

# Electrolytic Reduction of Oximes, I. Benzoinoxime

By

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Electrolytic reduction of oximes generally takes place so smoothly that some of the reaction is believed to afford the best mode of preparation for amines. As the works on this field, however, are rather few, and many points are left still untouched the author has taken up the problem to study it more thoroughly. The present communication dealing with the reduction of benzoinoxime forms the first report of the experimental works thus planned for carrying out.

Benzoinoxime ( $\alpha$ -compound melting at 150–151°) prepared from benzoin and hydroxylamine according to the method of H. Goldschmidt and N. Polonowska<sup>1</sup> was used. A solution formed by dissolving 10 grams of the oxime in 100 c.c. of alcohol with 10 c.c. of a concentrated sulphuric acid added was taken as the cathode solution in a beaker, into which a porous cell filled with a dilute sulphuric acid was dipped so as to form the anode compartment. Using a lead plate of 136 sq. cm. as the cathode a current of 0.6 ampere was passed for about 8 hours, during which the temperature of the bath was maintained at 25° by cooling it with water. When the current was passed for nearly 3 hours, the evolution of hydrogen in the cathode greatly increased, and the cathode became coated with very minute crystals.

After the electrolysis was over the yellow-coloured cathode solution was poured into water and left to stand over-night, and then

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<sup>1</sup> Ber. D. Chem. Ges., **20**, 492 (1887).

filtered. The precipitate (I) consisting of a white crystalline substance contaminated with some oily liquid was boiled with water for about 20 minutes with the object of separating the soluble part from the insoluble. The insoluble portion, when recrystallised from alcohol, formed colourless prisms melting at 135-137°, and having all the properties of benzoin; the soluble portion crystallized out from the aqueous solution in fine needles which, on further treatment with dilute alcohol, were separated into two parts, that is, the less soluble one crystallizing in plates, with the melting point at 137-138°, and the more soluble one crystallizing into fine needles, with the melting point at 119-120°. The former was proved to be hydrobenzoin, and the latter isohydrobenzoin.

The filtrate separated from the precipitate (I), after having been confirmed to contain hydroxylamine, was made alkaline by sodium hydroxide and left to stand for 12 hours. The precipitate, gradually changing from the amorphous to the crystalline, was gathered and purified by recrystallizing it from benzene. As it was deemed to be a mixture of normal and iso-diphenyloxyethylamine,<sup>1</sup> it was treated with benzene with the object of separating the two substances from each other, and by this process 2 grams of the normal compound (M. P. 160°) and 0.2 gram of the isocompound (M. P. 129°) were obtained. They were each analysed by Kjeldahl's method with the following results :

Substance taken gram.	$\frac{N}{20}$ HCl	N	
		Found	Calc. (C <sub>14</sub> H <sub>15</sub> NO)
0.4550	4.2 c.c.	6.98	6.57%
0.5010	4.6 „	7.02	

On standing the normal amine with alcoholic hydrogen chloride needle crystals<sup>2</sup> melting at 210° were produced, and that it was amine hydrochloride was confirmed by titrating it with  $\frac{N}{10}$  NaOH.

<sup>1</sup> H. G. Söderbaum: Ber. D. Chem. Ges., **28**, 2522 (1895)

<sup>2</sup> N. Polonowska: *ibid.*, **21**, 488 (1888)

In order to test the substance crystallized out on the surface of cathode during the electrolysis, it was dissolved in hot benzene, and recrystallized from alcohol, in which it is soluble only at a high temperature. The melting point of the needle crystals thus purified was found to be 207–208°. Possibly the substance may be benzoinpinacone, but as the true melting point of benzoinpinacone<sup>1</sup> is not yet settled, its determination affords no reliable means for its identification. So that it was subjected to elementary analysis, and the following results were obtained.

1. 0.1010 grm. substance gave 0.3000 grm. CO<sub>2</sub> and 0.0590 grm. H<sub>2</sub>O
2. 0.1248 „ „ „ 0.3760 „ „ „ 0.0770 „ „
3. 0.1234 „ „ „ 0.3763 „ „ „ 0.0778 „ „
4. 0.0984 „ „ „ 0.2880 „ „ „ 0.0607 „ „

	Found				Calc.	
	1	2	3	4	for C <sub>28</sub> H <sub>26</sub> O <sub>4</sub>	for C <sub>28</sub> H <sub>26</sub> O <sub>2</sub>
C	81.09	82.21	83.30	80.98	78.85	85.24 %
H	6.54	6.82	6.89	6.90	6.15	6.64 %

From the above results it is clearly seen that the substance used for the analysis is neither benzoinpinacone nor desoxybenzoinpinacone<sup>2</sup>, but a mixture of the two.

Drawing an inference from the reduction-products thus far identified, it may be concluded that benzoinoxime undergoes electrolytic reduction in an acid solution only partly, and some part of it is hydrolysed before it is electrolytically reduced, and benzoin produced by hydrolysis undergoes reduction simultaneously so as to form hydrobenzoin, benzoinpinacone, and desoxybenzoinpinacone.

To find out the most favourable condition of electrolysis for the

<sup>1</sup> Melting point of benzoinpinacone given by Goldenberg [Lieb. Ann., **174**, 332 (1874)] is 208°, while Zinke [(Lieb. Ann., **198**, 52 (1879))] announced it to be 233°, and Kauffmann [Zs. Elektrochemie **4**, 461 (1898)] 235°.

<sup>2</sup> As the melting point of desoxybenzoinpinacone, 213° (α-compound) and 172° (β-compound) are given by Blank [Lieb. Ann., **248**, 1 (1888)].

production of the amine a series of experiments were conducted, the results of which are summarized in the following tables.

1. Influence of the concentration of sulphuric acid

Cathode solution : 3.0 gm benzoinoxime  
100 c.c. alcohol  
sulphuric acid (1.83)  
Anode solution : dilute sulphuric acid  
Cathode : lead plate (136 sq. cm)  
Current strength : 0.4 amperes  
Time of electrolysis : 8 hours  
Temperature : 7-8°

Table [ I ]

Conc. of H <sub>2</sub> SO <sub>4</sub>	Benzoin	Hydrobenzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
%	gm.	gm.	gm.	gm.	%	%
5	0.36	0.08	—	1.30	20.14	46.70
10	0.22	0.01	trace	0.73	11.25	26.00
20	0.34	0.05	trace	0.70	10.81	18.17

2. Influence of current density

Cathode solution : 3.0 gm benzoinoxime  
100 c.c. alcohol  
10 c.c. H<sub>2</sub>SO<sub>4</sub> (1.83)

Other conditions are the same as in 1.

Table [ II ]

Current density	Benzoin	Hydrobenzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
amp./100cm <sup>2</sup>	gm.	gm.	gm.	gm.	%	%
0.3	0.22	0.01	trace	0.73	11.25	26.00
0.4	0.80	0.30	trace	0.65	10.25	23.60
0.5	1.12	0.38	trace	0.51	7.81	8.20

## 3. Influence of temperature

The conditions are the same as in 2.

Table [III]

Temperature	Benzoin	Hydrobenzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
	gm.	gm.	gm.	gm.	%	%
7- 8°	0.22	0.01	trace	0.73	11.25	26.00
19-20°	0.15	trace	little	1.31	20.16	46.78
50-52°	trace	trace	0.37	0.02	0.31	0.94

## 4. Influence of cathode material

Cathode solution : 3.0 gm benzoinoxime  
 100 c.c. alcohol  
 5 c.c. sulphuric acid (1.83)

Anode solution : dilute sulphuric acid

Temperature : 7-8°

Current strength : 0.6 amperes

Time of electrolysis : 8 hours

Table [IV]

Cathode		Benzoin	Hydrobenzoin	Pinacone	Amine	Current yield of Amine	Material yield of Amine
Material	Surface area						
Pb <sup>(Amalgam)</sup>	sq. cm.	gm.	gm.	gm.	gm.	%	%
Pb	136	0.08	trace	0.02	1.10	11.46	39.15
Pb	136	0.36	0.08	—	1.30	13.75	46.70
Sn	141	0.50	0.02	trace	1.39	14.87	49.55
Ni	66	2.55	0.10	—	trace	—	—

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From the above results it may be concluded that for the preparation of the amine the concentration of sulphuric acid in the cathode solution should not exceed 5 %, and the electrolysis should be conducted at 19—20° with current density of about 0.3 amperes per sq. cm., and as cathodes tin and lead are most preferable.

In an alkaline or neutral solution, hydrolysis of the oxime does not take place, but at the same time no appreciable reduction could be observed.

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