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CYCLIC VOLTAMMETRY OF p-TROPOQUINONES

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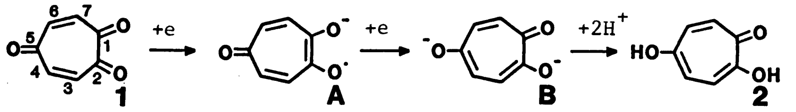
The first and the second half-wave potentials of p-tropoquinones measured by CV are linear to the Hammett's $\Sigma\sigma_p$ and $\Sigma\sigma_m$, respectively. Their smaller electrostatic repulsion than p-benzoquinones can be attributable to the characteristic three carbonyl system.

Recently, we have reported[1] a reversible one-electron redox process between p-tropoquinones (**1**)[2] and 5-hydroxytropolones (**2**). It is important to compare the half-wave potential of **1** by the cyclic voltammetry (CV)[3] with that of the reference benzenoid quinones (BQ). Herein, we will briefly describe the results.

The first half-wave potentials, E_1,[4] of **1** were higher than those of o- and p-BQ, and the total energy changes, $\Sigma E = E_1 + E_2$, of **1** were more positive than those



a: unsubstituted
b: 4,6-dichloro
c: 4-chloro
d: 3-chloro
e: 4-allyl
f: 4-propyl
g: 4-methyl
h: 3,6-diallyl
j: 4,6-dimethyl
k: 3,6-dipropyl
m: 3,7-dimethyl

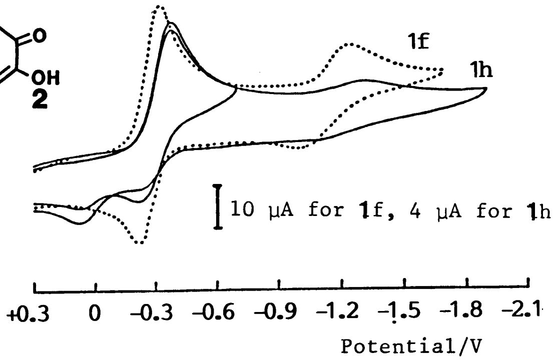


Fig. 1. CV of **1**f and **1**h.

Table 1. Reduction Potentials of Several **1** Derivatives.[a)]

	E_1	E_2	ΔE	ΣE		E_1	E_2	ΔE	ΣE		E_1	E_2	ΔE	ΣE
1a:	-0.21	-1.10	0.89	-1.31	**1**f:	-0.27	-1.16	0.89	-1.43	**1**m:	-0.37	-1.17	0.80	-1.54
1b:	0.04	-0.68	0.72	-0.64	**1**g:	-0.28	-1.15	0.87	-1.43	p-BQ:	-0.44	-1.55	1.11	-1.99
1c:	-0.09	-0.89	0.80	-0.98	**1**h:	-0.31	-	-	-	o-BQ:	-0.29	-	-	-
1d:	-0.10	-0.91	0.81	-1.01	**1**j:	-0.36	-1.24	0.88	-1.60	XQ:[b)]	-0.61	-1.72	1.11	-2.33
1e:	-0.25	-1.17	0.92	-1.42	**1**k:	-0.37	-1.22	0.85	-1.59					

a) Potentials in V were determined by CV method in a standard three-electrode cell (working electrode, Pyrex glass-sealed Pt wire; reference electrode, standard Ag/AgCl) at 22–23 °C in anhydrous DMF with 0.1 M Bu_4NBF_4 under N_2 with scan rate of 100 mV/s. b) XQ means 2,5-dimethyl-p-benzoquinone.

of BQ, and **1** are stronger oxidizing agents than the corresponding BQ. Moreover, for the energy difference, $\Delta E = E_1 - E_2$, which is known to reflect the electrostatic repulsion of two negative charges in the same molecular orbital, smaller values of **1** than those of p-BQ can be explained by the presence of three-carbonyl function in the molecule.

As shown in Table 1, E_2 of **1h** was absent. This might be due to the broad and irreversible second wave at ca. -1.2 V. In fact, a new oxidation wave was observed in the CV at ca. +0.06 V, which was also observed when the scanning was made between ca. +0.3 and -0.7 V. Consequently, this wave is attributable to the species derived from the anion radical (**A**). These new oxidation waves were also found in **1k** and **1m** around zero V, but they were weakened in the 4-substituted **1**; **1e** and **1j** showed a very weak wave, and **1g** and **1f** showed no such wave. Thus, C-3 and C-4 substituents play opposite roles for the appearance of new waves.$^{5)}$

Zuman$^{6)}$ has already found a linear correlation between the Hammett's substituent constants and reversible half-wave potentials for several benzo-, naphtho-, and other higher quinones. The E_1 of **1** are now shown to be also linear to the sum of the substituent constants, $\Sigma\sigma_p$, with a range of 0.41 V. The value of the reaction constant, ρ=+0.50 (correlation coefficient, r=0.998, and standard deviation, s= 0.010), showed a good agreement with the value of p-BQ (+0.53) in acetonitrile.$^{6b)}$ The observed linearity for E_1 should be explained in terms of the contribution of mesomeric effect of one electron to form **A**.

On the other hand, E_2, the energy changes to form the dianion (**B**), were not linear to $\Sigma\sigma_p$ but to $\Sigma\sigma_m$. Therefore, the shifts of E_2 are primarily dependent on inductive effect. The value of reaction constant, ρ=+0.57 (r=0.999, s=0.011), is almost same to that of E_1. The positive values for ρ indicate that the substituents with increasing electron-withdrawal strengthen the oxidizing ability.

Higher oxidizing ability of **1** than the BQ derivatives should be explained by the existence of o- and p-quinone functions in the molecules. Related studies are in progress.$^{7)}$

References

1) H. Takeshita, T. Kusaba, and A. Mori, Chem. Lett., 1982, 701; 1983, 1371.
2) For synthesis of **1a**, see S. Itô, Y. Shoji, H. Takeshita, M. Hirama, and K. Takahashi, Tetrahedron Lett., 1975, 1075.
3) The reduction potentials of 3,7-dimethyl-**1** and [2]paracyclo[2](3,7)-p-tropoquinonophane have already been determined by polarography. See A. Kawamata, Y. Fukazawa, Y. Fujise, and S. Itô, Tetrahedron Lett., 1982, 1083.
4) The potentials of **1** were calibrated by the redox potential (+0.465 V vs. Ag/AgCl) of ferrocenium/ferrocene couple as an internal standard.
5) This phenomenon may involve multiple processes, and detailed study will be published later.
6) a) P. Zuman, Collect. Czech. Chem. Commun., 27, 2035 (1962); b) P. Zuman, "Substituent Effects in Organic Polarography", Plenum Press, N. Y.(1967), Chap. VIII, pp. 273–308.
7) We thank The Ministry of Education, Science, and Culture for a financial support [the Grant-in-Aid for Scientific Research, No. 60470025 (to A. M.)].

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