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Carboxylates as Proton-Accepting Groups in Concerted Proton−Electron Transfers. Electrochemistry of the 2,5-Dicarboxylate 1,4-Hydrobenzoquinone/2,5-Dicarboxy 1,4-Benzoquinone Couple

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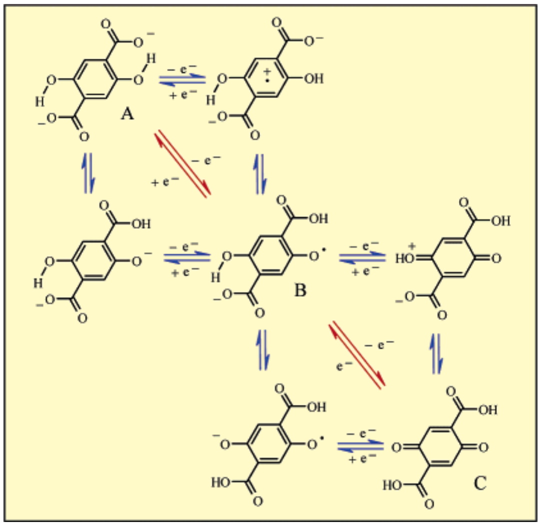
Association between single electron transfer and proton transfer in many reactions of electron transfer and radical chemistry is a well-recognized phenomenon. Molecular electrochemists, and especially organic electrochemists, have dedicated an active attention to this possible association as a particular case of the coupling between electron transfer and acid−base reactions in a general sense. Until very recently, however, proton transfer and electrochemical electron transfer have been viewed as separate individual steps. This conception ought to change if electrochemistry is to contribute to the interpretation of newly discovered clues pointing to the possibility that the two reactions may be concerted in several natural processes.[1] The most prominent of these involves photosystem II,[2] but evidence has been gathered that similar processes might be at work in the functioning of cytochrome *c* oxidase,[3] ribonucleotide reductase,[4] prostaglandin H synthetase,[5] galactose oxidase,[6] and superoxide dismutase.[7] Very likely, this is only the tip of the iceberg as electron transfer (and/or transport) and proton transfer (and/or transport) are associated in a considerable number of natural processes. One may even wonder if the remarkable efficiency of enzymatic systems in which proton and electron transfers are coupled is not the result of their acting in concert.

Coupling proton transfer to electron transfer entails an improvement of the driving force of the reaction. Two types of mechanisms may be followed (Scheme 1): (i) mechanisms in which the two reactions occur in a stepwise manner (in blue in the Scheme), with proton transfer first, followed by electron transfer (PET) or, vice versa, electron transfer first, followed by proton transfer (EPT) and (ii) a mechanism in which proton and electron transfer occur in a concerted manner (CPET pathway, in red in the Scheme). Only in the last case will the benefits of the additional driving force offered by the coupling with proton transfer be fully exploited, although there is a kinetic price to pay for this advantage. Recently a semiclassical model has been developed, showing that the Marcus−Hush−Levich rate law for outersphere electron transfers can be applied to electrochemical CPET reactions and providing procedures to estimate the reorganization factors, as well as the proton tunneling and isotope effects.[8]

So far, mostly nitrogen bases have been evoked as proton-accepting groups in the coupling of proton transfer with electron transfer in natural processes and in biomimetic studies,[8d,9] although amidinium−carboxylate salt bridges between an electron donor and an electron acceptor have been shown to allow the occurrence of a proton-coupled electron transfer.[10] See also the role of the D_1-aspartate 61 as the proton-accepting site in the oxygen evolution complex of photosystem II.[11]

We have explored the role of carboxylate groups as proton-accepting groups in CPET reactions by means of a cyclic voltammetric investigation of the 2,5-dicarboxy 1,4-benzoquinone/2,5-dicarboxylate 1,4-hydrobenzoquinone couple (Scheme 1) in a nonaqueous medium (*N,N*-dimethylformamide, DMF).

Scheme 1



The hydroquinone that bears two carboxylic acid groups in ortho, ortho′, shows (blue curve in Figure 1a) a broad two-electron irreversible wave on the anodic side and a thin two-electron irreversible wave on the reverse scan as expected for the oxidation of a standard hydroquinone.[12] The cyclic voltammetric behavior changes drastically upon addition of 2 equiv of a strong base (Me_4NOH), expected to deprotonate the two carboxylic acid functions, thus yielding 2,5-dicarboxylate 1,4-hydrobenzoquinone (top left of Scheme 1). Two closely spaced quasi-reversible one-electron waves are now observed (Figure 1).

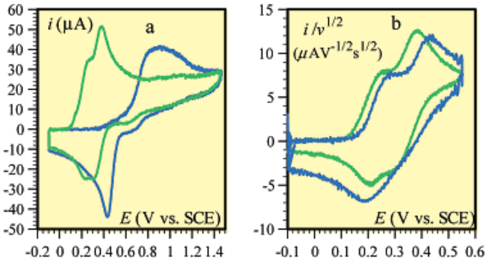


Figure 1. Oxidative cyclic voltammetry[13] of 2 mM 2,5-dicarboxy 1,4-hydrobenzoquinone in DMF + 0.1 M *n*-Bu_4NBF_4 at glassy carbon electrodes. (a) In the absence (blue) and presence of 2 equiv of Me_4NOH (green). Scan rate = 0.2 V/s. Electrode diameter = 3 mm. (b) In the presence of 2 equiv of a strong base (Me_4NOH): variation of the normalized voltammograms with scan rate. Green line, 0.2 V/s; blue line, 20 V/s. Electrode diameter = 1 mm.

10.1021/ja0621750 CCC: $33.50

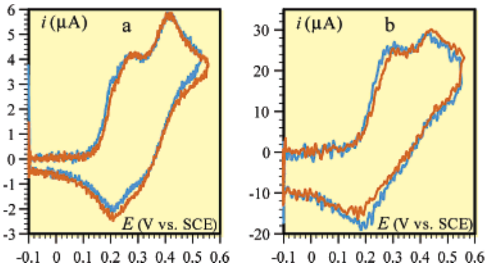


Figure 2. H/D kinetic isotope effect in the oxidative cyclic voltammetry[13] of 1.15 mM 2,5-dicarboxylate 1,4-hydrobenzoquinone at 0.5 V/s (a) and 20 V/s (b).[15] Blue, in light DMF; red, in DMF-d_7; 1 mm diameter glassy carbon electrode.

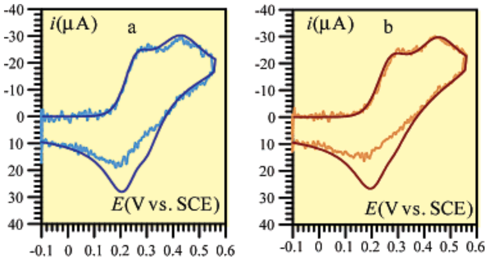


Figure 3. Oxidative cyclic voltammetry[13] of 1.15 mM 2,5-dicarboxylate 1,4-hydrobenzoquinone[13] at 20 V/s in light DMF (a) and in DMF-d_7 (b). Simulation of the cyclic voltammetric responses.[16]

Table 1. Experimental Thermodynamic and Kinetic Characteristics and Predictions for a Concerted (CPET) and Stepwise Square-Scheme (SQS) Mechanism

				k_S^{H} (cm/s)^c			k_S^{H}/k_S^{D}		
	E^0	$k_S^{H,ap}$	ϕ_2		predicted			predicted	
couple	(V vs SCE)	(cm/s)^a	(V)^b	exp$^{a/}$	CPET	SQS	exp$^{a/}$	CPET	SQS
A/B	0.235	0.20	0.05	0.010	0.0084	0.0005	2.5	2.5	1.0
B/C	0.345	0.03	0.07	0.005			1.4		

[a] Apparent standard rate constant. [b] Potential in the outer Helmoltz plane.[17] [c] Standard rate constant correct from the double layer effect.[13]

They exhibit (Figure 1b) a quasi-Nernstian behavior at low scan rate, while the anodic and cathodic peaks tend to move away upon raising the scan rate, as electron transfer kinetics start to interfere. These observations point to two successive reactions in which the transfer of each successive electron is coupled with proton transfer from the phenolic to the carboxylate position. The corresponding standard potentials ($E^0 = 0.235$ and 0.345 V vs SCE) are separated by only 110 mV, corresponding to a relatively weak Coulombic repulsion between the two negative charges, in line with their likely localization on the oxygen atoms of the carboxylate groups[14] and to stabilization of the dianion by H-bonds between the carboxylate and the phenolic groups.

The mechanism (Scheme 1) of these two successive proton-coupled electron transfers may be of the stepwise type (square scheme marked in blue) or of the concerted type (CPET marked in red). As seen in Figure 2, there is a small but definite hydrogen/deuterium kinetic isotope effect on both waves, which appears, as expected, only when the scan rate is large enough for electron transfer kinetics to interfere. This observation is a good indication that a CPET mechanism is followed for the two successive proton-coupled electron transfers. The kinetic characteristics of the two reactions as derived from the fitting[16] of the cyclic voltammetric responses at 20 V/s (Figure 3) are summarized in Table 1.

The stepwise square scheme mechanism is ruled out for two reasons: it is predicted to be slower than observed and to show no H/D kinetic isotope effect.[13]

Concerning the CPET mechanism, approximate predictions based on the theory of electrochemical concerted proton−electron transfers[8] led to an average value of $\lambda = 0.95$ eV for the reorganization energies of the two successive reactions and $Z = 822$ cm s^{-1} for their pre-exponential factors. The predicted value of the standard rate constant[13] is compatible with the experimental values (Table 1). This is also the case with the value of the H/D kinetic isotope effect predicted on the same basis.

In summary, the presence of carboxylate groups ortho to the phenol groups induces the removal of an electron to be coupled with the transfer of the phenolic proton to a carboxylate oxygen. The kinetics of the electrochemical reaction and the observation of a significant hydrogen/deuterium kinetic isotope effect unambiguously indicate that electron transfer and proton transfer are concerted. This is an additional demonstration that carboxylate groups may serve as proton-accepting sites in concerted proton−electron transfer reactions.

Supporting Information Available: Details on experimental and simulation procedures. Cyclic voltammetry in water. Estimation of the various theoretical parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Prepared as a salt and introduced in the DMF solution.[13] Cyclic voltammograms obtained in this way are closely similar to those obtained by in situ neutralization of 2,5-dicarboxy 1,4-hydrobenzoquinone in DMF + 0.1 M n-Bu$_4$NBF$_4$ (Figure 1).
(16) The simulations[13] do not quite fit the reverse trace in both cases. This is due to a relatively slow decay of the two reaction products, similarly, but to a stronger extent, to what has been previously observed with a phenol bearing an amino group as proton-accepting site.[8c] This behavior is presumably related to the deprotonation by DMF, or more likely by dimethylamine present as an impurity,[15] of the intermediate radical and the quinone. These reactions take place to a much larger extent in buffered aqueous media at pH values where the carboxylic acid groups are deprotonated, thus leading to irreversible patterns, exhibiting a H/D kinetic isotope effect, which is even more marked than that in DMF.[13] Work is in progress to decipher the mechanism of these reactions. For the moment, we may consider that this partial lack of chemical reversibility does not affect the determination of the kinetic characteristics significantly.
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JA0621750