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Oxidation Potential of Hydroxamic Acids and 4-Fluorophenol in the Presence of Added Base. Effect of Hydrogen-bonding[1]

MASAICHIRO MASUI,* YORIE KAIHO, TAKAHIRO UESHIMA and SHIGEKO OZAKI

Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka, 565, Japan

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The effects of a wide range of bases on the oxidation potentials of hydroxamic acids and 4-fluorophenol were examined by cyclic voltammetry mainly in acetonitrile and methylene chloride at a glassy-carbon electrode. Linear relationships between ΔE_p and the pK_a of the added bases were obtained for pyridines and for aliphatic amines, where $\Delta E_p = E_{pl} - E_{pe}$; E_{pl} is the potential for the original first wave and E_{pe} is that for the extra wave developed in the presence of the base. The results can be largely explained in terms of the formation of hydrogen-bonded complexes between the acids and the bases.

Keywords——cyclic voltammetry; oxidation potential; hydroxamic acids; hydrogen-bonding; basicity of amines; organic solvent; glassy-carbon electrode

In the previous communication[2] we showed that the anodic oxidation of hydroxamic acids in acetonitrile in the presence of an added base developed an irreversible extra wave at a less positive potential (E_{pe}) than that observed in the absence of the base (E_{pl}). The magnitude of the potential difference depends wholly on the strength of the base, and the height of the extra peak, without changing the potential (E_{pe}), on the amount of the base up to roughly two equivalents with respect to the acid.

An almost linear relationship between $\Delta E_p (= E_{pl} - E_{pe})$, and the p$K_a$ of the added base was obtained. Based upon the results, we considered that the formation of a hydrogen-bonded complex between the acid and the added base is mainly responsible for the development of the extra wave, and the potential shift, ΔE_p, depends mostly on the strength of the hydrogen bonding between them.

In the present paper we present details of a further investigation on the effects of pK_a, the structure of bases, the kind of solvent system and other factors on ΔE_p. Excellent linear correlations between ΔE_p and pK_a of the bases were observed for each series of bases, and the distance between the almost parallel plots increased with decreasing dielectric constant of the solvent and increasing acidity of acids used.

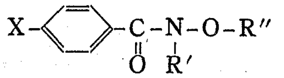
Results and Discussion

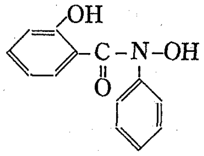
Peak potentials for the first oxidation step and pK_a values of the acids and a phenol used in the present study are summarized in Table I.

Bases used and their pK_a values are shown in Table II.

Cyclic voltammetry was performed with a glassy-carbon disk electrode (0.07 cm^2) and a scan rate of 0.05 V/s in acetonitrile containing 0.1 M sodium perchlorate or in methylene chloride containing 0.1 M tetraethylammonium perchlorate (TEAP). The concentration of the acid was 5 mM. As shown in Fig. 1, on addition of γ-collidine, for example, benzohydroxamic acid (BHA) showed an extra oxidation wave at a less positive potential, E_{pe}, than the original first wave at E_{pl},[2] and the current i_{pe} increased with the amount of γ-collidine, while the potential E_{pe} was actually fixed at a nearly constant value. When the acid used was a bifunctional one, N-phenylsalicylhydroxamic acid, development of two new waves was observed at 0.6 V and 0.9 V, as the amount of the base added was increased (Fig. 2). The two waves

Table I. pK_a and E_{pl} for Hydroxamic Acids and a Phenol



		X	R′	R″	pK_a	E_{pl}[a]
I	Benzohydroxamic acid	H	H	H	8.80[b]	1.35
II	N-Phenylbenzohydroxamic acid	H	C_6H_5	H	9.15[b]	1.05
III	O-Methylbenzohydroxamic acid	H	H	CH_3	8.89[b]	1.33
IV	p-Nitrobenzohydroxamic acid	NO_2	H	H	8.02[b]	1.51
V	N-Phenylsalicylhydroxamic acid				6.8[c]	1.22
VI	4-Fluorophenol				9.81[d]	1.53

[a] Volt *vs.* SCE.

[b] O. Exner and W. Simon, *Coll. Czech. Chem. Commun.*, **30**, 4079 (1965).

[c] Determined in 40% (v/v) aq. MeOH at 20°C according to the method of Parke *et al.* T. Parke and W.W. Davis, *Anal. Chem.*, **26**, 642 (1954).

[d] G. Kortüm, W. Vogel and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solutions," London, 1961.

Table II

No.	Base	pK_a	No.	Base	pK_a
1	Isopropylamine	10.72[a]	10	α-Picoline	6.0[a]
2	n-Butylamine	10.61[c]	11	β-Picoline	5.7[d]
3	Trimethylamine	9.74[a]	12	β, β, β-Trifluoroethylamine	5.59[d]
4	4-Dimethylaminopyridine	9.61[c]	13	Benzimidazole	5.50[b]
5	Benzylamine	9.37[a]	14	Pyridine	5.23[a]
6	Ammonia aq.	9.25[a]	15	Quinoline	4.8[a]
7	Propargylamine	8.15[c]	16	3-Acetylpyridine	3.26[d]
8	γ-Collidine	7.30[e]	17	Pyrazole	2.52[d]
9	Imidazole	7.0[b]	18	3-Cyanopyridine	1.39[c]

[a] R.C. Weast, "Handbook of Chemistry and Physics," 47th ed., The Chemical Rubber Co., Ohio, U.S.A. 1966.

[b] S. Sasaki, "The Chemistry of Heterocyclic Compounds," Tokyokagakudojin Co., Tokyo, 1972.

[c] D.D. Perrine, "Dissociation Constants of Organic Bases in Aqueous Solution," Butterworth and Co., Ltd., London, 1965.

[d] D. D. Perrine, "Dissociation Constants of Organic Bases in Aqueous Solution; Supplement 1972," Butterworth and Co., Ltd. London, 1972.

[e] P.G. Stecher, "The Merck Index," 8th ed., Merck and Co. Inc., Rahway, N.J., U.S.A., 1968.

showed heights each approximately equal to one-half of the original first wave when a sufficient amount of pyridine was present. The plot of i_{pe} against base concentration consisted of two straight lines, as can be seen in Fig. 2, and the lines bend at the points each equivalent to one acid proton. A similar result was seen for all the other acids and phenol used, except that the number of waves is only one for these compounds. Because N-phenylbenzohydroxamic acid (N-phenyl-BHA) and salicylaldehyde develop the oxidation peak at 0.56 V and 1.40 V, respectively, in the presence of pyridine, the first hydrogen bonding of N-phenylsalicylhydroxamic acid can be assumed to take place at the hydroxy proton of the hydroxamic acid moiety and the second at the phenol proton. In nominally dry ethanol, the effect of bases as above was also examined using N-phenylsalicylhydroxamic acid. Up to about 10 mM pyridine, the results were similar to those described above (Fig. 3). The effect of a much more greater amount of pyridine on the potential is also shown in Fig. 3, and a slight effect, that is, a potential shift of about −60 mV per log[pyridine], is apparent in the plot of E_{pe1} against log [pyridine].

In aqueous ethanol (1: 1 by volume), such an extra wave was not observed when the base added was pyridine, while with aliphatic amine which is a much stronger base than pyridine, an extra wave was still developed at a less positive potential. The results suggest that the effect of hydrogen bonding on the development of the extra wave is weaker in a more polar solvent system.

The reported[2] plot of ΔE_p against pK_a of the base was rather scattered from a straight line, but similar plots for aliphatic amines and substituted pyridines in the present work give

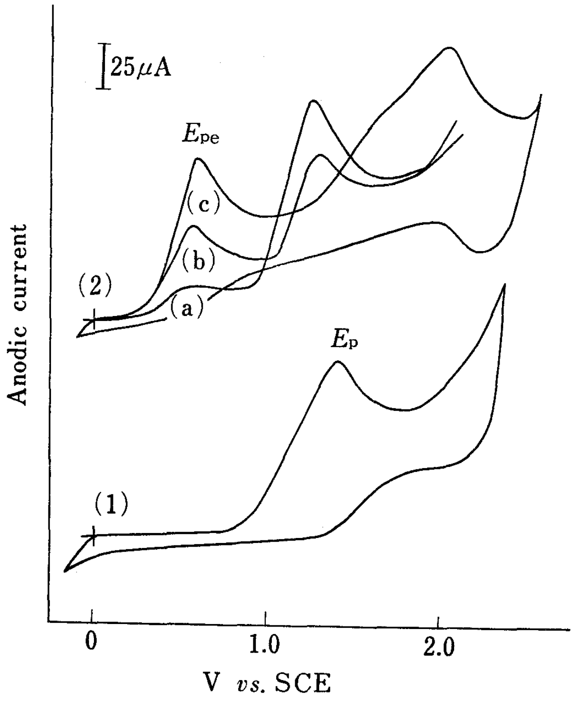


Fig. 1. Cyclic Voltammograms of BHA in the Presence and Absence of γ-Collidine

(1): BHA (5 mM).
(2): BHA (5 mM)+γ-collidine, (a); 1 mM, (b); 2.5 mM, (c); 5 mM, 10 mM.

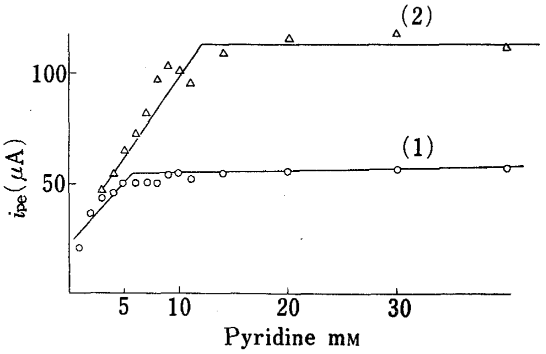


Fig. 2. Dependence of Peak Current of the Extra Waves for N-Phenylsalicylhydroxamic Acid (5 mM) on the Concentration of Base (Pyridine) at a Scan Rate of 0.05 V s^{-1}

○—○, (1): peak current of the 1st extra wave at 0.60 V vs. SCE.
△—△, (2): peak current of the 1st +2nd waves at 0.90V, v.s. SCE.

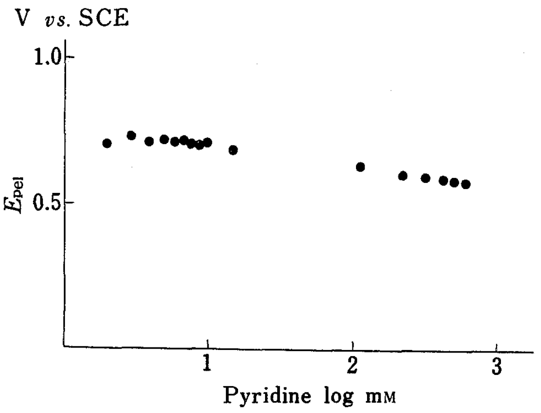


Fig. 3. Dependence of Peak Potential of the 1st Extra Wave, E_{pe1} for N-Phenyl salicylhydroxamic Acid (4.95 mM) on the Concentration of the Base (Pyridine) in Ethanol

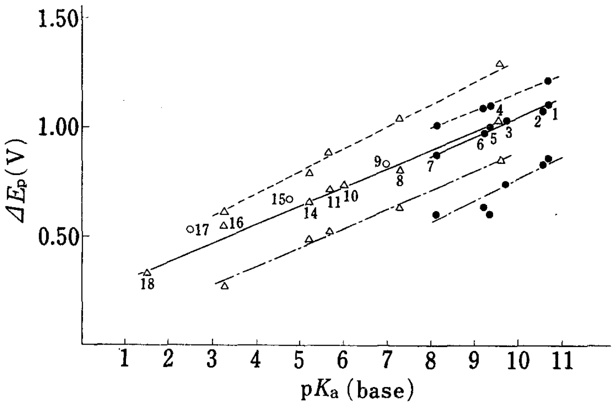


Fig. 4. Plot of ΔE_p against pK_a of the Added Base

△; pyridine derivatives, ●; aliphatic amines, ○; other bases.
——; BHA, ----; p-NO_2-BHA, —·—; N-phenyl-BHA.
The numbers refers to the bases as designated in Table II.

excellent straight lines (Fig. 4). Thus, the results indicate that a series of bases having a common functional center form a hydrogen bonding whose strength is linearly proportional to their pK_a value (Fig. 4 and Table II). The line for the series of pyridines is located at higher ΔE_p than that for aliphatic amines. The increased *s* character of the unshared pair orbital of pyridine may be responsible for the larger ΔE_p, and this is in accord with the result reported for the formation constant of hydrogen bonding between *p*-fluorophenol and bases studied by a nuclear magnetic resonance (NMR) method.[3] On comparing the ΔE_p values for the three BHA derivatives, the ΔE_p values increase in the order *N*-phenyl-BHA<BHA<*p*-NO_2–BHA, and this is in accord with their acidities. Thus, it can be said that a stronger acid forms a stronger hydrogen bond with a base and causes a larger potential shift. The distance between the straight lines for pyridines and aliphatic amines is larger in *p*-NO_2–BHA and *N*-phenyl–BHA than in BHA (Fig. 4). A clear-cut explanation is not possible at present, but some steric effect may be involved in the case of *N*-phenyl–BHA. The plots for *O*-methylbenzohydroxamic acid (O–Me–BHA) are located at a lower position than those for BHA (Fig. 5), and this is in accord with the order of acidity, though the acidic proton of O–Me–BHA is on nitrogen. Slightly different behaviors of the plots for the two acids are apparent in the figure, but the reason is not clear.

When methylene chloride was used as a solvent in place of acetonitrile, both the ΔE_p values observed for BHA and the distance between the couple of lines for the pyridine derivatives and aliphatic amines are larger than those observed in acetonitrile (Fig. 6).

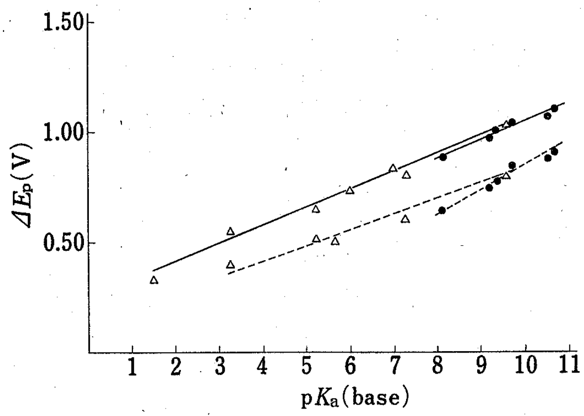


Fig. 5. Plot of ΔE_p against pK_a of the Added Base

△; pyridine derivatives, ●; aliphatic amines, ——; BHA, ----; O–Me–BHA.

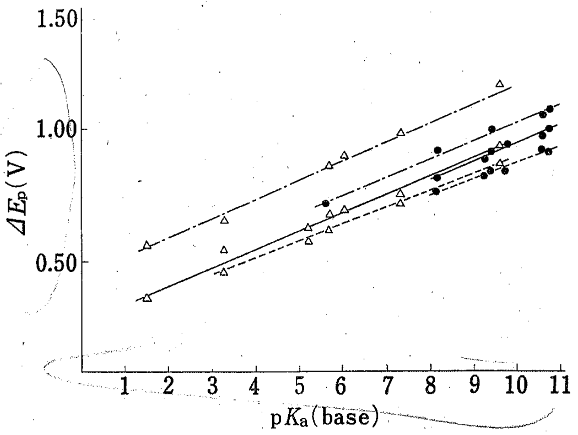


Fig. 6. Plot of ΔE_p against pK_a of the Added Base

△; pyridine derivatives, ●; aliphatic amines, ——; BHA in CH_3CN, ----; BHA in CH_2Cl_2, -·-·-; *p*-F-phenol in CH_3CN.

The results show that the hydrogen bonding between BHA and the bases is stronger in methylene chloride than in acetonitrile. In Fig. 6, it can be seen that *p*-fluorophenol, a slightly weaker acid than BHA and found to form a 1 : 1 hydrogen-bonded complex with bases in carbon tetrachloride by an F-NMR method,[3] is also shows a similar potential shift, ΔE_p. These results support our view that the extra wave observed above is derived mainly from hydrogen-bonded complexes between the acid and the bases.

The influence of the concentration of supporting electrolyte was examined by using 0.05 to 0.12 M sodium perchlorate in the presence of 5 mM BHA and 25 mM pyridine. As the concentration of sodium perchlorate decreased, a slight increase of both E_{pl} and E_{pe} was observed, and the differences of potentials between those observed at 0.05 and 0.12 M sodium perchlorate were 0.02 V for E_{pl} and 0.03 V for E_{pe}. The effect of the concentration of the acid was also investigated. Increased concentration of the acid caused a slight increase of oxidation potential, as is generally observed for an irreversible wave, and the difference of E_{pl} values observed at 3.85 mM and 11.5 mM of BHA was only about 0.04 V. Thus the influence of concentration of both supporting electrolyte and acid on E_{pl} or E_{pe} is actually negligible if the potential difference ΔE_{p} is measured under roughly constant conditions, for example about 0.1 M supporting electrolyte and about 5 mM acid in the same solvent. The water content of the solvent was not significant,$^{2)}$ except when the base used was strong compared with water.

Conclusion

The cyclic voltammetric behaviors of the compounds having an acidic proton, such as carboxamide,$^{4)}$ hydroxamic acids and *p*-fluorophenol, in the presence and absence of added base in organic solvent can be explained as shown in Chart 1, where AH is a free acid, B is a base, *n* is the number of bases concerned, and A^- is an anion of the acid. As judged from the intersection of two straight lines in the figures reported in the previous papers$^{2,4)}$ and Fig. 2 in the present paper, *n* should be one for each acidic proton. The oxidation potential E_{pl} is that for AH and E_{pe} should be that for hydrogen-bonded complex $[\overset{-}{\mathrm{A}}\text{–}\mathrm{H}\cdots\overset{+}{\mathrm{B}}]$. The oxidation potential of A^- is not known. If A^- is produced in solution containing a large excess of strong base, a wave corresponding to A^- could be developed at some very low potential. No indication of the wave for A^- has been obtained in the present study. The effects of sweep rate$^{2)}$ and a very large amount of pyridine (Fig. 3) on the current i_{pe} indicate that there is a slight kinetic contribution to the development of the extra wave, but the effect is not so large as to cause the potential shift of over one volt. This is a completely different phenomenon from that observed in aqueous solution for the polarographic reduction of free and dissociated forms of maleic and fumaric acids.$^{5)}$ The extra wave grows at a fixed potential as the amount of base increases, and the fixed potential depends completely on the $\mathrm{p}K_{\mathrm{a}}$ of the base. This can not be explained by an ordinary kinetic contribution to the electrochemistry of the system having the interconversion

$$\mathrm{AH}+\mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^- + \overset{+}{\mathrm{B}}\mathrm{H}.^{6)}$$

The effect of base on the oxidation potential of a compound having an acidic proton will be quite useful as a measure of the relative basicity of a base in a certain organic solvent and may also be applicable in electrochemical experiments to make the oxidation potential lower than the original one if the base does not disturb the reaction.

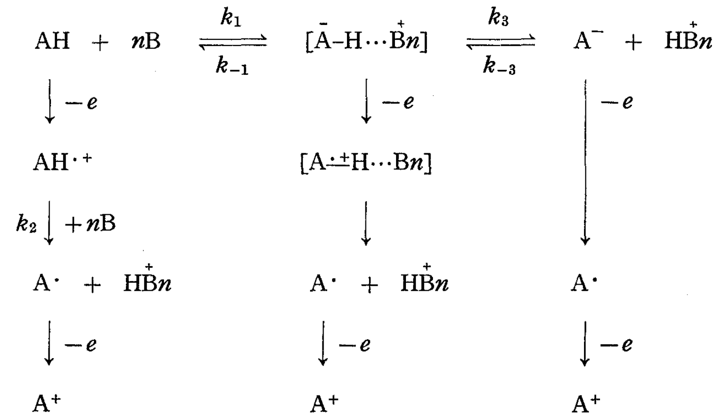


Chart 1

Experimental

Materials——Benzohydroxamic acid,[7] *N*-phenylbenzohydroxamic acid,[8] *O*-methylbenzohydroxamic acid,[9] and *p*-nitrobenzohydroxamic acid[10] were prepared by the reported methods. Commercial reagent-grade *p*-fluorophenol was used without further purification. All the bases used were of reagent grade. Tetraethylammonium perchlorate was prepared by the method of House *et al.*[11] Sodium perchlorate was purified by recrystallization from aqueous ethanol (*ca.* 95%) and dried over phosphorous pentoxide. Methylene chloride was purified by washing it with dilute hydrochloric acid and sodium bicarbonate solutions followed by distillation. Acetonitrile was purified by the method of Mann *et al.*[12]

Cyclic Voltammetry——Cyclic voltammetry was performed with a three-electrode system employing a linear scanning unit (Hokuto Denko Co., Model HB-101) equipped with a potentiostat (Hokuto Denko Co., Model PS-500B). The electrode system consisted of a glassy-carbon indicator electrode, a glassy-carbon counter electrode, and a saturated calomel electrode (SCE). Measurements were carried out at 25±0.05°C with a substrate concentration of *ca.* 5 mM and a sweep rate of 0.05 V s^{-1}.

References and Notes

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