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NOTES

Electrochemical Reduction of α-Ketoglutaric Acid Oxime

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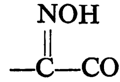
The electrochemical reduction behaviour of α-ketoglutaric acid oxime (α-KGO) has been studied at hanging mercury drop electrode (HMDE) and dropping mercury electrode (DME) in various supporting electrolytes using cyclic voltammetry, chronopotentiommetry and d.c. polarograpy. Mechanism of the reduction process was discussed and kinetic parameters evaluated and reported. The reduction product formed is shown to be glutamic acid.

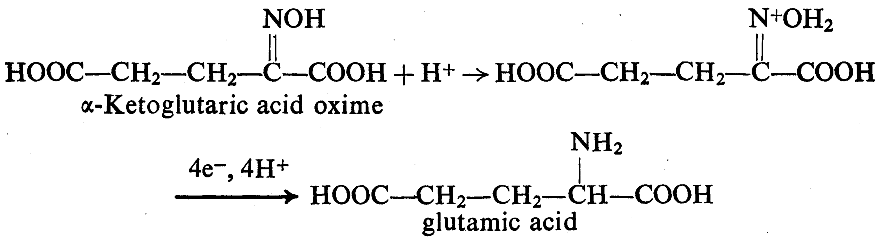
Among the azomethine derivatives oximes occupy an important place due to their wide spread application as analytical reagents[1], spectrophotometric reagents[2], in pharmacology[3] and as corrosion inhibitors[4]. Much electrochemical work has been done on oximes[5] and they are shown to get electrochemically reduced to amines[6]. It is worth investigating the feasibility of preparation of biologically important amino acids through the reduction of the corresponding α-keto acid oximes. We have not come across any reports connected with the electrochemical reductions and preparation of α-amino acids from their corresponding oximes.

In the present investigation, an attempt is made to study the reduction behaviour of the group  $-\overset{\overset{NOH}{\|}}{C}-COOH$ in the title compound as well as to get the reduction product by employing controlled potential electrolysis in various supporting electrolytes such as 0.1M $HC10_4$ and Clarks and Lubs buffer of pH 2.0 and acetate buffer of pH 4.0.

The title compound has been prepared by the procedures given in literature[7]. The purity of the compound was checked by the sharp melting point (153° C). The chemicals used were prepared from Analar grade without further purification. D.C. polarograms were recorded by 364 polarographic analyser (PARC) coupled with Kipp & Zonen x-t recorder. Cyclic voltammograms were recorded with Metrohm E506 polarecard coupled with E 6/2 VA Scanner, E 648 VA combistand, E 608 VA controller and digital electronic 2000 x-y/t recorder. Chronopotentiometric studies were performed with electroscan 30 (Beckman) apparatus. The DME of flow rate 2.5086 mg/sec and HMDE of area 0.03294 cm^2 were used as working electrodes. Reference electrode employed in the present work were saturated calomel electrode (SCE) for d.c. polarography, Ag/AgCl (s) Cl^- electrode and molybdenum electrode for chronopotentiometry.

α-Ketoglutaric acid oxime is found to undergo four electron reduction in all the supporting electrolytes studied through only one step in all the techniques employed. This step may be attributed to the reduction of oxime to amine. Intermediate imine formation is not found which was confirmed by the cyclicvoltammograms taken at higher sweep rates. In the supporting electrolytes of $pH > 4$ no reduction peak/wave is observed, due to the electron density decrease at the carbon atom, bearing nitrogen atom, because of the two carboxylate anion formation. The non-compliance of Tome's criterion and the log plot analysis indicated the irreversible nature of the reduction. This was also supported by the absence of anodic peak in cyclicvoltammetry, variation of peak potential with scan rate and the linear plots of E Vs. $\log\left(1 - \frac{t^{1/2}}{\tau^{1/2}}\right)$ with a slope larger than $0.05915/n$ where n is number of electrons, in the chronopotentiometry. The linear plots of i_p vs. $v^{1/2}$ not passing through origin in the buffer of 0.1M $HC10_4$ has indicated weak reactant adsorption in cyclicvoltammetric technique. The $E_{1/2}$ and E_p values are found to shift to more negative values with increase of the pH indicating participation of protons in the rate determining step. This was also confirmed from the linear plots of $E_{1/2}$ Vs. pH and E_p vs. pH. By employing millicoulometry technique[8], the number of electrons participated in the reduction processes was found to be four. The reduction product was identified as glutamic acid through controlled potential electrolysis in 0.1M $HC10_4$ by applying −0.70 V against SCE. The product was confirmed by paperchromotography. The factor $i_0\,\tau^{1/2}$ is seen to decrease with the current density i_0 and this variation of $i_0\,\tau^{1/2}$ with i may be interpreted as due to the protonation of the oxime group preceding the electrochemical reaction (CE Mechanism). This nature was also observed by the decrease of current function $(i_p/v^{1/2})$ with increase of the scan rate in cyclicvoltammetry in the buffer of pH 2.0 and 0.1M $HC10_4$.

Based on the above results the following reduction mechanism at DME as well as at HMDE may be proposed:



$$HOOC{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle NOH}{\|}}{C}{-}COOH + H^+ \rightarrow HOOC{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle N^+OH_2}{\|}}{C}{-}COOH$$

α-Ketoglutaric acid oxime

$$\xrightarrow{4e^-,\,4H^+} HOOC{-}CH_2{-}CH_2{-}\overset{\overset{\displaystyle NH_2}{|}}{C}H{-}COOH$$

glutamic acid

Controlled potential electrolysis is shown to be a good method for the preparation of glutamic acid from α-ketoglutaric acid oxime. Typical d.c. polarogram of α-ketoglutaric acid oxime before and after electrolysis is presented in Fig. 1. The heterogeneous rate constant values at different

TABLE 1

TYPICAL KINETIC DATA OF α-KETOGLUTARIC ACID OXIME

Concentration : 0.5 mM Applied current : 2.3 μA

Sweep Rate : 100mV S^{-1} Drop time : 3 Sec

Suporting electrolyte	Chronopotentiometry			Cyclivoltammetry			D. C. polarography		
	τ	D	$k^0_{f,h}$	$-E_p$	D	$k_f^0,_h$	$-E_{1/2}$	D	$k^0_{f,h}$
	Sec.	$cm^2\ s^{-2}$	$cm\ s^{-1}$	V	$cm^2\ s^{-1}$	$cm\ s^{-1}$	V	$cm^2\ s^{-1}$	$cm\ s^{-1}$
0.1 M HC10$_4$	7	1.216 $\times 10^{-6}$	6.940 $\times 10^{-15}$	0.27	2.310 $\times 10^{-7}$	1.670 $\times 10^{-5}$	0.564	3.168 $\times 10^{-6}$	3.180 $\times 10^{-7}$
Clarks and Lubs buffer pH—2.0	9	1.638 $\times 10^{-6}$	7.050 $\times 10^{-19}$	0.78	5.856 $\times 10^{-6}$	4.610 $\times 10^{-12}$	0.644	8.940 $\times 10^{-6}$	3.300 $\times 10^{-7}$
Acetate buffer pH—4.0	9	1.488 $\times 10^{-6}$	1.600 $\times 10^{-23}$		No wave		1.01	6.566 $\times 10^{-6}$	2.220 $\times 10^{-8}$

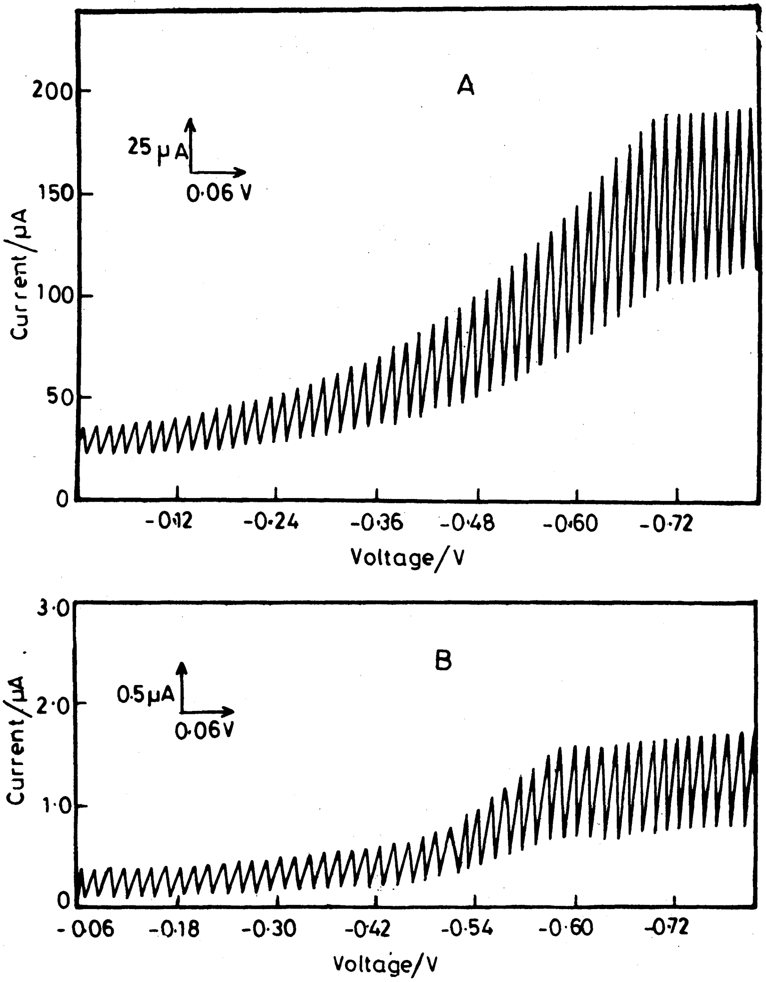


Fig 1. Typical d.c. polarograms of α-ketoglutaric acid oxime in 0.1M $HClO_4$ (A) before and (B) after electrolysis (12 hrs) at —0.70V. Drop time : 3 sec.

pH values are calculated[9] and reported in Table 1. The value of $K^{\circ}_{f,h}$ is found to decrease with increase of pH of the supporting electrolyte indicating that the electrode reaction becomes more and more irreversible with increase in pH. Diffusion coefficient values obtained by d.c. polarographic technique may be considered as more reliable compared to other techniques in view of the advantages associated with renewable nature of the DME.

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