# Xenic Acid: Reduction at the Dropping-Mercury Electrode

Abstract. *Xenic acid is reduced at the dropping-mercury electrode in a single step to xenon. The half-wave potential for the reduction of xenic acid changes from approximately — 0.10 to — 0.360 volt against a saturated* $Hg_2SO_4$*-Hg reference electrode in the* pH *range 4.60 to 8.00. The diffusion current varies linearly with concentration of xenic acid.*

Investigation of xenic acid reduction at the dropping mercury electrode was initiated with the hope of establishing whether xenic acid is reduced in steps with the formation of stable intermediate species of lower oxidation states or whether it is reduced directly to atomic xenon.

Aqueous solutions of xenic acid, $XeO_3 \cdot xH_2O$, may be obtained by the hydrolysis either of xenon tetrafluoride, $XeF_4$, or xenon hexafluoride, $XeF_6$, as has been described by Dudley *et al.* (*1*) and Williamson and Koch (*2*). Xenic acid is a very weak acid, comparable to orthotelluric acid, $H_6TeO_6$, and has an oxidation potential which is possibly as negative as periodic acid.

A Sargent model XXI recording polarograph and an H-polarographic cell equipped with a thermostat were used for the polarographic study. Buffered or unbuffered 0.1*M* potassium sulfate solution was used as the supporting electrolyte and the concentration of the xenic acid was adjusted in the range $4 \times 10^{-5}$ to $2.0 \times 10^{-4}M$. Nitrogen, purified by passing it over hot copper turnings, was bubbled through the solutions to deaerate them.

This process was carried out in the absence of mercury to prevent the reduction of the xenic acid, and a polarogram was made immediately. A typical polarogram of xenic acid in the potassium sulfate electrolyte is shown in Fig. 1, and the results are summarized in Table 1.

In the potassium sulfate electrolyte, xenic acid forms a well-defined cathodic wave. This wave is preceded by a very small anodic wave which eventually coalesces with the cathodic wave as the concentration of xenic acid increases. Well-defined anodic waves preceding the reduction of periodate and of orthotellurate have been reported by Jensovsky (*3*), and Jaselskis and Lanese (*4*), respectively. Thus it appears that xenic acid, in the first step, oxidizes mercury and forms an unstable and slightly soluble mercurous xenate. The cathodic wave corresponds to a six electron reduction process. The number of electrons taking part in the reduction process has been calculated by comparing the periodate reduction to iodic acid at *p*H 6.4. For the same concentration, the reduction wave for xenic acid is three times greater than that of periodate, which has been established to be a two electron reduction. The half-wave potential $E_{1/2}$, becomes more negative with increasing *p*H, as would be expected for the reduction reaction

$$XeO_3 \cdot xH_2O + 6H^+ + 6e \longrightarrow Xe + (3 + x)H_2O$$

For a reversible process the change of *p*H by one unit should produce a shift of the half-wave potential by 0.06 volt. However, this is not the case, as shown in Table 1, indicating that the reduction process is irreversible.

The cathodic current is proportional to the square root of the mercury head and changes approximately by 2 percent per degree Celsius indicating that the reduction process is primarily diffusion controlled.

That the cathodic wave is directly proportional to the concentration of xenic acid present, in the range $4 \times 10^{-5}$ to $2 \times 10^{-4}M$ is supported by the constancy of $i/Cm^{2/3}t^{1/6}$, where $i$ is the diffusion current, $C$ is the concentration of xenic acid, $m$ is the mass flow of mercury in milligrams per second, and $t$ is the drop time in seconds.

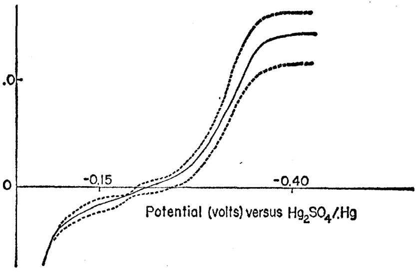

Fig. 1. Polarogram of $8.24 \times 10^{-5}M$ xenic acid in 0.1*M* potassium sulfate. Dashed lines, maximum and minimum current; solid line, average current.

Table 1. Polarographic characteristics of xenic acid.

| Conc. of xenic acid ($M \times 10^5$) | *p*H of supporting electrolyte | $E_{1/2}$ volt against $Hg_2SO_4$-Hg | Diffusion current (μamp) | $i/Cm^{2/3}t^{1/6} \times 10^1$ |
|---|---|---|---|---|
| 4.12 | 6.4* | − 0.29 | 0.62 | 0.993 |
| 8.24 | 6.4* | − 0.32 | 1.38 | 1.105 |
| 12.36 | 6.4* | − 0.32 | 2.04 | 1.090 |
| 16.48 | 6.4* | − 0.32 | 2.70 | 1.082 |
| 20.60 | 6.4* | − 0.32 | 3.35 | 1.074 |
| 8.24 | 4.6† | − 0.10 | 1.30 | 1.042 |
| 8.24 | 5.3† | − 0.24 | 1.36 | 1.090 |
| 8.24 | 8.0‡ | − 0.36 | 1.40 | 1.021 |

* Unbuffered 0.10*M* potassium sulfate solution used as the supporting electrolyte. † Supporting electrolyte of 0.1*M* potassium sulfate and 0.02*M* acetic acid, with the *p*H adjusted by the addition of KOH. ‡ Supporting electrolyte of 0.1*M* potassium sulfate and 0.2*M* $NaH_2PO_4$ with the *p*H adjusted by the addition of KOH.

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### References and Notes

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5. I thank Messrs. Malm and Appelman from the Argonne National Laboratories for the sample of xenic acid.

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# Hydrogen Energy Levels: Perturbation Caused by Proton Structure

Abstract. *The shifts in the lowest electronic energy levels of the hydrogen atom caused by the extended charge distribution of the proton have been calculated and found to be of the order of the unexplained portion of the Lamb shift for these levels.*

The analysis of high-energy electron scattering from hydrogen has shown that the proton is not a point charge (*1*). Satisfactory agreement with the experimental data is obtained by representing the proton as a spherically symmetric cloud of charge whose density is an exponentially decreasing function of the radial distance from its center and whose radius (root mean square) is approximately $0.80 \times 10^{-13}$ cm. Such a charge-density distribution, suitably normalized, is given by the equation

$$\rho(r) = (e\alpha^3/8\pi) \exp(-\alpha r) \quad (1)$$

where $\rho$ is the charge density, $r$ is the radial coordinate, $e$ is the electronic charge, and $\alpha = 4.32 \times 10^{13}$ cm$^{-1}$.