

SHORT COMMUNICATIONS

A.C. WAVES AND D.C. POLAROGRAPHIC MAXIMA*

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It is well known that under some conditions, the D.C. polarographic step of nitrobenzene shows a maximum. Here, it is shown that the nature of the corresponding A.C. wave depends on whether or not such a maximum is present.

For instance, in "Universal" buffer (Prideaux and Ward 1924) of pH 1.8, the D.C. polarogram shows two steps, the first, corresponding to a four-electron reduction of nitrobenzene to phenylhydroxylamine, and the second, to a two-electron reduction of the latter to aniline (cf., for example, Seagers and Elving

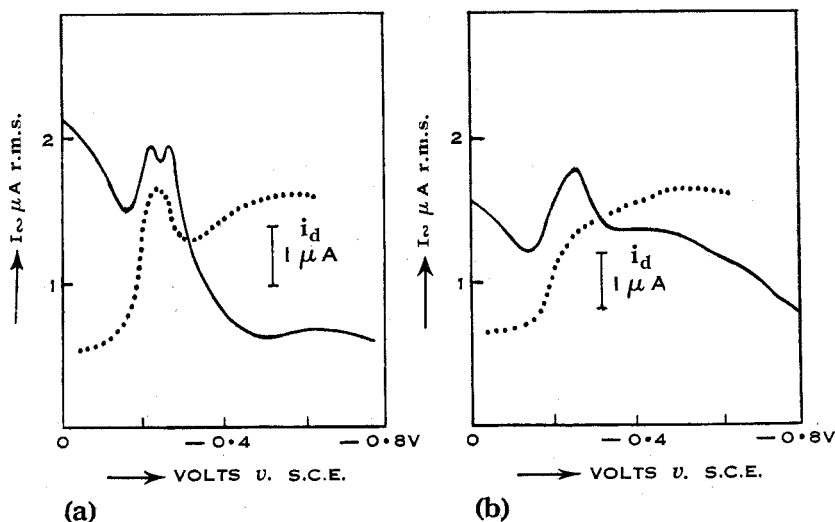


Fig. 1.—A.C. (—) and D.C. (...) polarograms of nitrobenzene, $2 \times 10^{-3}M$.

(a) In "Universal" buffer pH 1.8.

(b) In "Universal" buffer pH 1.8 + 0.5M potassium nitrate.

1951); the first step has a maximum. The A.C. curve shows two peaks corresponding in potential to the first D.C. step (Fig. 1 (a)). When the solution contains 0.5M potassium nitrate in addition to the buffer, the D.C. maximum is suppressed and the corresponding A.C. curve (Fig. 1 (b)) appears to have only a single peak in the region of the first D.C. step. On close examination, however, also this wave is shown to be a composite one (see below).

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At pH 7.3, with low concentrations of nitrobenzene in "Universal" buffer, no maximum is present on the D.C. polarogram and the A.C. wave is well defined. At higher concentrations a maximum appears on the D.C. step, but the A.C. wave is not distorted; however, it increases in height far more than would be expected. Thus for an increase in concentration of nitrobenzene from 10^{-4}M to $3 \times 10^{-4}\text{M}$, the magnitude of the D.C. diffusion current increases to three times its former value, while the A.C. wave increases in height by about five times (Fig. 2).

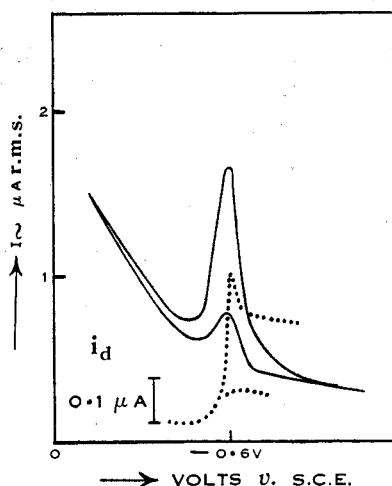


Fig. 2.—A.C. (—) and D.C. (...) polarograms of nitrobenzene in "Universal" buffer pH 7.3. Lower curves 10^{-4}M , upper curve $3 \times 10^{-4}\text{M}$.

Summarizing

The process responsible for the appearance of a maximum on the D.C. polarographic step of nitrobenzene also gives rise to an increase in the alternating current. This increase might appear as a separate peak on the A.C. curve (as at pH 1.8, see Fig. 1) or the current increase might occur at the same potential as the main A.C. wave, thus adding to its height (as at pH 7.3, see Fig. 2).

Even when no D.C. maximum is present, the A.C. waves of nitrobenzene appear, on close examination, to be composite; they show a kink which, though small, is invariably present (Fig. 3). This is best seen when smaller alternating voltages than the usual 15 mV r.m.s. are used, and when readings are taken at small intervals of applied direct potential (5 mV or less).

This kink may be due to:

- (i) An incipient maximum; that is, even where no maximum is visible on the D.C. step, the process which gives rise to maxima may nevertheless be proceeding, albeit to a minor extent.
- (ii) A combined polarographic-tensammetric process; in other words, the A.C. wave may in fact consist of two waves, the one a result of the reduction process and the other brought about by a concomitant

adsorption process. Such combined processes have been discussed in detail elsewhere (Breyer, Bauer, and Hacobian 1954).

- (iii) A reduction process occurring in more than one step, since the overall transfer of four electrons is involved. Thus the potential of the kink and the peak potential of the main A.C. wave might correspond to different stages in the reduction of nitrobenzene to phenylhydroxylamine.

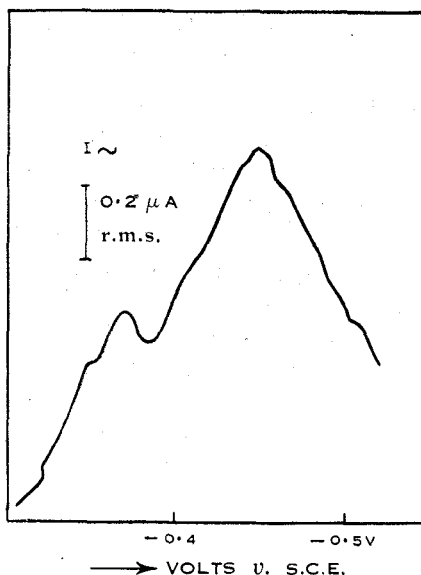


Fig. 3.—A.C. wave of 4×10^{-4} M nitrobenzene at pH 4.9. Superposed alternating voltage 5 mV r.m.s.

Possibilities (i) and (ii) obviously may be correlated with the observation reported here, namely, the production of an A.C. peak by the process which gives rise to D.C. maxima. The third possibility seems of great theoretical interest, since it would supply information about the mechanism of the particular reduction process.

Further experimental work is needed to decide which of the proposed hypotheses is valid.

References

- BREYER, B., BAUER, H. H., and HACOBIAN, S. (1954).—*Aust. J. Chem.* **8**: 312.
PRIDEAUX, E. B. R., and WARD, A. T. (1924).—*J. Chem. Soc.* **125**: 426.
SEAGERS, W. J., and ELVING, P. J. (1951).—*Proc. 1st Int. Congr. Polarography Prague* **1**: 281.