were not especially studied.

After boiling the mixture for two or three hours there always remained a small quantity of unoxidized nitro-toluene. This was distilled off with water-vapor. After the nitro-toluene had been removed, the fluid was filtered from some ferric oxide which always separated, and the filtrate was acidified with hydrochloric acid and extracted with ether. On distilling off the ether a residue remained, which proved to be a mixture of two acids. These were separated partly by the different solubility of the acids in water and partly by the different solubility of their barium salts.

One barium salt crystallized in thin yellow prisms which were difficultly soluble in cold water. The acid separated from these fused at 240° (corrected). The analyses of the barium salt gave 24.62 and 24.90 per cent. of Ba, and 15.93 and 16.06 per cent of H_2O, calculated for $(C_6H_4\left\langle\begin{smallmatrix}COO,\\NO_2\end{smallmatrix}\right.)_2\ Ba+5H_2O$, Ba = 24.51 per cent. and H_2O = 16.10 per cent.

These properties and all others so far as studied correspond with those of para-nitro-benzoic acid ($C_6H_4\left\langle\begin{smallmatrix}COOH\ 1.\\NO_2\ \ 4.\end{smallmatrix}\right.$) and its barium salt. This evidently came from the para-nitro-toluene which was mixed with the ortho-nitro-toluene.

The second barium salt proved far more soluble in water. From a very concentrated solution it separated in concentrically grouped crystals of an orange yellow color. The acid separated from a portion of these fused at 146° (corrected). Claus and Mallmann 1. give 146°.5 as the fusing point of ortho-nitrobenzoic acid.

The analysis of the barium salt gave 26.30 and 26.32 per cent. B_a and 10.69 and 10.64 per cent. H_2O; calculated for $(C_6H_4\left<\begin{smallmatrix}COO\\NO_2\end{smallmatrix}\right.)_2\ B_a+_3H_2O$, $B_a=26.20$ and $H_2O=10.33$ per cent. A portion of the salt was re-crystallized. It crystallized in the same form but the color of the crystals was a lighter orange. An analysis of the re-crystallized salt gave 10.54 per cent. H_2O. Unfortunately the barium estimation was lost.

The free acid dissolved in caustic potash with an intense yellow color.

These properties correspond with those of ortho-nitro-benzoic acid and its barium salt.

An approximate estimate was made of the yield from the oxidation, but not much weight is to be attached to it, as there was unavoidable loss at several points and no especial care was taken with the weights. From 8 grains of nitro-toluene 2 grains of unoxidized nitro-toluene were recovered and barium salts were obtained corresponding to about 1.2 grains of para-nitro-benzoic acid and 1.7 grains of ortho-nitro-benzoic acid.

It was thought that something might be learned about the relative ease with which ortho and para compounds are oxidized by oxidizing the portion of nitro-toluene which had been left unacted upon by the mixture. If this should have only ortho-nitro-benzoic acid, it would indicate that the para compound was most easily acted upon and had been entirely oxidized, leaving only ortho-nitro-toluene.

The oxidation was conducted as before and again a mixture of two acids was obtained. One of these fused at 139° - 140° and the other at 239° The amount obtained was not sufficient for complete purification and analysis, but there can be little doubt that both ortho- and para-nitro-benzoic acid were present. Hence there is no indication as yet as to whether the ortho or para group is oxidized most readily.

Ber. XI, 760.

I. Claus & Mallmann, Ber. XI, 760.

The work described above is really sufficient proof that para-nitro-toluene is oxidized by potassium ferricyanide and caustic potash, but, for the sake of completeness, one grain of pure para-nitro-toluene (from Kahlbaum, fuses 53° – 54°) was oxidized in the same manner as described above. As the para acid is quite insoluble in water, instead of extracting with ether the solution was concentrated and the potassium ferrocyanide was allowed to crystalize out. The acid was then precepitated from the mother-liquor with hydrochloric acid, separated from the solution with the filter-pump and converted into the Ba salt. An analysis of this gave 24.48 per cent. Ba and 16.06 per cent. H_2O. Calculated for $(C_6H_4 \langle\genfrac{}{}{0pt}{}{COO}{NO_2})_2 Ba + 5 H_2O$, Ba= 24.51, H_2O– 16.10. The acid separated from this salt fused at 240° – 241° (corrected.)

The results obtained prove that so far as the nitro-toluenes are concerned the oxidizing action of potassium ferricyanide and caustic potash is similar to that of potassium permanganate in alkaline solution. It would seem probable that the same analogy would hold true in the case of other benzene derivatives, but such a conclusion would be unsafe without a further study of the subject.

Some work has already been done with ortho-brom-toluene, and I had hoped to have the work complete enough to report at this meeting. But unexpectedly, the oxidation takes place with far greater difficulty than was the case with the nitro-toluene and apparently runs in a much more complicated manner. The investigation will be resumed in that direction so soon as the pressure of other duties shall permit.