

POLAROGRAPHIC REDUCTION OF BENZOATE IN ACETONITRILE

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ABSTRACT

The polarographic wave observed for acetonitrile solutions of benzoic acid is due to reduction of the acid proton; the apparent diffusion current constant for the wave increases with concentration of benzoic acid as expected for the reduction of the acidic proton of a slightly dissociated acid. No wave was observed for ethyl benzoate.

The situation in respect to the electrochemical reduction of benzoic acid and the benzoate functionality at the dropping mercury electrode is not entirely clear. The reduction wave observed for benzoic acid in unbuffered aqueous solution would seem to be due to the reduction of hydrogen ion; the acid is not reduced in buffered aqueous media [1]. On the other hand, there seems to be some uncertainty in the literature (cf. below) due to the work of Stackelberg and Stracke [2], who apparently presented evidence for the reduction of benzoic acid in 75% dioxane, which was 0.05 M in Et_4NBr . In the latter medium, benzoic acid itself gave two waves (Table 1), tetraethylammonium benzoate also gave two waves, but ethyl benzoate gave only one wave. Stackelberg and Stracke wanted to assign the first benzoic acid wave to a hydrogen-ion reduction but were deterred by the presence of the wave in the tetraethylammonium salt. The possible presence of free benzoic acid in the salt and ester or its formation during test solution preparation was apparently not considered. In earlier work, Wawzonek and co-workers [3] had referred to the reduction of ethyl benzoate in 50% dioxane solution (0.1 M in $n\text{-Bu}_4\text{NI}$) ($E_{1/2} = -2.18$ v. vs. S.C.E.; $i_d/C = 7.62$) and had implied that benzoic acid might be reduced ($E_{1/2} = -1.87$ v. vs. S.C.E.; $i_d/C = 2.12$).

The implied polarographic reduction of the benzoate functionality, apparently based on the work of Stackelberg and Stracke, is indicated in several standard works, e.g., references [4], [5] and [6]. The first

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listed reference [4], which indicates an iodide instead of the bromide background electrolyte for the Stackelberg-Stracke data, also lists data for the reduction in 0.1 M tetra-*n*-butylammonium iodide in 50% dioxane of benzoic acid ($E_{1/2} = -1.87$ v.; $i_d/C = 2.12$) and of ethyl benzoate (-2.18; 7.62) (the source is not indicated, but is apparently reference [3]).

TABLE I

Polarographic Reduction of Benzoic Acid and Related Species in 75% Dioxane^a

Compound		$E_{1/2}^b$ v.	i_d/C $\mu\text{a./mM}$	I^c
Benzoic Acid	I	-1.94	1.1	1.9
	II	-2.46	1.7	3.3
Et ₄ N Benzoate	I	-1.98	1.1 - 0.9 ^d	1.9 - 1.6
	II	-2.38	2.9 - 2.7 ^d	5.6 - 5.2
Ethyl Benzoate		-2.14	3.5 - 2.7 ^d	6.1 - 4.7

a. Data of Stackelberg and Stracke [2]. Background electrolyte: 0.05 M Et₄NBr.

b. Reported as vs. aqueous S. C. E. and corrected for iR drop; the reference electrode used was a mercury pool, which had a potential of -0.19 v. vs. aqueous S. C. E.

c. $I = i_d/Cm^{2/3}t^{1/6}$; calculated from $m^{2/3}t^{1/6}$ values (0.58 at -2.0 v. and 0.46 at -2.6 v.) given in original paper.

d. Concentration-dependent.

From the large-scale electrolysis of aromatic carboxylic acids and their esters, including benzoic acid and ethyl benzoate, in highly acidic aqueous ethanolic solution, it was concluded that at lead cathodes the carboxyl group is selectively reduced to alcohol or ether, while at platinized platinum the phenyl group is reduced to cyclohexyl [7].

Consequently, it was decided to investigate the benzoate reduction in acetonitrile solution, which was 0.1 M in Et₄NClO₄. Coetzee and Kolthoff [8] reported a half-wave potential of -2.1 v. vs. S. C. E. and a diffusion current constant of 1.95 for a 1 mM solution of benzoic acid in acetonitrile, which was also 0.1 M in Et₄NClO₄.

Experimental

Benzoic acid was a U. S. National Bureau of Standards standard sample; ethyl benzoate was Eastman white label grade; acetonitrile (Burdick and Jackson Laboratories) had been purified by distillation in glass; tetraethylammonium perchlorate (Eastman white label grade) was repeatedly recrystallized from benzene-acetonitrile mixture and polarographically checked before use. Nitrogen used for purging solutions of oxygen was suitably purified and equilibrated.

A Sargent Model XXI Polarograph was used in conjunction with an operational amplifier-based three-electrode system [9], which corrected for the solution resistance of about 3 kilohms. The potential settings of the Polarograph were checked potentiometrically.

A jacketed three-compartment cell was used; the middle compartment contained the test solution and the D. M. E.; the other two compartments contained a platinum counter electrode in background solution and the silver-silver nitrate reference electrode (Ag/AgNO_3 , 0.1 M in acetonitrile), respectively. Temperature of observation was 25°C.

Characteristics of the D. M. E. in the background solution (0.1 M Et_4NClO_4 in acetonitrile) were as follows: $m = 0.86 \text{ mg. sec.}^{-1}$ at the mercury height of 50 cm. and $t = 2.81 \text{ sec.}$ at -2.2 v. ($m^{2/3}t^{1/6} = 1.07 \text{ mg}^{2/3} \text{ sec.}^{-1/2}$).

Potentials cited are contrasted with the Ag/AgNO_3 (0.1 M in acetonitrile) electrode, which is stated [10] to have a potential of +0.337 v. vs. the aqueous S. C. E. (including the liquid junction potential). The decomposition potential of the background solution, i. e., the potential at which the current reaches a magnitude of 1 $\mu\text{a.}$, is -2.44 v. vs. the silver reference electrode used.

Results and Discussion

Solutions of benzoic acid gave well-defined curves, whose characteristics are summarized in Table II.

TABLE II

Polarographic Reduction of Benzoic Acid in Acetonitrile^a

Concn. mM	$E_{1/2}$, vs.		i_1/C $\mu\text{a.}/\text{mM}$	I^c
	$\text{Ag}/\text{AgNO}_3^b$ v.	S. C. E. v.		
0.26	-2.21	-1.87	1.29	1.21
0.51	-2.21	-1.87	1.67	1.56
0.76	-2.19	-1.85	1.69	1.58
0.99	-2.19	-1.85	1.75	1.64
>1.5	(rounded maximum)			

a. Background electrolyte: 0.1 M Et_4NClO_4

b. Ag/AgNO_3 , 0.1 M, in acetonitrile, which is stated to have a potential of +0.337 v. vs. aqueous S. C. E.

c. $I = i_1/Cm^{2/3}t^{1/6}$

Ethyl benzoate (concentration of 1 to 3 mM) did not give a reduction wave in acetonitrile. If the reduction of benzoic acid involved a portion of the molecules other than the acid proton, one would normally expect the ester to be more readily reduced. A possible exception would involve the situation where tautomerism involving a readily migratory proton produces a reducible or more readily reducible function; however, this situation is quite unlikely in the case of benzoic acid.

Consequently, the one wave observed for acetonitrile solution of benzoic acid may be safely attributed to the reduction of the acid proton and not to a reduction of the carboxyl group or aromatic ring.

The diffusion current constants observed in the present study (Table II) are compatible with the notion of a hydrogen ion reduction being the cause

of the wave. If a one-electron process in aqueous solution is assumed to have a diffusion current constant value of 2, which is of the magnitude found for many organic and inorganic reductions, a one-electron process in acetonitrile would be expected to have a diffusion current constant value of about 3, since the constant is inversely proportional to the square root of the viscosity of the solvent (viscosities: water, 0.894; acetonitrile, 0.345); actually, Kolthoff and Coetzee [8] did find a value of 3.04 for solutions of perchloric acid in acetonitrile, in agreement with conductivity data. The values of the diffusion current constant in Table II are obviously too small for an ordinary one-electron process. However, the limiting current-concentration ratio (as would also be true of the corresponding diffusion current constant value) for organic acids in aqueous solution (presumably due to proton reduction) is known to decrease with decreasing dissociation constant of the acids [4]. If this tendency is also maintained in variation of solvent for a given acid, as seems reasonable, the magnitude of the diffusion current constant values in Table II for benzoic acid is comparable to that expected for a one-electron reduction of the acid proton, since the dissociation of the acid would be appreciably suppressed in acetonitrile (pK_a of benzoic acid is 4.2 in water and 12.0 in acetonitrile [11]). The increase in diffusion current constant with acid concentration is also compatible with acid proton reduction being involved. Coetzee and Kolthoff [8] observed a diffusion current constant of 1.95 for 1 mM benzoic acid in acetonitrile (cf. subsequent comment).

It is quite probable that the first benzoic acid wave reported by Stackelberg and Stracke [2] ($E_{1/2} = -1.94$ v. vs. S.C.E.) corresponds to the benzoic acid wave observed in the present study ($E_{1/2} = -1.87$ v. vs. S.C.E.); the difference between the half-wave potential values may be attributed to the dissimilarities both in the media themselves, e.g., dielectric constant, and in the liquid junction potentials between nonaqueous test solution and aqueous potassium chloride solution of the S.C.E. Both of these values are somewhat more positive than that reported by Coetzee and Kolthoff [8] for benzoic acid in acetonitrile ($E_{1/2} = -2.1$ v. vs. S.C.E.); it is possible that the more negative half-wave potential and the larger diffusion current constant observed by the latter were due, at least in part, to the maximum, which begins to appear at the millimolar level or above (cf. previous discussion).

The origins of the waves reported [2] for tetraethylammonium and ethyl benzoates are not clear; the available potential range in the present study was sufficient to have at least allowed detection of the ester wave.

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