CXL.—*The Electrolytic Reduction of Nitrourea.*

By G. W. F. HOLROYD.

THIELE AND LACHMAN (*Annalen*, 1895, **288**, 303) obtained evidence of the formation of nitrosourea as the primary reduction product of nitrourea. This nitroso-compound appears to be very unstable, being readily decomposed by mineral acids or acetic acid, and although rather more stable in alkaline solution, it decomposes, even in such a solution, at a little above 0°.

With the object of reducing the nitrosourea before it decomposes and so preparing semicarbazide from nitrourea, Thiele and Heuser (*ibid.*, 311) added, in small quantities at a time, a mixture of nitrourea and hydrochloric acid to a mixture of zinc dust and ice. Since the temperature must be kept at about 0°, this operation is very laborious. The semicarbazide was separated from solution in the form of the compound $[(CH_3)_2C{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2]_2,ZnCl_2$; the yield of this compound obtained by the authors was 40 to 55 per cent. of the calculated amount.

The experiments described below were undertaken in order to see whether the conditions necessary for the reduction might not be obtained more easily by using the electric current. The result was to show that the reduction may be effected electrolytically with the expenditure of very little labour. An aqueous solution of ammonium chloride served, in the majority of experiments, as the electrolyte.

The following are the conditions which I found most favourable for the reduction. Ten grams of nitrourea, prepared according to Thiele and Lachman's directions (*loc. cit.*, 281), are placed in a jar, and 80 grams of commercial ammonium chloride and 300 grams of water are added. The cathode and anode each consist of a sheet of wrought iron, the area of one side of the portion of each of these which is immersed in the liquid is 70 sq. cm. The anode must be at least 3 mm. thick. A current of 2 amperes is passed during 20 hours. The cell is immersed in a large vessel of cold water. Since the resistance of such a cell, although it increases as the electrolysis proceeds, does not exceed more than about one ohm, a large number of such cells can easily be arranged in series, the anode of one cell being bent round so as to dip into the next and form the cathode of this second cell, and so on.

In experiment 15, several cells of double the size and with double the charge of nitrourea, ammonium chloride, and water were placed in series. The yield given in the table refers to one of these cells; the rest of the product obtained in this experiment was not recrystallised.

After interrupting the current, the contents of the cell are filtered at the pump, the precipitated ferrous hydroxide is washed twice with water, the turbid filtrate rendered clear by acidifying with hydrochloric acid, the liquid again filtered if necessary, and 10 grams of benzaldehyde are added for every 10 grams of nitrourea used, in order to separate out the semicarbazide. The mixture is shaken in a bottle for a few minutes, allowed to stand for an hour, and the precipitated benzylidenesemicarbazide is then filtered off and washed with water.

The benzylidenesemicarbazide so obtained may be directly converted into semicarbazide hydrochloride. According to Thiele and Stange (*Annalen*, 1894, **283**, 21), benzylidenesemicarbazide gives 89 per cent. of the theoretical yield of semicarbazide hydrochloride. If the benzylidenesemicarbazide is required in a state of purity, it may be recrystallised from commercial alcohol (methylated spirit). The reduction gave a yield of recrystallised benzylidenesemicarbazide equal to 60 per cent. of the theoretical yield. The crude product probably contains 66 per cent. of the calculated amount, for 1 gram of pure benzylidenesemicarbazide gave 0·9 gram when recrystallised in the same manner.

I found this the most economical method of preparing semicarbazide hydrochloride.

Subjoined is a table showing the results of electrolysis under various conditions of temperature, size of electrodes, and density of current.

In calculating the density of current, both sides of the cathode have been counted as area of the cathode, with the exception of those cases where the iron box was used and of experiment 17, where the electrodes were very close to one another.

For purposes of estimation, the semicarbazide was converted into the benzylidene derivative.

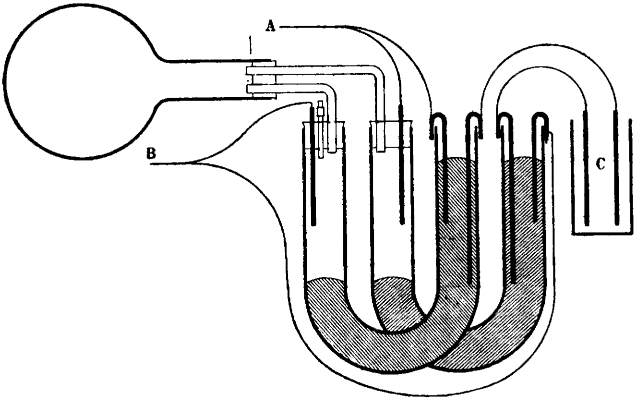
0·1160 of the product in experiment 15 gave 26·1 c.c. of nitrogen at 17° and 758 mm. N = 26·05.

$C_8H_9ON_3$ requires N = 25·76 per cent.

Number of experiment.	Nature of electrolyte.	Nature and size of electrodes.	Amperes.	Density of current in amperes per sq. cm. of cathode.	Temperature.	Per cent. of current effective in producing semicarbazide.	Hours during which current was passed.	Grams of nitrourea used.	Grams of recrystallised benzylidenesemicarbazide.	Per cent. of theoretical yield.
1	24 grams of ammonium chloride, 90 grams of water.	Cathode, a wrought iron box containing the electrolyte, 115 sq. cm. in contact with liquid; anode, 70 sq. cm. wrought iron.	1	0·0087	20°	12·9	6	1	0·79	50·9
2	,,	Cathode same as in 1, with iron plate attached; total area, 286 sq. cm.; anode as in 1.	1	0·0035	,,	12·1	,,	,,	0·74	47·7
3	,,	Cathode and anode as in 1.	1	0·0087	,,	19·6	4	,,	0·80	51·6
4	,,	,,	1	,,	−5	12·7	6	,,	0·78	50·3
5	,,	Cathode as in 1; anode, 360 sq. cm. wrought iron.	1	,,	20	20·3	4	,,	0·83	53·5
6	,,	Cathode, a strip of wrought iron 15 sq. cm.; anode as in 1.	1	0·066	,,	15·7	6	,,	0·96	61·9
7	,,	Cathode, a strip of wrought iron 7 sq. cm.; anode as in 1.	1	0·143	,,	18·4	4	,,	0·75	48·4
8	,,	,,	1	,,	,,	16·03	6	,,	0·98	63·2
9	,,	Cathode and anode as in 1.	1	0·066	,,	29·9	2	,,	0·61	39·35
10	8 grams of ammonium chloride, 30 grams of water.	,,	1	,,	,,	22·5	4	,,	0·92	59·35

11	24 grams of ammonium chloride, 90 grams of water.	Cathode, a strip of wrought iron 30 sq. cm.; anode, 70 sq. cm. wrought iron.	2	,,	,,	16·3	3	,,	1·0	64·51
12	,,	Cathode and anode as in 6.	0·3	0·02	,,	24	15	,,	1·1	70·90
13	80 grams of ammonium chloride, 300 grams of water.	Cathode, a wrought iron plate 150 sq. cm.; anode, ditto.	2	0·013	,,	22·9	20	10	9·34	60·25
14	,,	,,	2	,,	,,	18·1	25	,,	9·24	59·61
15	150 grams of ammonium chloride, 600 grams of water.	Cathode, a wrought iron plate 300 sq. cm.; anode, ditto.	3	0·01	,,	21·1	27	20	17·46	56·32
16	25 grams of ammonium chloride, 73 of water, 22 of ammonia of sp. gr. 0·880.	The electrodes were sheets of zinc; 70 sq. cm. of each were in contact with the liquid.	4	0·114	,,	7·7	20	10		40·58
17	8 grams of ammonium chloride, 25 of water, 5 of ammonia of sp. gr. 0·880 (the nitrourea was added gradually.)	The electrodes were discs of zinc placed one above the other, the area of one side of each was 50 sq. cm.	5	0·1	,,	13·6	1⅓	1	0·928	59·9
18	50 grams of sodium chloride, 150 of water in outer cell; same solution in a porous inner cell.	Cathode, platinum foil, 72 sq. cm. in outer cell; anode, carbon in inner cell.	1·9	0·026	−2	17·4	8	5	2·69	34·7
19	200 grams of 18 per cent. hydrochloric acid in outer cell; hydrochloric acid of same strength in inner porous cell.	Cathode and anode as in 18.	1·9	,,	−5	15·4	,,	,,	2·39	30·8
20	200 grams of 18 per cent. hydrochloric acid in outer cell; hydrochloric acid of same strength in inner cell	,,	1·9	,,	,,	6·4	,,	2	0·99	32·1

In experiment 16, the electrolysis was interrupted after 10 hours and begun again on the following day; the nitrourea was added in portions of 1 gram at intervals of 2 hours. When electrolysis was at an end, the solution was filtered and 5 grams of acetone were added, a crystalline deposit of the compound $[(CH_3)_2C:N\cdot NH\cdot CO\cdot NH_2]_2,ZnCl_2$ was formed. This precipitate was filtered off after some hours, and dried on a porous plate; it then weighed 5·95 grams. One gram of this precipitate was dissolved in water, 1 gram of benzaldehyde added, and the solution heated to boiling; the benzylidenesemicarbazide thus formed was collected and recrystallised from alcohol; it then weighed 0·73 gram. The 5·95 grams of zinc compound would, therefore, have given 4·34 grams of recrystallised benzylidenesemicarbazide; this corresponds to a yield of 28 per cent. of the theoretical. 1·95 grams of recrystallised benzylidenesemicarbazide were obtained from the filtrate from the zinc compound; this corresponds to a yield of 12·58 per cent. A total yield of 40·58 per cent. of the theoretical was, therefore, obtained in this experiment.



In all the other experiments, the semicarbazide was precipitated directly as the benzylidene derivative.

Experiment 17 shows that a good yield may be obtained when zinc poles are used, if the nitrourea be added very gradually.

In the case of experiments 16 and 17, where zinc poles were used, an alternating current was employed to prevent the formation of a bridge of zinc from pole to pole.

A little piece of apparatus which I found very useful for alternating a direct current, depends on an observation made some years ago by Mr. A. G. Vernon Harcourt. If a vessel containing air be heated and connected, by means of glass tubing, with a U-tube containing mercury, and an oscillatory motion be imparted to the mercury, this motion is maintained so long as the vessel containing air is heated.

I proposed to use this arrangement as a source of energy to work an ordinary rocking alternator. I am, however, indebted to Mr. D. H. Nagel, of Trinity College, for the suggestion that I should use the oscillating mercury in the U-tube directly for making and breaking contact. This I did in the following manner.

I placed a flask of 250 c.c. capacity in a horizontal position above an argand burner and connected it, by means of a doubly-bored cork and bent glass tubes, with two U-tubes half-filled with mercury. By imparting simultaneously to the mercury in both U-tubes an oscillatory motion (by depressing the mercury in the outer limbs by two corks fixed on the ends of little rods), I obtained the necessary movement of the mercury. This movement is maintained so long as the flask is heated. By the arrangement of wires shown in the figure (p. 1330), a current may be sent first in one direction and then in the opposite direction through an electrolytic cell. The wires which come in contact with the mercury should be of iron.

Thiele and Lachman remark with respect to primary nitrosoamines: "These nitrosoamines are generally very unstable bodies, and it is owing to their production that the reduction of primary nitroamines generally gives such unsatisfactory yields" (*loc. cit.*).

A method similar to the above may probably be applied with advantage to the reduction of other nitroamines and nitrosoamines. This I hope to test in the near future.

I wish to express my thanks to Mr. D. H. Nagel, of Trinity College, Oxford, for kindly allowing me to carry out these experiments in the Laboratory of Balliol and Trinity Colleges.

CHRIST CHURCH, OXFORD.