water which has not been boiled fully one-half of the tellurium remains as metal: $H_2Te + O = H_2O + Te$. When treated with ninety-five per cent. alcohol no reaction takes place, even on boiling. This would seem to be the best one of the tellurides from which to make the organic salts as it does not decompose in the air so quickly as the alkali tellurides.

SEPARATION FROM COPPER BY THE ELECTRIC CURRENT.

Tellurium is easily deposited by the current, either from acid or alkaline solutions; even the feeblest current throws out the metal, but unfortunately not in the reguline state.

It has been found possible to separate tellurium fron copper by adding an excess of sodium hydroxide and about three grams of potassium cyanide for each gram of copper present. With this solution, a current such as is used for depositing copper, will throw out all the tellurium present, as a black non-adherent precipitate. After twelve hours, the tellurium is filtered off and weighed, either as metallic tellurium on a weighed filter or as tellurium dioxide. The solution is now made slightly acid with sulphuric and the copper precipitated in the usual way. If the proper amount of potassium cyanide has been added and the current has not been allowed to run too long, the tellurium is perfectly free from copper, and if the current is strong enough, none of it will adhere to the cathode.

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THE ELECTROLYTIC REDUCTION OF PARANITRO COMPOUNDS IN SULPHURIC ACID SOLUTION.[1]

BY ARTHUR A. NOYES AND JOHN T. DORRANCE.

Received September 9, 1895.

INTRODUCTION.

IT was shown some time ago by Noyes and Clement[2] that nitrobenzene in sulphuric acid solution is transformed by electrolytic hydrogen into paraamidophenolsulphonic acid. It has since been proved by the extended investigations of Gattermann and his students[3] that this behavior is characteristic of aromatic nitro compounds in general, one of the oxygen atoms

[1] Read at the Springfield meeting.

[2] *Ber. d. chem. Ges.*, 26, 990.

[3] *Ibid*, 26, 1844, 2810; 27, 1927.

of the nitro group always migrating during the reduction to the para position with the production of a hydroxyl group. It is evident, however, that this cannot take place when the position para to the nitro group is occupied by another element or group than hydrogen. The purpose of our investigation was to determine the nature of the reduction-products of a number of such compounds with the view of ascertaining any general principle that may exist. Only three such para compounds have been previously studied, namely, paranitrotoluene and paranitroorthotoluidine by Gattermann[1] and paranitrobenzoic acid by Noyes and Clement.[2] We have now investigated three additional ones, paranitraniline, paranitrophenol, and parachlornitrobenzene.

THE METHOD OF REDUCTION.

The method of carrying out the reduction was essentially the same in all cases. The apparatus consisted of a small beaker, to the sides of which a large platinum electrode was closely fitted, and in which was placed a cylindrical porous cup containing a small platinum electrode. Concentrated sulphuric acid was placed within the cup at the start, and small quantities of diluted acid were occasionally added during the electrolysis to prevent the acid from becoming fuming. The solution to be electrolyzed was placed outside; it was prepared by dissolving twenty or thirty grams of the substance in two and a half to three times its weight of strong sulphuric acid. A current of one or two amperes was passed through for forty or fifty hours.

The reduction-product precipitated either during the electrolysis or after cooling. It was filtered out upon a hardened filter with the aid of suction and dried by spreading on porous plates. The filtrate was diluted with an equal bulk of water, and any further precipitate added to the original one. The subsequent purification varied in the different cases, and will be described under the separate substances.

REDUCTION OF PARANITRANILINE.

The paranitraniline used was in part a Kahlbaum preparation and was in part prepared by ourselves by the method given by

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[1] *Ibid.* 26, 1850, 1852.

[2] *Am. Chem. J.*, 16, 511.

Nölting and Collin.[1] It gave the correct melting-point of 146°.

The reduction-product was isolated by extracting the precipitate dried on the porous plates with boiling water, boiling the solution with animal charcoal, filtering, and causing to crystallize by cooling.

It was found to consist of paradiamidobenzene sulphate. It was very difficultly soluble in cold water.[2] Its solution was colored purple by ferric chloride, and it gave the following results on analysis:

0.2193, 0.2847, and 0.3581 gram substance gave respectively 0.0985, 0.1262, and 0.1638 gram water and 0.2822, 0.3672, and 0.4605 gram carbon dioxide.

0.3147, 0.2077, 0.3938, and 0.4525 gram substance gave respectively 0.3481, 0.2340, 0.4363, and 0.5066 gram barium sulphate.

	Found.				Calculated for
	I.	II.	III.	IV.	$C_6H_{10}N_2SO_4$.
Carbon	35.10	35.18	35.08	....	34.94
Hydrogen	4.99	4.92	5.08	....	4.85
Sulphur trioxide	38.32	38.68	38.04	38.44	38.84

REDUCTION OF PARANITROPHENOL.

A sample of the substance from Kahlbaum having the correct melting-point (113°) was employed.

The reduction-product was practically insoluble even in boiling water, but dissolved readily in sodium hydroxide or carbonate. It was purified by dissolving in the latter, filtering, and precipitating immediately with hydrochloric acid. The precipitate was washed successively with water, alcohol, and ether, and dried at 125°. Twelve grams were obtained from thirty grams of nitrophenol.

The physical and chemical properties and the analysis of the body established its identity as paraamidophenolsulphonic acid, It reduced silver nitrate solution in the cold with the production of a purple color, and turned brown rapidly in alkaline solution owing to oxidation. It was decomposed by heating with strong

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[1] *Ber. d. chem. Ges.*, 17, 262.

[2] Contradictory statements exist in the literature as to the solubility of this salt. Nietski, in *Ber. d. chem. Ges.*, 11, 1098, states that it is readily soluble. Vignon, in *Bull. Soc. Chim.*, 50, 153, that it requires 714 parts of water at 15°. The latter statement is, according to our experience, the correct one.

hydrochloric acid in a closed tube to 180°; the hydrochlorate of the base crystallized out upon cooling, and from this, by the addition of potash, the base itself was set free. Like paraamidophenol, it melted at 183°, undergoing decomposition. It also showed the characteristic color reactions of that substance with chloride of lime and ferric chloride.

The analysis of the sulphonic acid gave the following results:

0.2361 gram substance gave 0.0879 gram water and 0.3295 gram carbon dioxide.

	Found.	Calculated for $C_6H_3.NH_2.OH.SO_3H$.
Carbon	38.06	38.08
Hydrogen	4.13	3.70

REDUCTION OF PARACHLORNITROBENZENE.

A Kahlbaum preparation (melting-point 83°) was employed in this case also. The reduction-product proved to be a sulphonic acid, and was purified exactly as that obtained from the reduction of nitrophenol. It was first tested qualitatively for chlorine and found to contain none. It exhibited in fact all the characteristic properties of paraamidophenolsulphonic acid, being almost insoluble in hot water, oxidizing very rapidly in alkaline solution, and readily reducing silver nitrate solution. It was subjected to just the same treatment as the reduction-product of the nitrophenol with identical results. In addition to the confirmatory tests described under that substance, the diacetyl derivative of the base was prepared by boiling with acetic anhydride, and this was found to melt at 149°. Diacetylparaamidophenol melts according to Ladenburg at 150°-151° C.

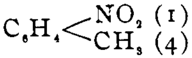
The sulphonic acid gave the following results on analysis:

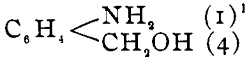
0.2912 gram substance gave 0.1002 gram water and 0.4059 gram carbon dioxide.

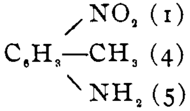
	Found.	Calculated for $C_6H_3.NH_2.OH.SO_3H$.
Carbon	38.02	38.09
Hydrogen	3.90	3.70

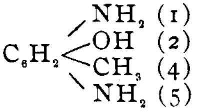
SUMMARY OF THE RESULTS.

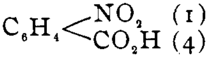
The paranitro compounds, which up to the present time have been submitted to electrolytic reduction are tabulated below together with their reduction-products:

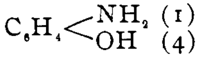

$C_6H_4\left\langle\begin{array}{ll} NO_2 & (1) \\ CH_3 & (4) \end{array}\right.$

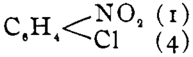

$C_6H_4\left\langle\begin{array}{ll} NH_2 & (1) \\ CH_2OH & (4) \end{array}\right.$[1]

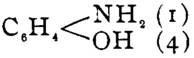

$C_6H_3\begin{array}{ll} / NO_2 & (1) \\ -CH_3 & (4) \\ \backslash NH_2 & (5) \end{array}$

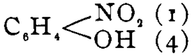

$C_6H_2\begin{array}{ll} / NH_2 & (1) \\ \langle OH & (2) \\ \langle CH_3 & (4) \\ \backslash NH_2 & (5) \end{array}$

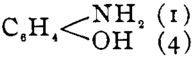

$C_6H_4\left\langle\begin{array}{ll} NO_2 & (1) \\ CO_2H & (4) \end{array}\right.$

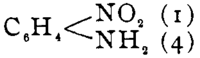

$C_6H_4\left\langle\begin{array}{ll} NH_2 & (1) \\ OH & (4) \end{array}\right.$


$C_6H_4\left\langle\begin{array}{ll} NO_2 & (1) \\ Cl & (4) \end{array}\right.$


$C_6H_4\left\langle\begin{array}{ll} NH_2 & (1) \\ OH & (4) \end{array}\right.$


$C_6H_4\left\langle\begin{array}{ll} NO_2 & (1) \\ OH & (4) \end{array}\right.$


$C_6H_4\left\langle\begin{array}{ll} NH_2 & (1) \\ OH & (4) \end{array}\right.$


$C_6H_4\left\langle\begin{array}{ll} NO_2 & (1) \\ NH_2 & (4) \end{array}\right.$


$C_6H_4\left\langle\begin{array}{ll} NH_2 & (1) \\ NH_2 & (4) \end{array}\right.$

The most striking of the results are those obtained with the paranitrobenzoic acid and with the parachlornitrobenzene, the group para to the nitro group being driven out in each case. It seems not improbable that this behavior is a general characteristic of nitro compounds with negative para groups, but an investigation of others would be needed in order to establish it as a fact.

It is also worthy of note that, contrary to what might be expected, in only one of the six cases, that of the nitrotoluidine, does the oxygen atom display any tendency to migrate to any other than the para position.

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PERIODIDES OF PYRIDINE.[2]

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PYRIDINE ALKYL PERIODIDES.

1. *Pyridine Methyl Pentiodide.*—This was obtained in the manner given in detail below, very satisfactorily in preparation I, and with slight impurity in two other preparations, II and III, by different ways, through separation from other periodides.

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[1] The substance isolated was a condensation-product of this with a second molecule of nitrotoluene; but this is undoubtedty the primary reduction-product.

[2] Read at the Springfield meeting of the American Association for the Advancement of Science, September 2, 1895.