681. *Polarographic Reduction Half-wave Potentials of Some Phosphonic Acids.*

By Gennady M. Kosolapoff and Charles J. Jenkins, tert.

Polarographic reduction half-wave potentials were determined for nine nitro-substituted phenylphosphonic acids. Polarographic reduction with a dropping-mercury electrode could not be effected for *o*- and *p*-bromo-, *o*-chloro-, or 3-amino-4-bromo-phenylphosphonic acid.

Much work has been reported on polarographic reduction of organic compounds on a dropping-mercury electrode, but none for organophosphorus compounds. An examination of this class of compound was warranted for theoretical reasons and because the data might be utilised for electrolytic syntheses.

The nearest analogue that has been subjected to polarographic reduction is *m*-nitrobenzenesulphonic acid;[1] in buffers ranging from acidic to pH 8 this acid yields one polarographic wave whose half-wave potential moves steadily to more negative values with increase of pH; at pH 8—12 it gives two waves, the first following the pattern set by the single wave described above, whilst the second wave tends to lower the negative magnitude of its half-wave potential with increase of pH. The data reported also indicated the irreversibility of the reduction both by the form of the curves and by the fractional electron requirement calculated by the conventional route.

---

[1] Korschunov, Vertyulina, and Malyergina, *J. Gen. Chem.* (*U.S.S.R.*), 1955, **25**, 261.

With this background, we felt that polarographic reduction of nitrophenylphosphonic acids should be possible and this proved justified. We expected that halogen-substituted phosphonic acid would also be reducible on a dropping-mercury electrode, for halogenobenzoic acids are; but it is known that halogenophenylphosphonic acids can be readily dehalogenated by catalytic hydrogenation under mild conditions.[2] However, *o*- and *p*-bromo-, *o*-chloro-, and 3-amino-4-bromo-phenylphosphonic acid were not reduced on the dropping-mercury electrode in buffer solutions with pH 10 or pH 2·15. In these cases the curve was that obtained from the buffer alone. It is possible to rationalise this failure by regarding the electron-withdrawing effect of the phosphonic acid group as being sufficiently strong as to prevent the rupture of the carbon–halogen bond in any of the three isomeric positions in the phenyl ring.

TABLE 1. *Substituted phenylphosphonic acids.*

No.	Subst.	$-E_{1/2}$ (first wave)			$-E_{1/2}$ (second wave)
		pH 2·3	6·9	10·0	pH 10·0
1	2-Br-4-NO_2	0·195	0·544	0·687	1·389
2	4-Cl-3-NO_2	0·126	0·638	0·738	—
3	4-HO-3-NO_2	0·211	0·604	0·750	1·571
4	4-MeO-3-NO_2	0·255	0·668	0·836	—
5	3-Br-2-NO_2	0·217	0·648	0·695	1·083
6	*o*-NO_2	0·206	0·549	0·73	0·91
7	*m*-NO_2	0·230	0·639	0·773	—
8	*p*-NO_2	0·244	0·629	0·747	1·483
9	4-Nitrobenzylphosphonic acid	0·254	0·557	0·782	1·60

The polarograms of the various nitrophenylphosphonic acids were obtained in each instance at pH 2·3, 6·9, and 10·0, in order to secure data for acidic, neutral, and basic media, and to compare the resulting values with the results secured for the nitrophenylsulphonic acid.[1] The results are in Table 1. It is evident that the polarographic reduction of these acids in neutral or acidic media results in a single polarographic wave. In alkaline media, however, six of the compounds showed a second polarographic reduction wave, whilst three showed but one wave. The trend of the values of the half-wave potential of the first wave with variation of pH is invariably toward increasing negative values of the reduction potential, which agrees with the results for the sulphonic acid analogue.[1] Nevertheless, it is curious that the *m*-nitrophenylphosphonic acid displayed but one reduction wave in alkaline media, unlike its sulphonic analogue which gave two.

The relative ease of reduction of the mononitrophenylphosphonic acids, varies with alteration of the pH of the medium: in acid the order of increasing difficulty is *o*-, *m*-, *p*-; in neutral solution it is *o*-, *p*-, *m*-; in alkaline solution it becomes *o*-, *p*-, *m*-. The results indicate the greater difficulty of polarographic reduction of the nitrophenylphosphonic acids in comparison with the nitrobenzoic acids.[3]

EXPERIMENTAL

The polarograms were taken by a manually operated polarograph (Fisher Elecdropode), with the polarographic cell immersed in a thermostat at 25·0° ± 0·01°.

The phosphonic acids, prepared by conventional methods, were reduced in 0·002M-solutions containing 0·01% of gelatin for the (at least partial) suppression of maxima. Lower concentrations of gelatin were tried without success. We also failed to suppress maxima by employing a rotating " hoe." [4]

The buffer solutions consisted of citric acid–disodium hydrogen phosphate for pH 2·3, mono- and di-sodium phosphate for pH 6·9, and glycine–sodium chloride–sodium hydroxide or boric acid–potassium chloride–sodium hydroxide for pH 10·0. The decomposition potentials of these were, respectively, −0·80 v for pH 2·3, −1·5 v for pH 6·9, and −1·8 v for pH 10·0 (referred to a saturated calomel electrode).

[2] Freeman and Doak, *J. Org. Chem.*, 1956, **21**, 238.

[3] Kolthoff and Lingane, "Polarography," Interscience Publ., Inc., New York, 2nd edn., Vol. I, p. 754.

[4] Skobeta and Kavetskii, *Zavodskaya Lab.*, 1949, **15**, 1299.

The capillary characteristics were:

Drop time (sec. per drop)	2·992	3·135	3·260	3·363	3·540	3·694	3·880	4·097
Capillary const. ($C = m^{2/3}t^{1/6}$)	2·277	2·222	2·179	2·141	2·096	2·046	1·996	1·936

Table 2 lists the values of the diffusion current, as microamp. The second wave obtained for six of the acids in alkaline solution was too diffuse in its appearance to permit a reasonable estimate of the diffusion current. The numbering of the acids in Table 2 corresponds to that in Table 1.

TABLE 2.

No.	pH 2·3	6·9	10·0	10·0 (second wave)	No.	pH 2·3	6·9	10·0	10·0 (second wave)
1	5·61	3·53	1·4	—	6	5·73	5·49	2·5	3
2	5·31	4·37	1·3	—	7	6·30	4·21	1·3	—
3	5·64	3·47	0·22	5	8	5·81	3·38	1·3	3
4	5·61	3·38	1·2	—	9	5·98	4·42	2·1	3
5	5·60	4·30	1·9	2					

The solutions used were freshly prepared and the pH of each was checked potentiometrically before use. It was noted that the solutions of the nitrophenylphosphonic acids in the above buffers, with added gelatin, readily develop bacterial cultures in contact with air for >1 day under local conditions.

The estimation of the half-wave potentials was performed graphically by determination of half the ordinate distance between the initial and the final current–voltage curves. Some of the half-wave potentials were also estimated by differential plotting. The results agreed with each other well within 0·003 v.

ROSS CHEMICAL LABORATORY, ALABAMA POLYTECHNIC INSTITUTE,
AUBURN, ALABAMA, U.S.A.

[*Received, March 28th,* 1957.]