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# Electrolysis of Sodium Nitrite in the Presence of Ketones

## (Preparation of Ketoximes by the Electrolytic Method)

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Reduction of an aqueous mixture containing an aliphatic or cyclo-aliphatic ketone and an inorganic nitrite gave good yields of the ketoxime. Optimum conditions which gave yields of up to 60% are: pH 5.0, temperature, preferably below 15°C, nitrite concentration of about 10%, and a rotating zinc cathode. Ketones used include acetone, methyl ethyl ketone, cyclopentanone, and cyclohexanone. Acetophenone gave no oxime and the reasons are discussed.

### Introduction

The reduction of sodium nitrite with zinc in the presence of acetone has been reported to give an acetoxime in a high yield, 95%.<sup>1)</sup> A number of studies<sup>2)</sup> have been made for the preparation of ketoximes in the past, but no attempt has been made for the direct utilization of hydroxylamine prepared by the electrolytic method except the case reported by Hoshino et. al.<sup>3)</sup> who have prepared the cyclohexanone oxime by the reaction of cyclohexanone with hydroxylamine prepared by the electrolytic reduction of nitric acid.

In this paper, it is intended to discuss the direct preparation of ketoximes by the electrolytic reduction of sodium nitrite in the presence of ketones. According to the literature,<sup>4)</sup> in the electrolytic reduction of neutral or alkaline nitrite solution, the hydroxylamine was found in appreciable amounts, 16—70%, at Ni, Cu, Zn, Pt, and Hg cathodes. In general, low overvoltage cathode must be used in order to isolate the hydroxylamine during the electrolysis of nitrite and the solution must be either feebly acid or neutral. In addition, the formation of oximes can be affected by the acidity of the solution and it is believed that the best result can be obtained at pH 3—5.

The effect of various factors on the formation of oximes has been examined along these lines and the best yields were obtained using a rotating zinc cathode in a neutral solution. Carbon dioxide was passed through the solution during the electrolysis.

### Experimental

**Materials.** Sodium nitrite was a c.p. product obtained from Baker Chemical Co. (U.S.A.) Cyclohexanone, obtained from Eastman Kodak Co. (U.S.A.) was fractionated using an effective column, b.p. 153°C. Cyclopentanone, obtained from Reaction Products Inc. was used directly without further purification, b.p. 130—131°. Acetone, methyl ethyl ketone, and acetophenone were of analytical purity.

**Cathodes.** Platinum: Cylindrical gauze (100 sq. cm.) Nickel: Sheet (100 sq. cm.)

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Copper: Plate (100 sq. cm.) Zinc: Plate (100 sq. cm.) Lead: Plate (100 sq. cm.) Magnesium: Plate (100 sq. cm.) The rotating zinc cathode was also prepared using a zinc block (50 sq. cm.) mounted at the end of a brass rod which was held in a chuck of a variable speed motor and passed through the rubber stopper on the porous cup.

**Cell.** The anode was a sheet of lead (10×20 cm.) in the form of a cylinder around the cathode chamber which was an unglazed porcelain cylinder, 17 cm long and 7 cm in a diameter. (Coors Porecelain Co.)

**Technique.** The porous pot forming the cathode chamber contained 250 ml. of the electrolyte was surrounded by the lead anode and the whole placed in a breaker which was cooled in an ice-bath to keep the desired temperature. The carbon dioxide was passed through the catholyte during the electrolysis at a constant speed which was measured by a flow meter. A thermometer was also passed through the rubber stopper and the temperature was checked directly from the catholyte. Anolyte was a saturated sodium carbonate solution. (see Fig. 1)

**Isolation of Products.** After completing the electrolysis, the catholyte was transferred to a beaker and the excess of carbonate was neutralized with dil. hydrochloric acid at pH 5-7. Then the catholyte was heated on a steam-bath at 70° for 10 min. and kept overnight at room temperature. The solution was extracted with ether and dried over anhydrous calcium sulfate. After evaporating the ether, the residual solution was distilled under diminished pressure. In the case of acetone and methyl ethyl ketene, the ether and unreacted ketones were distilled off using a Vigreux column to prevent any loss of ketoximes during the ether evaporation. In the case of cyclohexanone, cyclopentanone and acetone the corresponding oximes were obtained in a solid form after distillation of the unchanged ketones.

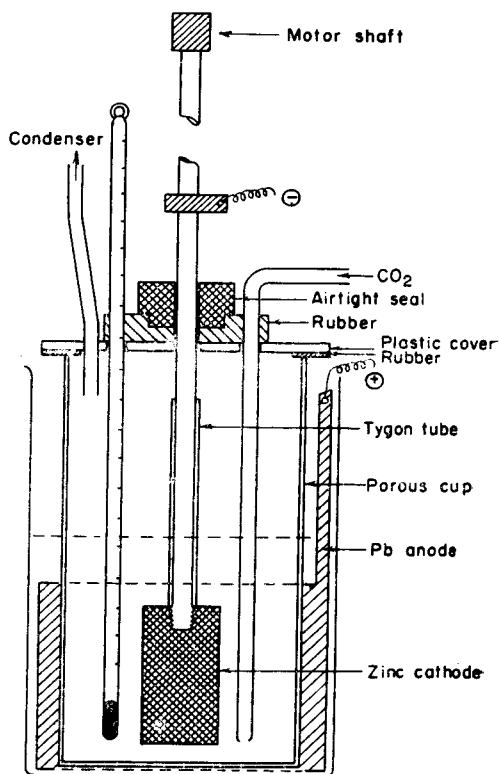


Fig. 1. Electrolysis Cell.

### Typical Experiments

(i) Cyclohexanone oxime. Cyclohexanone (19.6 g., 0.2 mole) in 250 ml. of water containing sodium nitrite (25 g., 0.36 mole) was electrolyzed in a separate cathode cell at a zinc cathode (100 sq. cm.). A current of 2.0 amp. (current density of 0.02 amp./sq.cm.) was passed for 10 hrs. (20 amp.hrs., theoretical for 19.6 g., cyclohexanone, 21.4 amp.hrs.) at

10–12°. The carbon dioxide supplied from dry-ice was also passed through the catholyte at a rate of 0.6 liter/min. during the electrolysis. When the electrolysis was completed, the catholyte was transferred to a beaker and neutralized with dil. hydrochloric acid at pH 5–7 and heated rapidly on the steam-bath at 70° for 10 min. The solution was kept at room temperature for 24 hrs. and extracted with ether. After evaporating the ether, the residue was distilled under diminished pressure.

A fraction (4.5 g.) coming over at 46–53°/15 mm.Hg was collected and was found that it contained mainly cyclohexanone together with small amounts of cyclohexanone (ca. 30%, estimated by an infrared spectra analysis.)

The residue (11.5 g.) from the distillation which solidified when cooled in ice was recrystallized from a petroleum ether (b.p. 30–65°). it melted at 90.0–90.5° and there was no depression on taking melting point measurement with an authentic sample. The yield of cyclohexanone oxime was 50.9%, (current efficiency, 54.6%) based on the theoretical yield from cyclohexanone, and the total recovery of the cyclohexanone was 74%.

(ii) Cyclopentanone oxime. Cyclopentanone (17 g., 0.2 mole) in 250 ml. of water containing sodium nitrite (25 g., 0.36 mole) was electrolyzed in a separate cell at a rotating zinc cathode (50 sq. cm.). A current of 1.5 amp. (current density of 0.03 amp./sq. cm.) was passed through the electrolyte for 11.3 hrs. (17 amp. hrs, theoretical for 17 g. cyclopentanone, 21.4 amp. hrs.) at 8–10°. The speed of rotation of the cathode was 2000 r.p.m. (measured by STROBATIC). The carbon dioxide was passed through the catholyte at a rate of 0.5 liter/min. during the electrolysis.

After completing the electrolysis, the catholyte was neutralized with dil. hydrochloric acid at pH 5–7 and then heated on a steam-bath at 70° for 10 min. The solution was kept at room temperature for 24 hrs. and extracted with ether. The ether was evaporated and the residual solution was distilled at a reduced pressure. A fraction (6.0 g.) coming over at 34–36.5°/20 mm. was collected and found to be mainly unchanged cyclopentanone together with small amounts of cyclopentanol (ca. 25%, estimated by an infrared spectra analysis.)

The residue (9.5 g.) from the distillation which solidified on cooling was recrystallized from petroleum ether (b.p. 30–65°), and m.p. 56.0–56.5°. There is no depression of melting point upon taking a mixed melting point with an authentic sample. The yield of cyclopentanone oxime was 48%, (current efficiency, 62.4%) based on the theoretical yield, and the total recovery of cyclopentanone was 81%.

(iii) Acetone oxime. Acetone (12 g., 0.2 mole) in 250 ml. of water containing sodium nitrite (25 g., 0.36 mole) was electrolyzed in a separate cell using a rotating zinc cathode (50 sq. cm.). A current of 1.5 amp. (current density of 0.03 amp./sq. cm.) was passed through the electrolyte for 10 hrs. (15 amp. hrs., theoretical for 12 g. acetone, 21.4 amp. hrs.) at 7–9°. The speed of rotation of the cathode was 2000 r.p.m. The carbon dioxide was also passed through the catholyte at a rate of 0.5 liter/min. during the electrolysis.

When the electrolysis was completed, the catholyte was neutralized with dil. hydrochloric acid at pH 5–7 and then heated on a steam-bath at 40° for 10 min. The solution was kept at room temperature in a stoppered flask for 24 hrs. and then extracted with

ether. The ether and unreacted acetone was distilled off very carefully using a Vigreux column to prevent any evaporation of the oxime. The residue (5.8 g.) which solidified when cooled in an ice was recrystallized from petroleum ether (b.p. 30—65°). It melted at 58—61°. The yield of acetone oxime was 39.7%, (current efficiency, 57.6%).

(iv) Methyl ethyl ketone oxime. Methyl ethyl ketone (14.5 g., 0.2 mole) in 250 ml. water containing sodium nitrite (25 g., 0.36 mole) was electrolyzed in a separate cell at a zinc cathode (100 sq.cm.). A current of 2.0 amp. (current density of 0.02 amp./sq.cm.) was passed through the electrolyte for 10 hrs. (20 amp.hrs., theoretical for 14.5 g. methyl ethyl ketone, 21.4 amp.hrs.) at 11—13°. The carbon dioxide was passed through the catholyte at a rate of 0.6 liter/min. during the electrolysis.

After completing the electrolysis, the catholyte was neutralized with dil. hydrochloric acid at pH 5—7 and then heated on a steam-bath rapidly at 60° for 10 min. The solution was kept at room temperature for 24 hrs. and extracted with ether. The ether and unchanged methyl ethyl ketone were distilled off using a Vigreux column and the residue was distilled under diminished pressure. A fraction (6.5 g.) coming over at 62—64/15 mm. was collected and was identified as methyl ketone oxime.

Anal.	Calc'd for C <sub>4</sub> H <sub>9</sub> ON	N, 16.09
	Found.	N, 16.15

The yield of methyl ethyl ketone oxime was 37.4%, (current efficiency, 40%).

(v) Acetophenone oxime. Acetophenone (25 g., 0.2 mole) was electrolyzed in a separate cell using a rotating zinc cathode (50 sq.cm.) A current of 1.5 amp. (current density of 0.03 amp./sq.cm.) was passed through the electrolyte for 10 hrs. (15 amp.hrs., theoretical for 24 g. acetophenone, 21.4 amp.hrs.) at 10—11°. The speed of rotation of the cathode was 2000 r.p.m. The carbon dioxide was also passed through the catholyte at a rate of 0.5 liter/min. during the electrolysis.

When the electrolysis was over, the catholyte was neutralized with dil. hydrochloric acid at pH 5—7 and heated on the steam-bath at 70° for 10 min. The solution was kept at room temperature for 24 hrs. and extracted with ether. After evaporating the ether, the residue was distilled under reduced pressure to give following fractions:

- 1) b.p. 80—83°/8 mm.Hg      4.8 g. Unchanged acetophenone.
- 2) b.p. 84—86°/8 mm.Hg      8.8 g.  $\alpha$ -Methyl phenylcarbinol.
- 3) residue.                      8.8 g.

Redistillation of fraction (2) gave a colorless liquid, b.p. 90—94°/15 mm.Hg. The residue from the distillation was redistilled at a reduced pressure and there obtained high boiling fractions (0.3 g.) coming over at 140—145°/2 mm.Hg. It solidified upon cooling, m.p. 118—120° and was identified as pinacol.

### Discussion of Results

As mentioned before, in the reduction of nitrite, Ni, Zn, Cu, Pt and Hg cathodes gave fairly good yields of hydroxylamine in a neutral or alkaline solution. It is of interest, in

this respect, to see the effect of cathode materials on the reduction of nitrite in regard to the formation of oxime. In the present study, Pt, Ni, Cu, Zn, Mg, and Pb metals were examined and it was found that only the zinc cathode gave a good yield of cyclohexanone oxime as well as other aliphatic ketone oximes. (Table I.)

Table I. Effect of Cathode Materials.

Catholyte: Cyclohexanone, 19.6 g. (0.2 mole), sodium nitrite, 25 g. (0.36 mole), water, 250 ml. Anolyte: Saturated sodium carbonate solution.  
Cathode: Pt, Ni, Cu, Pb, Zn and Hg. Anode: Lead sheet.  
Current density: 0.02 amp./sq.cm. Quantity of current: 20 amp.hrs.  
(Theory, 21.4 amp.hrs.) Flow of carbon dioxide: 0.6 liter/min.  
Temp.: 10–12°C.

Run No.	Cathode	Yield of cyclohexanone oxime <sup>a)</sup>			Recovered cyclohexanone (g)	Cyclohexanol <sup>b)</sup> (%)
		(g)	(%)	C.E. (%)		
1	Pt	1.5	6.6	7.0	10.8	trace
2	Ni	2.0	8.9	9.6	9.0	10
3	Cu	2.5	11.1	12.0	9.0	20
4	Pb	5.5	24.1	26.9	6.1	50
5	Zn	11.5	50.9	54.6	4.5	30
6	Mg	3.0	13.3	14.3	9.5	trace

a) M.p. 90–90.5°C (recrystallized from petroleum ether (b.p. 30–65°).

b) Amount estimated by the Infrared spectra analysis in the recovered cyclohexanone.

In the case of Pb cathode, a high overvoltage cathode, appreciable amount of cyclohexanol were obtained in the product showing that the reduction of ketone was also taking place under these conditions.

As is seen in Table II, when the concentration of nitrite is low, the reduction tends to go further to the attack of ketone group giving cyclohexanol even in the case of the zinc cathode. This fact shows that there are two competing reactions, that is, reduction

Table II. Effect of Concentration of Sodium Nitrite.

Catholyte: Cyclohexanone, 19.6 g., Sodium nitrite, 15, 20, 25, 30 and 45g.,  
Water: 250 ml. Anolyte: Sat. sodium carbonate solution.  
Cathode: Zinc (100 sq. cm.) Anode: Lead sheet.  
Current density: 0.02 amp./sq. cm.  
Quantity of current: 20 amp.hrs. (Theory, 21.4 amp.hrs.)  
Flow of carbon dioxide: 0.6 liter/min. Temp.: 10–12°.

Run No.	NaNO <sub>2</sub>		Yield of cyclohexanone oxime <sup>b)</sup>			Recovered cyclohexanone (g)	Cyclohexanol <sup>b)</sup> (%)
	(g)	(%)	(g)	(%)	C.E. (%)		
1	15	6	3.0	12.4	13.3	10.3	42
2	20	8	8.0	36.4	38.9	5.5	45
3	25	10	11.5	50.9	54.6	4.5	30
4	30	12	10.4	46.0	49.2	4.0	trace
5	45	18	7.5	33.2	35.5	6.0	trace

a) M.P. 88.5–89°C.

b) see Table I.

of the nitrite and the reduction of the ketone group under these conditions. On the other hand, if we use rather high concentration of nitrite, again, the formation of cyclohexanone oxime is decreased even though less cyclohexanol is obtained in the product. When the concentration of sodium nitrite is too high, there would be expected less possibility for the cyclohexanone to react with the hydroxylamine produced on the cathode surface and also greater possibility would be expected for the hydroxylamine to undergo further reduction to ammonia. This result suggests that there must be some proper ratio for the concentration of both species, sodium nitrite and cyclohexanone, for this reaction. The best result was obtained using a 10% solution of sodium nitrite (molar ratio of  $\text{NaNO}_2/\text{cyclohexanone}$  was 1.8) for the formation of cyclohexanone oxime. The results are shown in Table II and also Fig. 2.

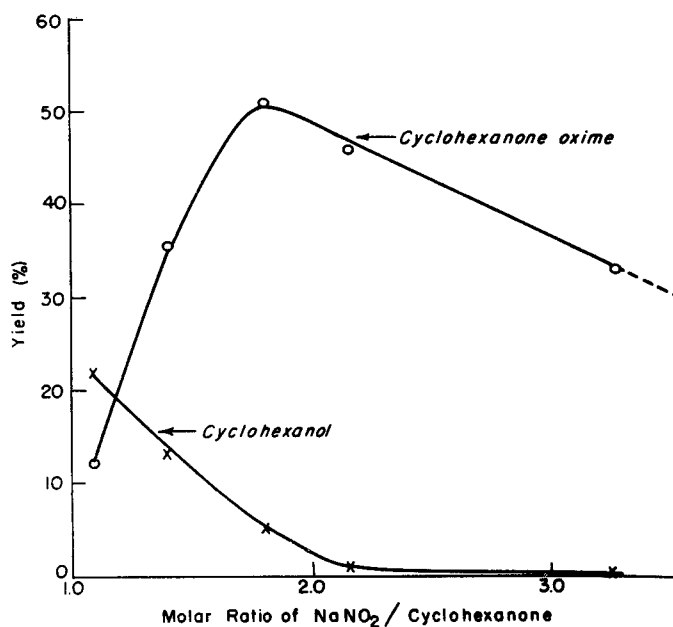


Fig. 2. Effect of Concentration of Sodium Nitrite.

The effect of current density on the formation of cyclohexanone oxime was not so great, but the best yield was attained using a 0.02 amp./sq. cm. rather than 0.01 or 0.03 amp./sq. cm. (see Table III).

The higher the temperature, the larger the quantity of cyclohexanol obtained under the same current density. (Table IV).

The study was further extended to the oximes of cyclopentanone, acetone, methyl ethyl ketone, and also acetophenone. As is seen in the experimental part, all aliphatic ketones gave fairly good yields of corresponding ketoximes. However, in the case of acetophenone, the result is quite different from those of aliphatic ketones. It was found that the main product from the acetophenone was  $\alpha$ -methyl phenylcarbinol<sup>5)</sup> rather than acetophenone oxime.

This result can be easily explained by the fact that acetophenone is a much better

depolarizer at a cathode than the nitrite under these conditions. This phenomenon was also in agreement with the polarographic study of both compounds.\*

The study was also made on the influence of the rotating cathode on the formation of oximes in the present experiment, and it was found that the best yields of oximes were obtained using a high speed rotating zinc cathode. The results are summarized in Table V.

Table III. Effect of Current Density.

Catholyte: Cyclohexanone, 19.6 g. (0.2 mole), sodium nitrite, 25 g. (0.36 mole), water, 250 ml. Anolyte: Sat. sodium carbonate solution.  
Cathode: Zinc sheet (100 sq. cm.) Anode: Lead sheet.  
Quantity of current: 20 amp. hrs. (Theory, 21.4 amp. hrs.)  
Flow of carbon dioxide: 0.6 liter/min. Temp.: 10–12°.

Run No.	Current density (amp./sq.cm.)	Yield of Cyclohexanone oxime <sup>a)</sup>			Recovered cyclohexanone (g)	Cyclohexanol <sup>b)</sup> (%)
		(g)	(%)	C.E. (%)		
1	0.01	9.0	40.0	42.8	6.0	30
2	0.02	11.5	50.9	54.6	4.5	30
3	0.03	9.8	43.4	46.4	8.0	45

a) M.P. 88.5–89°C.

b) see Table I.

Table IV. Effect of Temperature.

Catholyte: same as in Table III.  
Anolyte : "  
Cathode : Zinc sheet (100 sq. cm.) Anode: Lead sheet.  
Current density: 0.2 amp./sq. cm. Quantity of current: 20 amp. hrs.  
(Theory, 21.4 amp. hrs.) Flow of carbon dioxide: 0.6 liter/min.

Run No.	Temp. (°C)	Yield of cyclohexanone oxime <sup>a)</sup>			Recovered cyclohexanone (g)	Cyclohexanol <sup>b)</sup> (%)
		(g)	(%)	C.E. (%)		
1	10–12	11.5	50.9	54.6	4.5	30
2	40–45	7.8	34.5	37.0	7.0	43

a) M.P. 88.5–89°C.

b) see Table I.

Table V. Effect of Rotating Zinc Cathode.

Catholyte: 0.2 mole ketones in 250 ml. of water containing 25 g. sodium nitrite.  
Anolyte: Saturated sodium carbonate solution.  
Cathode: Rotating zinc cathode<sup>a)</sup> (50 sq. cm.) and Zinc sheet cathode (100 sq. cm.)  
Current density: 0.03 amp./sq. cm. Temp.: 10–15°C.

Ketone	Current efficiency of oxime formation (%)	
	Rotating cathode	Stationary cathode
Cyclohexanone	56	46
Cyclopentanone	62	54
Acetone	57	40
Methyl ethyl ketone	55	40

a) 2.5 cm in diameter, 6 cm long, speed of rotation, 2000 r.p.m.

\* Acetophenone was recorded to give half-wave potentials in neutral medium such as, –1.33 volt at pH 4.9 and –1.58 volt at pH 7.2, while sodium nitrite gave no reduction waves in the same medium. (Cf. A. G. Stromberg and L. M. Reinus, J. Gen. U. S. S. R., **16**, 1431 (1946); C. A. **41**, 5479 (1946).



### Conclusions

An attempt was made for the direct preparation of ketoximes by the electrolytic reduction of sodium nitrite in the presence of ketones.

The yield of ketoximes was found to be very sensitive to the condition of electrolysis as well as to the cathode materials.

Among the cathodes studied in the present study, on zinc cathode (preferably rotating zinc cathode) gave good yield of ketoximes.

Optimum conditions which gave fairly good yield of ketoximes are: pH 5.0, temperature below 15°C, nitrite concentration about 10%.

The following ketoximes were prepared using a rotating zinc cathode. Acetoxime (57%), Methyl ethyl ketone oxime (55%), Cyclopentanone oxime (62%), Cyclohexanone oxime (56%).

Acetophenone was found to give no oxime under the same condition and it gave mainly  $\alpha$ -methyl phenyl carbinol.

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