

Electronic Supplementary information

Proton Coupled Electron Transfer of Ubiquinone Q₂ Incorporated in Self-Assembled Monolayer

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Determination of the pK_{ai} values using the Hammett correlation.

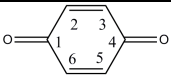
For the right part of the nine-member square scheme, the different pK_{ai} collected in the literature are summarized in Table 1. We decided to correlate all these data using the Hammett sigma plots.¹ Indeed, the Hammett equation was successfully applied to quinones,²⁻³ and the change in the pK_{ai} values can be described by a Hammett-type approach analog to the changes of the redox potential.⁴

The slope of the straight line expresses the sensitivity of the protonation reaction to substituent effect. The Hammett substitution constant, σ , reflects the influence of the substituent on the pK_{ai} value. When the quinone is substituted by more than one group, the substituent constant is the sum of the individual substituent constant $\Sigma\sigma_i$.²⁻³

It was demonstrated that the best correlations were obtained using the σ_{para} constants in benzene derivatives.^{2, 4-5} Moreover, in the case of the halogeno substituents, the σ_{meta} constants were used instead of the σ_{para} constants because they reflect more accurately the inductive effects of the halogeno group in the quinone system.⁵⁻⁶ In Table 1, $\Sigma\sigma_i$ corresponds to the sum of the σ_{para} constants except for the halogeno substituents for which we used σ_{meta} values.

The variations of pK_{a4}, pK_{a5} and pK_{a6} with $\Sigma\sigma_i$ are presented in Fig. 1. They show good correlations with regression coefficients from 0.914 to 0.96.

Table1: Acidity constants of substituted 1,4-benzoquinones

	$\Sigma\sigma_i$	pK _{a4}	pK _{a5}	pK _{a6}
<i>Substituents</i>				
2,6-dichloro	0.74		7.3 ¹⁴	10 ¹⁴
2,5-dichloro	0.74		7.9 ¹⁵	10 ¹⁵
2-nitro	0.71		7.42 ¹⁶	10.11 ¹⁶
2-bromo	0.23		8.67 ¹⁶	10.68 ¹⁶
2-chloro	0.23		8.9 ¹⁵	11 ¹⁵
	0.23		8.81 ¹⁶	10.78 ¹⁶
2-sulfonate	0.05		9.57 ¹⁵	11.9 ¹⁵
None	0	4.1 ⁷	9.85 ¹⁴	11.4 ¹⁴
	0	4 ⁸	9.9 ¹⁷	11.9 ¹⁷
2- <i>tert</i> -butyl	-0.10	4.3 ⁹		
2-methyl	-0.17	4.45 ¹⁰	10.1 ¹⁴	11.6 ¹⁴
2,3-dimethyl	-0.34	4.65 ¹⁰	10.43 ¹⁵	12.6 ¹⁵
2,5-dimethyl	-0.34	4.6 ¹¹⁻¹²	10.38 ¹⁵	12.5 ¹⁵
2,6-dimethyl	-0.34	4.75 ¹⁰	10.35 ¹⁵	12.4 ¹⁵
	-0.34		10.2 ¹⁸	12.8 ¹⁸
2,3-dimethyl-5-nonaprenyl (plastoquinone)	-0.50	4.7 ¹³	10.8 ¹⁹	
2,3,5-trimethyl	-0.51	4.95 ¹⁰	10.8 ¹⁵	12.9 ¹⁵
tetramethyl (duroquinone)	-0.68	5.1 ¹¹⁻¹²	11.3 ¹⁴	12.7 ¹⁴

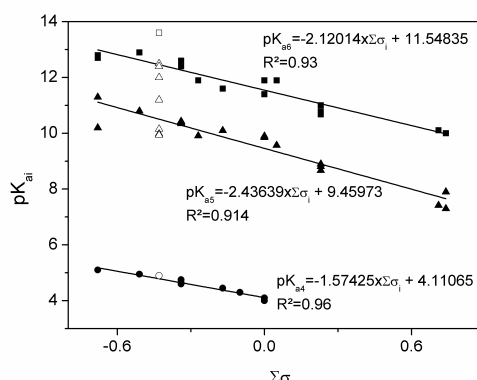


Fig. 1: Hammett correlations: plots of pK_{a4} (dark circle), pK_{a5} (dark triangle) and pK_{a6} (dark square) with $\Sigma\sigma_i$ for the different substituted 1,4-benzoquinones of Table 1. Values of pK_{a4} (open circle), pK_{a5} (open triangle) and pK_{a6} (open square) for the different UQ_n collected in Table 2 ($\Sigma\sigma_i = -0.43$).

Using these correlations it is now possible to estimate the pK_{ai} values of UQ_2 and more generally UQ_n . Prince demonstrated that the σ_{para} value for the prenyl substituent is -0.16 .² No significant difference was observed between polyprenyl chains when $1 < n < 10$.² Concerning the methoxy group, it was established that a single methoxy group has a σ_{para} value of -0.27 but when two methoxy groups are adjacent like in UQ_n , the apparent σ_{para} value is only -0.10 for both.^{2, 5} This is attributed to the steric inhibition of resonance when the two methoxy groups are adjacent.^{2, 20} Rubinson²¹ proposes a more geometric picture of the correlations and comes to the same conclusion if the methoxy group blocked the normal preferred path. The $\Sigma\sigma_i$ value for UQ_n is thus $\Sigma\sigma_i = \sigma_{prenyl} + \sigma_{2 \text{ adjacent OMe}} + \sigma_{Me} = -0.16 - 0.10 - 0.17 = -0.43$. By reporting this value into the graph of Fig. 1, we obtained $pK_{a4} = 4.79 \pm 0.09$, $pK_{a5} = 10.51 \pm 0.16$ and $pK_{a6} = 12.46 \pm 0.13$.

Let us compare these values to data collected in the literature. They are indicated in Table 2 for different chain lengths (UQ_n with $n=2, 6, 9, 10$) and reported on the graph of Fig. 1.

Table2: Acidity constants of coenzymes UQ_n

Coenzyme Q_n	pK_{a4}	pK_{a5}	pK_{a6}
UQ_2		12.4 ²²	
UQ_6		10.15 ²³	
UQ_9		9.98 ²³	
UQ_{10}	4.9 ¹³	12 ¹⁶	13.6 ¹⁶
		9.94 ²³	
		11.2 ¹⁹	
		12.5 ²²	

The pK_{a4} value obtained by pulse radiolysis¹³ for UQ_{10} is in good agreement with the Hammett treatment.

Only one pK_{a6} value was determined.¹⁶ It is quite high compared to those deduced from the Hammett correlation (Fig.1) may be due to the fact that UQ_{10} is adsorbed flat on the mercury electrode, therefore the environment is completely different and may induce a higher pK_{a6} value.

Concerning pK_{a5} , the literature results were essentially obtained for UQ_{10} . There is a great discrepancy between the values from 9.94²³ to 12.5.²² Ksenzhek et Al.²³ studied three coenzymes, UQ_6 , UQ_9 and UQ_{10} , by thin layer voltammetry on carbon electrode. In the entire pH range, the variation of $E^{o'}$ with pH is equal to -60 mV / pH unit. The authors supposed that in basic medium ($pH > 10.1$) the oxidized form exists as an anion due to an OH^- conjugated with one of the oxygen atoms. Therefore pK_{a5} must have nearly the same value to explain the slope of -60 mV / pH unit. The other literature result concerns UQ_{10} incorporated in supported phospholipid layers.²² The authors recorded the voltammograms at different pH and at a scan rate of 0.1 Vs⁻¹. They reported the variations of the anodic (E_{pa}) and cathodic (E_{pc}) peak potentials with pH at this scan rate. Both varied linearly with pH. The slopes are respectively -60 mV and -60 mV for $pH < 9$, -120 mV and 0

for $9 < \text{pH} < 12.5$ and -60 mV and 0 for $\text{pH} > 12.5$. We wanted to compare these results with ours. We plotted the graph E_{pa} and E_{pc} in function of pH at 0.1 V s^{-1} (Fig. 2). We obtained exactly the same variations and the same slopes. The change in slopes were observed for $\text{pH}=8.8$, i.e. approximately the same as those obtained for UQ_{10} .²² It should be noted that working at only one scan rate gives a partial view of the electrochemical behavior of the system. Indeed, the existence of a nine member square scheme implies that the cathodic and anodic peak potentials vary diversely with scan rate. Moreover, the reaction kinetics depending on pH , it is not possible to have access to the exact value of E° . The only way to obtain E° is to extrapolate its value by superimposing the theoretical curve²⁴ with the variations of E_{pa} and E_{pc} with $\log v$ as presented in Fig. 4 of the article. Therefore, until now the literature results on UQ_n present a great deal of uncertainty that can explain the discrepancy between the values collected in Table 2.

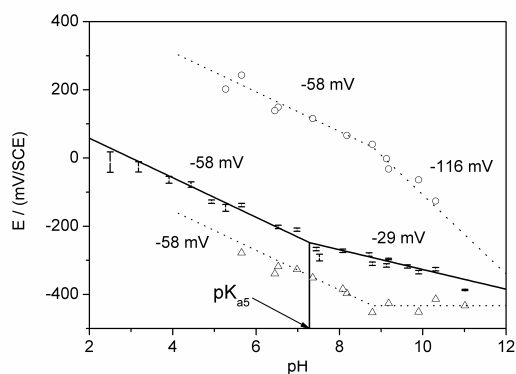


Fig. 2: pH dependence of E° , cathodic (open triangle) and anodic peak potentials (open circle) at a scan rate of 0.1 V s^{-1} .

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