POLAROGRAPHIC STUDY OF SOME BISAMINATED BENZOQUINONES

D.W. Cameron,[*] R.G.F. Giles,[†] and M.H. Pay[†]

[*]Department of Organic Chemistry, University of Melbourne, Australia

[†]Department of Chemistry, University of Cape Town, South Africa

Empirical data obtained from the [1]H n.m.r. spectra of a series of bisaminated benzoquinones suggest that the half wave potentials of the compounds investigated would be expected to alter on changing the nature of the amino substituents.[1]

Accordingly, the half wave potentials of the compounds shown in the Table were measured at various pH values.   The $E^O_{\frac{1}{2}}$ and $\Delta E^O_{\frac{1}{2}}$ values $[\Delta E^O_{\frac{1}{2}} = E^O_{\frac{1}{2}}(A) - E^O_{\frac{1}{2}}(H)]$ obtained at pH 7 are indicated.   From both the Table and the Figure it is seen that these values increase in the order monomethylamino < pyrrolidino ≮ azetidino < dimethylamino < piperidino < aziridino, this indicating a corresponding decreasing resistance to reduction.

The changes in the slopes of some of the curves as the pH is lowered indicate protonation of the reduced species in more acid media.   The aziridino compound could not be studied in acid (HCl) solution as it undergoes ring-opening to give 2,5-bis (2-chloroethylamino)-1,4-benzoquinone,[2] a change which could be followed polarographically at pH values just below 7 by the slow disappearance of the original wave and the appearance of a new wave whose half wave potential is 0.275v. more negative.
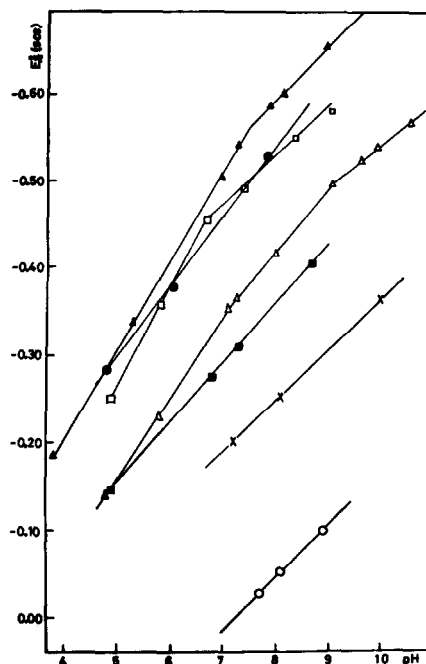
The relative order of the $E^O_{\frac{1}{2}}$ values quoted above is in qualitative agreement with that obtained from the spectroscopic data of the preceding communication.   Further work on related systems is currently in progress.
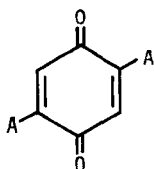
FIGURE

Variation of $E^O_{\frac{1}{2}}$(sce) with pH, for substituted quinones.

TABLE*

A	$E^O_{\frac{1}{2}}$(sce)	$\Delta E^O_{\frac{1}{2}}$	Legend for figure
H	+0.015		o
aziridino	-0.184	-0.199	x
azetidino	-0.448	-0.463	●
pyrrolidino	-0.466	-0.481	▢
piperidino	-0.284	-0.299	◼
monomethylamino	-0.495	-0.510	▲
dimethylamino	-0.331	-0.346	Δ

*Measured in Britton-Robinson buffer at pH 7.00

REFERENCES

1.   See preceding communication.

2.   I. Baxter, D.W. Cameron, and R.G.F. Giles, J. Chem. Soc. (C), 1969, 1325.