

Electrolytic Reduction of Oximes, II. γ -Isonitrosovaleric Acid and α -Isonitrosopropionic Acid.

By

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Acid-oximes are generally liable to undergo hydrolysis so as to change into the corresponding ketonic acid and hydroxylamine. The case with which hydrolysis takes place seems to depend upon the constitution of the acid oximes, that is to say, on the relative position of the carbon atom to which the oximido group is attached toward the carboxyl group, and so far as the fatty acid oxime is concerned, α -acid oxime seems less hydrolysable than β , and β than γ . This may be looked upon as accounting for the reason why it has hitherto been impossible to transform γ -isonitrosovaleric acid into the corresponding amine by the action of tin and hydrochloric acid, while α and β -isonitroso fatty acids undergo reduction under similar treatment.

In the electrolytic reaction the causes of hydrolysis—concentration of acid and temperature—may, without much difficulty, be suppressed to a certain extent, so the author planned to reduce γ -isonitrosovaleric acid electrochemically with the hope of realizing the reaction which purely chemical methods failed to bring about.

Electrochemical reduction of α -isonitrosopropionic acid was also studied with the object of learning how α and γ -acid oxime differ in their behaviour towards reduction.

The comparison of the conditions for their reduction and of the yield of Amines is shown below :

	α -isonitrosopropionic acid	γ -isonitrosovaleric acid
Current density	4—5 Amp. /100 ² cm.	0.5 Amp. /100 ² cm.
Temperature	7—10°	3—5°
Sulphuric acid	8%	5%
Yield {Material	95%	84%
{Current	93%	61%

The figures in the above table show how much more hydrolysable γ -isonitrosovaleric acid is than α -isonitrosopropionic acid.

EXPERIMENTAL PART.

1. Electrolytic Reduction of γ -Isonitrosovaleric Acid.

γ -Isonitrosovaleric acid can be reduced to the corresponding amino-compound neither with tin and hydrochloric acid nor with sodium amalgam¹. Tafel² could prepare γ -aminovaleric acid only by reducing the phenylhydrazone of lavulinic acid with sodium amalgam in an alcoholic solution acidified with acetic acid. Isolation of the amino acid thus formed, however, is very troublesome and the yield is never more than 50%. In the electrolytic reduction the formation of the amino acid takes place smoothly and gives a very satisfactory result as is described below.

The γ -Isonitrosovaleric acid used in the experiment was prepared from lavulinic acid and hydroxylamine according to the method of P. Rischbieth³.

It melted at 95—96°. The solution containing 5 grams of the acid oxime and 100 c.c. of water acidified with 10 c.c. of sulphuric acid (1.83) was taken as the cathode solution and dilute sulphuric acid as the anode solution. Lead being used as the electrodes a current of 0.5 Amp. /1 sq. dm. was passed for 10 hours, during which the temperature of the bath was maintained at 6—8°.

After the electrolysis was over the cathode solution was treated with barium carbonate to precipitate sulphuric acid, and filtered.

¹ Ad. Müller : Ber. D. Chem. Ges., **16**, 1618 (1883).

² Ber. D. Chem. Ges. **19**, 2415 (1886).

³ Ber. D. Chem. Ges. **20**, 2669 (1887).

On evaporating the filtrate an oily substance slightly yellowish brown coloured was obtained which quickly solidified on standing. It was washed with ether and recrystallized from its concentrated aqueous solution on addition of alcohol-ether. It crystallizes in small plates and its solution reacts neutrally. The melting point was found to be far higher than that given by Tafel, that is 217—218° against 193°. The melting point of its hydrochloride was found to be 151°, which just agrees with Tafel's determination. It was analysed with the following results :

0.0901 grm. substance gave 0.0782 grm. H₂O and 0.1686 grm CO₂

0.3120 grm. substance by Kjeldahl's method required 26.4 c.c. $\frac{N}{10}$ HCl

	Found	Calc. for C ₈ H ₁₁ O ₂ N
C	51.07	51.28%
H	9.59	9.40%
N	11.80	11.97%

In order to learn the influence of external conditions on the reduction several experiments were conducted, results of which are tabulated as below :

I. Influence of the degree of concentration of the sulphuric acid.
Cathode solution : 3 gram the acid oxime + 100 c.c. water + sulphuric acid.

Anode solution : dilute sulphuric acid.

Cathode : lead (100³ cm.); Anode : also lead.

Current strenght : 0.5 amperes.

Current quantity : 3.3 ampere-hours.

Temperature : 6—8°.

Conc. of H ₂ SO ₄ %	Ketonic acid gram.	Amino acid gram.	Current yield %	Material yield %
5	0.27	2.12	58.73	80.30
8	0.28	2.12	58.73	80.30
15	1.02	1.40	38.78	53.03

II. Influence of current density.

Cathode solution : 3 gram the acid oxime + 100 c.c. water + 5 c.c. $H_2SO_4(1.83)$.

Other conditions the same as in I.

Current density amps./100 ² cm.	Ketonic acid gram.	Amino acid gram.	Current yield %	Material yield %
0.25	0.35	1.95	54.01	71.59
0.50	0.28	2.12	58.73	80.30
1.00	0.12	2.45	67.87	92.80
2.00	0.11	2.48	68.70	93.93
3.00	0.12	2.46	68.14	93.14

III. Influence of temperature.

Current of 0.5 amperes was used, all other conditions being the same as in II.

Temperature	Ketonic acid gram.	Amino acid gram.	Current yield %	Material yield %
3—5°	0.21	2.21	61.22	83.71
6—8°	0.28	2.12	58.73	80.30
18—20°	2.30	0.15	4.16	5.67

IV. Influence of cathode material.

The solution, current strength, current quantity and temperature are all the same as in the previous experiments.

Cathode		Ketonic acid gram.	Amino acid gram.	Current yield %	Material yield %
Material	Surface- area				
Hg	17.0 sq cm.	0.15	2.40	66.48	90.90
Pb	100.0	0.28	2.12	58.73	80.30
Sn	100.0	0.30	2.10	58.17	79.54
Ni	66.0	2.55	—	—	—

From the above table it appears that mercury is most effective as the cathode and that lead or tin come next.

2. Electrolytic Reduction of α -Isonitrosopropionic Acid.

α -Isonitrosopropionic acid¹ was prepared from pyrrocemic acid² obtained by treating tartaric acid with potassium bisulphate.

A solution of 20 grams of the acid oxime in 400 c.c. of 8% sulphuric acid was used as the cathode solution, and with lead as electrodes a current of 4.5 amperes/100² cm. was passed slightly in excess. The Temperature of the bath was maintained at 7–10°. After reduction was over, sulphuric acid in the cathode solution was precipitated as barium salt and filtered. The filtrate was evaporated to dryness in a water bath, and the pale yellow coloured residue was recrystallized from dilute alcohol. The material yield was more than 95%.

α -Aminopropionic acid thus obtained crystallizes in needles and has a strong sweet taste. It is hardly soluble in absolute alcohol and absolutely insoluble in ether. Its aqueous solution has a faint acid and is optically inactive. These properties well agree with those of α -alanine, but its melting point, determined to be 276–278°, is different from any of the values hitherto found by Weyl³ (255°), Emil Fischer and Lenchs⁴ (285°), and by Zelinsky and Stadnikoff⁵ (264–265°), among whose determinations there could not be found any conformity.

It was analysed with the following results :

0.1030 grm. substance gave 0.1516 grm. CO₂ and 0.0832 grm. H₂O

0.5054 grm. substance by Kjeldahl's method required 58.6 c.c. $\frac{N}{10}$ -HCl

	Found	Calc. for C ₃ H ₇ O ₂ N
C	40.17	40.42
H	8.07	7.92
N	16.27	15.73%

The amino-acid was mesotomised according to the method of Emil Fischer¹ and l-benzoylalanine was isolated, whose melting point and specific rotation were determined to be 164–165° and $[\alpha]_D^{25}$ = –32.1° respectively.

¹ V. Meyer and Janny: Ber. D. Chem. Ges., **15**, 1525 (1882).

² Döbner: Lieb. Ann., **242**, 269 (1887).

³ Ber. D. Chem. Ges., **21**, 1529 (1888).

⁴ Ibid. **35**, 3793 (1902).

⁵ Ibid. **41**, 2061 (1908).

42 *Masayoshi Ishibashi; Electrolytic Reduction of Oximes, II.*

The molecular weight of the amino-acid was determined by the cryoscopic method, water being used as the solvent.

Water	Substance	Mol. depression	Mol. weight	Degree of ionisation
18.5930 grm.	0.1540 grm.	0.201°	76.6	0.16
„	0.2302	0.292°	78.5	0.13
„	0.3137	0.387°	81.3	0.10

The degree of ionisation was calculated by the formula $\frac{M-M'}{M'}$ where M is the molecular weight calculated from $C_3H_7NO_2$ and M' that found experimentally.

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¹ Ibid. 32, 2451 (1899).