

Behaviour of oximes at a nickel black cathode

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1. Introduction

A nickel black cathode was successfully employed by Krishnan *et al.* [1] in the electroreduction of $-C\equiv N$. To assess the efficiency of this cathode in the reduction of $C=N$, the reduction of four oximes: benzophenone oxime, salicylaldoxime, β -furfuraldoxime and cyclohexanone oxime, are investigated in aqueous ethanolic hydrochloric acid and aqueous ethanolic $(NH_4)_2SO_4$ media and the results reported in this paper. The reductions yielded benzhydramine, salicylamine, furfurylamine and cyclohexylamine, respectively.

Generally, for simple oximes, the presence of a phenyl group or other negative groups favours reduction and the influence of substituents on the reductivity of oxime is reported to be phenyl $>$ H $>$ alkyl [2]. The influence of substituents in the electroreduction of four oximes at a nickel black cathode is also discussed in this paper.

2. Experimental details

Pure samples of four oximes were prepared [3, 4], and pure grade chemicals and redistilled rectified spirit were used.

Deposition of nickel black onto a graphite substrate of effective area 0.8 dm^2 was carried out from an aqueous solution (500 ml) of crystalline nickel sulphate (3.0 g) and ammonium sulphate (5.0 g) under the conditions given in literature [5].

2.1. Reduction in aqueous ethanolic acid medium

A solution of an oxime (except benzophenone oxime) (4.0 g) in aqueous ethanolic hydrochloric acid (500 ml, 1N, 30% alcohol) served as the catholyte. For solubility reasons, 1N rectified ethanolic hydrochloric acid was used for benzophenone oxime. The nickel black cathode (0.8 dm^2) was flanked on either side by two

ceramic diaphragms containing a graphite anode and aqueous hydrochloric acid (1N) anolyte. Provision was made to draw out Cl_2 from the anode chambers during electrolysis, through a Cl_2 trap connected to gentle suction. The catholyte was efficiently stirred during the reduction. Charge in excess of the theoretical was passed in order to obtain a high yield of the amine. All reductions were carried out at $30 \pm 2^\circ C$.

After electrolysis, the catholyte was distilled to near dryness under reduced pressure and it was ether extracted several times to remove the unreacted oxime. The residue was treated with 40% NaOH solution in ice cold conditions. The amine liberated was ether extracted, dried and characterized.

2.2. Reduction in an aqueous ethanolic ammonium sulphate medium

A solution of an oxime (except benzophenone oxime) (5.0 g) in a 4% solution of $(NH_4)_2SO_4$ in 30% aqueous ethanol (500 ml) served as the catholyte. For benzophenone oxime a 3% solution of $(NH_4)_2SO_4$ in 60% ethanol was used. The pH of the catholyte was kept at 8.0 by adding ammonia solution.

The nickel black cathode (0.8 dm^2) was flanked on either side by two ceramic diaphragms containing a Pb anode and a 5% aqueous sulphuric acid anolyte. No Cl_2 trap was needed in this experiment and other conditions were identical to those given above.

After electrolysis the catholyte was concentrated by distilling under pressure. The unreacted oxime was ether extracted. Solid sodium hydroxide was added to the residual liquid under ice cold conditions with stirring to liberate the amine. The amine was ether extracted, dried and characterized.

Benzophenone oxime yielded benzhydramine

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Table 1. Amine yield in acid medium

Current density ($A\ dm^{-2}$)	Benzophenone oxime			Salicylaldoxime			β -Furfuraldoxime			Cyclohexanone oxime		
	Cell voltage (V)	Amine yield (%)	C.E. (%)	Cell voltage (V)	Amine yield (%)	C.E. (%)	Cell voltage (V)	Amine yield (%)	C.E. (%)	Cell voltage (V)	Amine yield (%)	C.E. (%)
1.0	3.0	91.81	31.87	3.5	46.24	30.11	4.5	Black resinous mass	3.5	15.48	9.89	
3.0	4.0	79.20	27.40	4.5	40.36	26.32	7.0	Black resinous mass	3.0	11.90	7.60	
5.0	4.5	68.79	23.18	6.0	34.33	21.97	10.5	Black resinous mass	6.0	8.10	5.10	

C.E. is current efficiency.

of m.p. 33° C (Lit. 34° C); salicylaldoxime gave salicylamine of m.p. 124° C (Lit. 125° C); β -furfuraldoxime yielded furfurylamine of b.p. 145° C (Lit. 145° C); and cyclohexanone oxime produced cyclohexylamine of b.p. 132° C (Lit. 132–3° C).

3. Results and discussion

The results of the electroreductions at several current densities are presented in Tables 1 and 2.

A higher yield of amine is obtained at low current densities. Since nickel black is a low hydrogen over voltage electrode, the reduction at this electrode is believed to occur via adsorbed hydrogen atoms [1]. At higher current densities hydrogen evolution competes with the reduction thereby diminishing reduction efficiency.

Reduction of β -furfuraldoxime in aqueous ethanolic hydrochloric acid medium yielded a black resinous mass instead of the amine. Furan derivatives are known for their sensitivity towards acid and heat; since polarographic reduction data on this oxime in acid medium [6] is available, it is probable that the oxime underwent reduction

and the amine, thus formed, suffered resinification during working up of the catholyte. The fact that the catholyte remained colourless throughout the reduction but slowly turned brown and finally black during working up may support the above conclusion. The isolation of furfurylamine, though in low yield, from aqueous ethanolic ammonium sulphate medium confirms the occurrence of reduction of this oxime at the nickel black cathode.

The mechanism of oxime reduction is well known. Oxime consumes four electrons and yields amine. The reduction is shown to be pH dependent [2]. Most of the oximes are reducible in acid medium and only a few in alkaline medium. Polarographic reduction studies reveal that the protonated oxime is the reducible species in acid and neutral solution. Generally, for simple oximes the presence of a phenyl group or other negative substituent favours reduction. The influence of substituents on the reactivity of oxime is phenyl > H > alkyl [2]. Consequently, the order of reactivity of four oximes may be benzophenone oxime > salicylaldoxime > β -furfuraldoxime > cyclohexanone oxime.

Table 2. Amine yield in ammonium sulphate medium (pH = 8.0)

Current density ($A\ dm^{-2}$)	Benzophenone oxime			Salicylaldoxime			β -Furfuraldoxime			Cyclohexanone oxime		
	Cell voltage (V)	Amine yield (%)	C.E. (%)	Cell voltage (V)	Amine yield (%)	C.E. (%)	Cell voltage (V)	Amine yield (%)	C.E. (%)	Cell voltage (V)	Amine yield (%)	C.E. (%)
1.0	7.0	52.20	14.11	6.0	50.26	18.70	5.0	25.60	12.30	6.0	74.84	46.19
3.0	9.0	42.24	10.61	7.0	42.06	14.55	8.0	20.60	9.78	8.0	69.89	42.00
5.0	12.0	36.46	8.87	9.0	21.80	6.82	10.5	16.34	7.67	10.5	59.50	34.20

The yield of amine obtained from the four oximes in acid medium (see Table 1) is consistent with the expected behaviour. But in ethanolic $(\text{NH}_4)_2\text{SO}_4$ medium where the pH is maintained around 8, the proton activity will be necessarily low. Hence, one would expect a lower yield of amine from this medium than from the acid medium. The results shown in Table 2 are in agreement with the above conclusion except for cyclohexanone oxime.

In the case of cyclohexanone oxime, it is probable that the oxime is unusually sensitive to the nickel black cathode under the reduction conditions employed. One may expect a similar sensitivity of this oxime in an aqueous ethanolic hydrochloric acid medium also and the production of high yield of amine. However, its low reduction efficiency in acid medium may be traced to an appreciable hydrolysis of the oxime in the acid medium [7].

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