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Experimental and Theoretical Studies of Redox Reactions of *o*-Chloranil in Aqueous Solution

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The electrochemical reduction of *o*-chloranil (OCA) in aqueous solution has been studied experimentally and theoretically. The effects of temperature and pH on various thermodynamic parameters were studied by means of cyclic voltammetry. The pH dependence of the redox activity of OCA in aqueous solution at temperatures in the range 25–40 °C was used for the experimental determination of the standard reduction potentials of both the one-proton–two-electron (0.67 V) and two-proton–two-electron (0.79 V) reduction processes. The temperature dependency of the equilibrium constants of studied reactions has been used in order to determine enthalpy, entropy, and Gibbs energy changes of the reactions. It is found that the two studied redox reactions of OCA are strongly affected by solvation effects and controlled by entropy contributions to the Gibbs free energies. High-level *ab initio* calculations (G3 and CBS-QB3 using the CPCM solvation model) have been employed to calculate the reduction potentials of OCA in aqueous solution for the one-proton–two-electron (0.65 and 0.69 V at the respective levels of theory) and two-proton–two-electron (0.81 and 0.83 V) reactions, which are in excellent agreement with the corresponding experimental values. The acidic strength of the reduced form of OCA in aqueous solution, pK_a , has been also calculated (5.2) and is also in excellent agreement with the experimental value (5.0). The agreement mutually verifies the accuracy of experimental method and the validity of the mathematical model.

1. Introduction

Quinones are electroactive organic compounds of wide interest in chemistry, biochemistry, and electrochemistry.^{1–5} They play a vital role in a number of biochemical processes, especially those involving electron and/or proton transport, such as respiration,⁶ photosynthesis,^{7–9} and various antitumor activities.^{10–12} They are also intercalating agents of DNA,¹³ bioreductive alkylating agents of biomolecules,¹⁴ and promoters of reactive oxygen radical formation.¹⁵ In addition, compounds containing the quinone group can act as inhibitors of electron transfer¹⁶ and are also efficient in inhibiting the growth of bacteria,¹⁷ fungi,¹⁸ and parasites.¹⁹ The biological activities of quinones are closely related to their standard redox potential, E° , and the acidic dissociation constant, K_a , of the quinone and hydroquinone species; hence, obtaining accurate values of these quantities is important.

In the present work we study the redox chemistry of tetrachloro-1,2-benzoquinone, or *o*-chloranil (OCA; Figure 1). Chloranils are important oxidants in organic chemistry, and OCA is particularly interesting as there has been no report for any coupled chemical reaction for its redox forms. That is, its reduction mechanism is believed to be purely electrochemical (E) in nature, whereas the coupled chemical reaction can be observed for most monosubstituted *o*-benzoquinones.^{20–26} Despite the importance of this compound, it has not been widely studied. While there are a few studies of its electrochemical

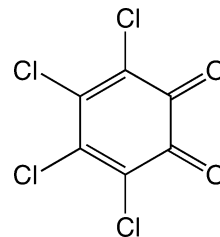


Figure 1. Structure of *o*-chloranil.

behavior in nonaqueous solvents,²⁷ its behavior in aqueous solution does not appear to have been studied. In the present work, which builds on our previous studies of other quinone derivatives,^{20–26,28–30} we have studied the electrochemical reduction of OCA in aqueous solution using standard experimental and theoretical methods. According to the literature and to the best of our knowledge, this is the first study of this kind on OCA and should also be relevant to other catechol derivatives.

2. Experimental Section

2.1. Equipment and Reagents. Electrochemical measurements were carried out using a computer-controlled potentiostat, PGATAT 30 (Eco-Chemie, Utrecht, Netherlands) with a standard three-electrode configuration. A glassy carbon working electrode (GC, 2 mm diameter) together with a platinum auxiliary electrode and a saturated calomel reference electrode (SCE) were purchased from Azar Electrode [Uromieh, Iran] and used for the electrochemical experiments. All potentials have been measured versus this reference electrode. Room temperature and elevated temperature experiments were performed in a double-walled glass cell, of 20 cm³ volume, which was connected to a

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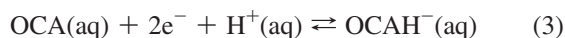
heated water bath at the appropriate temperature. pH measurements were performed using a Metrohm 691 pH/mV meter. In order to obtain a clean renewed electrode surface, the glassy carbon electrode was cleaned by successive polishing with 0.05 μm alumina–water slurry prior to its use in electrochemical experiments.

o-Chloranil (OCA) and all other reagents were purchased from Merck and used without further purification. The solutions were prepared with doubly distilled water. Phosphate buffer solutions (0.1 M) were prepared from 0.1 M H_3PO_4 – NaH_2PO_4 and pH adjusted with 0.1 M H_3PO_4 or 2.0 M NaOH.

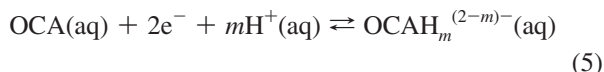
2.2. Thermodynamic Analysis. It is generally known that quinones and its derivatives (here *o*-chloranil) are reduced to corresponding hydroquinones by a one-step, two-electron redox reaction including protonation in aqueous solution.^{28–31} The overall reactions of OCA relative to the standard hydrogen electrode (SHE) are



Subtracting the half-reaction of SHE, these two-electron processes are



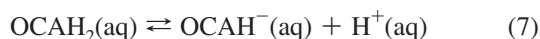
which are one-proton–two-electron and two-proton–two-electron reduction processes, respectively. These two processes can be summarized as follows:



Here OCA and OCAH_m stand for *o*-chloranil and its two-electron reduced forms, respectively, and m is the number of protons involved in the redox reactions ($m = 1$ or 2 , in this case). In this reaction scheme, the conditional formal potential, $E^{\circ'}$, is given by the following equation:³²

$$E^{\circ'} = E^{\circ} - \frac{2.303mRT}{2F}\text{pH} \quad (6)$$

where E° is the standard redox potential (or formal potential at pH 0); R , T , and F are the gas constant, temperature, and Faraday constant, respectively. As can be seen from eq 6, the conditional formal potential, which is approximated by the midpoint potential between the anodic and cathodic peaks, $E^{\circ'} = (E_{\text{p,a}} + E_{\text{p,c}})/2$, of OCA is pH-dependent and it is shifted to negative potential as pH is increased. Also, based on eq 6, for variation of $E^{\circ'}$ versus pH, two linear segments are found with the theoretical slope value of -0.0592 V/pH (for $m = 2$) and -0.0296 V/pH (for $m = 1$) in ranges of $\text{pH} < \text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a1}} < \text{pH} < \text{p}K_{\text{a2}}$, respectively. Then, the $\text{p}K_{\text{a1}}$ of OCAH_2 , which is the reduced form of OCA as shown in reactions 2 and 4, can be determined from the intersection of these two linear plots of $E^{\circ'}$ versus pH.^{30,32} This acidic constant corresponds to the deprotonation of OCAH_2 in aqueous solution:



It is worth noting that, if the pH is smaller than $\text{p}K_{\text{a1}}$, then two protons are involved in the redox reaction; if the pH lies between $\text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a2}}$, then only one proton is involved. Based on the relation between the formal potential of the redox couple, $E^{\circ'}$, and pH, eq 6, the standard redox potential of OCA, E° , can be obtained from the intercept of eq 6, at pH 0.

Standard redox potentials relative to the reference electrode (SHE) can be measured at different temperatures in order to calculate changes of enthalpy and entropy of studied reactions based on the following equations given in standard textbooks:^{32,33}

$$\Delta S^{\circ} = nF\left(\frac{\partial E^{\circ}}{\partial T}\right)_P \quad (8)$$

$$\Delta H^{\circ} = -nF\left[E^{\circ} - T\left(\frac{\partial E^{\circ}}{\partial T}\right)_P\right] \quad (9)$$

where T , F , and E° are the temperature, Faraday constant, and standard electrode potential, respectively. In this study, electrode potentials have been measured versus saturated calomel electrode (SCE) and then converted to electrode potentials vs SHE using the exact potential of SCE at each temperature.³⁴ Using the standard redox potentials and its variation relative to temperature, ΔH° and ΔS° of the corresponding reactions (1 and 2) can be obtained.

2.3. Computational Details. Gaussian 03³⁵ has been used for all ab initio molecular orbital theory³⁶ and density functional theory calculations.³⁷ The Gibbs free energy of each species was obtained at the G3³⁸ and CBS-QB3³⁹ levels of theory. The G3 method approximates QCISD(T)/6-31G(d) calculations in conjunction with additivity corrections, obtained at the MP2 and MP4 levels of theory.³⁸ The complete basis set method (CBS-QB3) is a model chemistry that makes use of a complete basis set extrapolation of the correlation energy, which is performed at the MP2 level of theory and then corrected to the CCSD(T) level via additivity corrections.³⁹ The G3 method employs the geometries which are optimized at the MP2(Full)/6-31G(d) level, but CBS-QB3 employs B3-LYP/CBSB7 optimized geometries.^{38,39} These high-level composite procedures have been designed particularly for the prediction of reliable energies of molecules in the gas phase and have been demonstrated to provide an accuracy of 1 kcal mol^{−1} when assessed against large test sets of thermochemical data.^{38,39} In order to calculate solvation energies, a continuum model of solvation, the conductor-like polarizable continuum model (CPCM) has been used at the RHF/6-31+G(d,p) level of theory.⁴⁰ This level of theory has been recommended for the calculation of solvation energies.⁴¹ The radii of the united atom topological model, optimized for the RHF methods (UAHF), have been chosen for solvation energies as recommended, and the rest of the parameters of the models have been kept as default values.⁴² All geometries of the studied species have been optimized fully in the presence of solvent. The literature values of 26.0 cal mol^{−1} K^{−1},⁴³ 1.5 kcal mol^{−1},⁴⁴ and -264.0 kcal mol^{−1},⁴⁵ have been used for the gas-phase entropy, enthalpy, and aqueous Gibbs free energy of solvation of the proton (H^+), respectively.

3. Results and Discussion

3.1. Cyclic Voltammetric Responses *o*-Chloranil as a Function of pH and Temperature. The effect of pH on the OCA response was investigated by cyclic voltammetry using 0.1 M phosphate buffer containing 0.5 mM OCA at different temperatures and at various pH values ranging from 2.0 to 7.0. Figure 2A shows the cyclic voltammetry responses at 25 °C. As can be seen in Figure 2B, the formal potential, $E^{\circ'} = (E_{\text{p,a}} + E_{\text{p,c}})/2$, of OCA was pH dependent and two linear segments were found with slope values of -0.055 V/pH and -0.029 V/pH in the ranges of $\text{pH} < \text{p}K_{\text{a1}}$ and $\text{p}K_{\text{a1}} < \text{pH} < \text{p}K_{\text{a2}}$, respectively. Based on the procedure described in section 2.2, the intersection of these two linear segments corresponds to $\text{p}K_{\text{a1}}$ of OCAH_2 , and was found to be 5.05 at 25 °C. In order to obtain standard

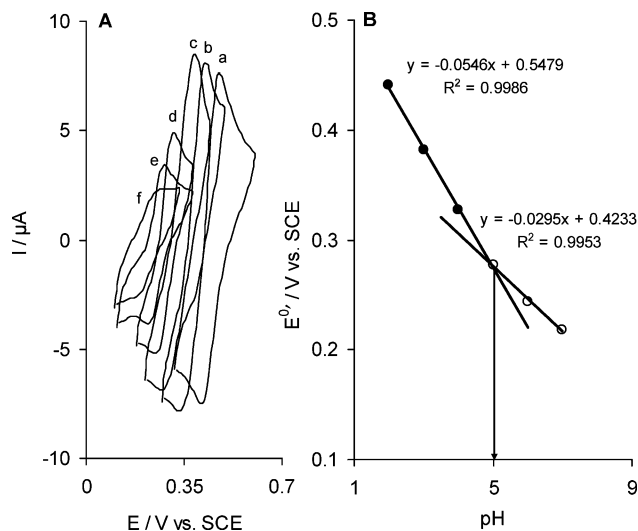


Figure 2. (A) pH dependence of the cyclic voltammetric response (at 25 °C) of a 0.1 M phosphate buffer containing 0.5 mM *o*-chloranil at a glassy carbon electrode. The scan rate is 25 mV s⁻¹. pH values are (a) 2, (b) 3, (c) 4, (d) 5, (e) 6, and (f) 7. (B) Plot of formal potential versus pH.

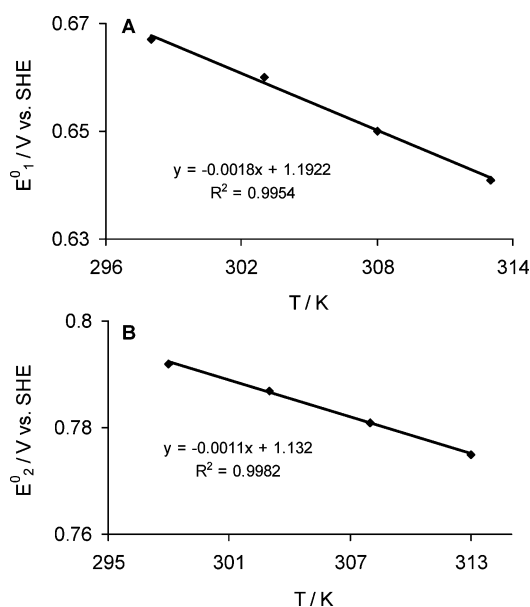


Figure 3. Effect of temperature on the redox potentials of *o*-chloranil. (A) Redox potential for one-proton–two-electron reaction, reaction 1. (B) Redox potential for two-proton–two-electron reaction, reaction 2.

redox potentials of OCA, the formal redox potentials have been extrapolated to pH 0, which corresponds to unit activity of proton in solution, $a_{\text{H}^+} = 1.0$. The standard redox potentials are found to be 0.67 and 0.79 V vs SHE for one-proton–two-electron and two-proton–two-electron reactions, respectively (reactions 1 and 2, respectively). The slope of lines is $-2.303mRT/2F$ as demonstrated in eq 6, where m is the number of protons involved in the redox reaction.

To investigate the effect of temperature, the cyclic voltammetric responses of OCA at various pH values were also studied at elevated temperatures in the range 25–40 °C (Supporting Information, Figures 1s–3s). Figure 3 shows the resulting variation of redox potentials with temperature for each reaction. In both cases the plots were linear, with an R^2 value of not less than 0.995. The slope of E vs T was used to calculate the enthalpy and entropy changes for reactions 1 and 2 using eqs 8

TABLE 1: Experimental Redox Potentials and Thermodynamic Functions for Reactions 1 and 2 for 0.5 mM OCA Aqueous Solution in the Range 25–40 °C (298–313 K)

property	temperature (K)			
	298	303	308	313
E_1^{aq}/V	0.667	0.660	0.650	0.641
E_2^{aq}/V	0.792	0.787	0.781	0.775
$\Delta H_1^{\circ}/\text{kcal mol}^{-1}$	−55.0	−55.0	−55.0	−55.0
$\Delta H_2^{\circ}/\text{kcal mol}^{-1}$	−52.2	−52.2	−52.2	−52.2
$\Delta S_1^{\circ}/\text{cal mol}^{-1} \text{K}^{-1}$	−81.2	−81.2	−81.2	−81.2
$\Delta S_2^{\circ}/\text{cal mol}^{-1} \text{K}^{-1}$	−52.6	−52.6	−52.6	−52.6
$\Delta G_1^{\circ}/\text{kcal mol}^{-1}$	−30.8	−30.4	−30.0	−29.6
$\Delta G_2^{\circ}/\text{kcal mol}^{-1}$	−36.5	−36.3	−36.0	−35.7
$\ln K_1$	52.0	50.6	49.0	47.5
$\ln K_2$	61.7	60.3	58.9	57.5

^a Relative redox potentials vs SHE; the conversion has been carried out using the exact values of SCE at each temperature.³⁴

^b The changes of enthalpies and entropies for reactions 1 and 2, respectively, are temperature independent in the studied range of temperature (linear relation of E vs T , see Figure 3).

and 9, and these are listed in Table 1. The enthalpy changes for these reactions were found to be −55.0 and −52.2 kcal mol⁻¹, respectively. These values are temperature independent in the studied range of temperature and are in agreement with the values of −54.9 and −52.2 kcal mol⁻¹ obtained directly from the slope of line of $\ln K$ vs $1/T$ based on the van't Hoff equation³³ (see Table 1s in the Supporting Information for more details).

From Table 1 it can be observed that under similar conditions the equilibrium constant K_1 is smaller than K_2 even though the absolute value of ΔH° for reaction 1 is greater than the absolute value of ΔH° for reaction 2. The reason for a greater value of K_2 is the contribution of $T\Delta S^{\circ}$ to the Gibbs free energies and therefore to the equilibrium constants. Changes of entropies for reactions 1 and 2 are −81.2 and −52.6 cal mol⁻¹ K⁻¹, respectively, obtained using eq 8. Interestingly, reaction 2 is significantly more entropically favorable than reaction 1, despite the fact that the translational degrees of freedom are reduced on reaction in this case. As we will show in the next section, this is the result of the differing effects of solvation on the two reactions.

3.2. Theoretical Calculations of the Redox Potential. The standard Gibbs free energy change of a redox reaction, $\Delta G^{\circ}(t)$, is related to the absolute reduction potential via eq 10:^{32,33}

$$E^{\circ} = -\Delta G^{\circ}(t)/nF \quad (10)$$

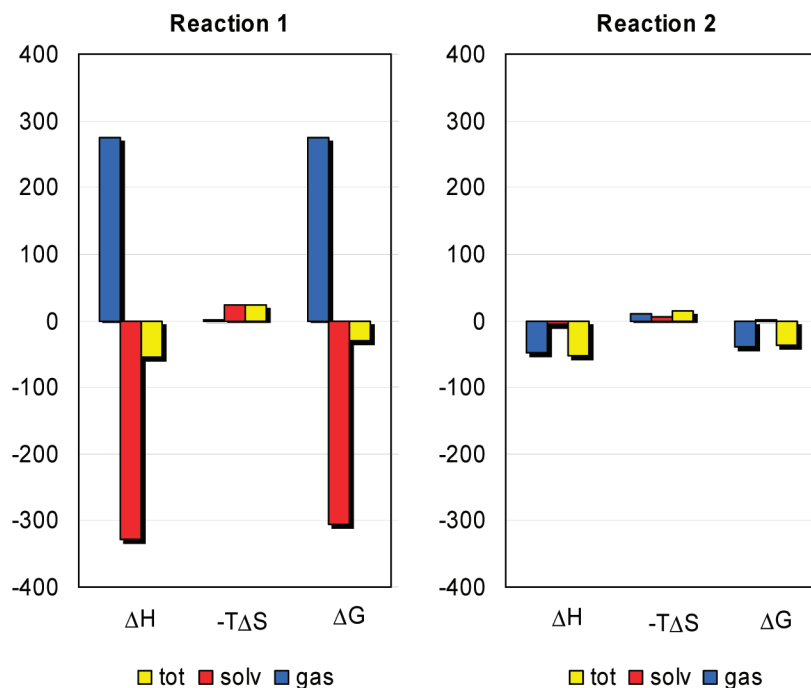
where n is number of electrons transferred and F is the Faraday constant (96 485 C mol⁻¹ or 23.061 kcal mol⁻¹).³³ In order to calculate $\Delta G^{\circ}(t)$, we have used the same methodology that we have reported previously for other quinone derivatives.^{24,26} In short, the total Gibbs energies of studied reactions are the sum of gas-phase Gibbs energies and corresponding total change of Gibbs energies of solvation. As detailed in section 2.3, the gas-phase Gibbs energies are calculated accurately using ab initio calculations at the G3³⁸ and CBS-QB3³⁹ levels of theory; solvation energies are calculated using the CPCM⁴⁰ model of solvation.

Table 2 presents the calculated values of the thermodynamic parameters associated with the various reduction processes. We first note that the values obtained from the G3 and CBS-QB3 methods are in close agreement with one another (within 1 kcal mol⁻¹ or better), which helps to support the validity of these alternative high-level composite procedures. Using the G3

TABLE 2: G3 and CBS-QB3 Calculations of Enthalpy and Gibbs Free Energy of Studied Reactions Together with Calculated/Experimental Redox Potentials at 298 K

	reaction 1		reaction 2		reaction 7	
	G3	CBS-QB3	G3	CBS-QB3	G3	CBS-QB3
$\Delta H^\circ(\text{gas})/\text{kcal mol}^{-1}$	273.9	272.4	-47.2	-48.2	321.0	320.5
$\Delta S^\circ(\text{gas})/\text{cal mol}^{-1} \text{ K}^{-1}$	-5.8	-5.1	-30.3	-30.4	24.5	25.2
$\Delta G^\circ(\text{gas})/\text{kcal mol}^{-1}$	275.6	273.9	-38.2	-39.1	313.7	313.0
$\Delta G^\circ(\text{tot soln})^a/\text{kcal mol}^{-1}$	-30.2	-31.9	-37.3	-38.2	7.1	6.3
$E^\circ(\text{calcd})^b/\text{V}$	0.65	0.69	0.81	0.83	—	—
$E^\circ(\text{expt})^{b,c}/\text{V}$	0.67		0.79		—	

^a Considering changes of Gibbs free energies of solvation of -307.7, 0.9, and -308.6 kcal mol⁻¹ for reactions 1, 2, and 7, respectively, calculated at the CPCM RHF/6-31+G(d,p) level of theory. See Supporting Information for the details of solvation energies. Standard state corrections are also considered.⁴⁷ ^b Standard redox potentials are relative to SHE. ^c Experimental redox potentials have been measured in this work using cyclic voltammetry.

**Figure 4.** Contributions (kcal mol⁻¹) of the gas-phase (gas) and solvation energies (solv) to the total (tot) change of enthalpy (ΔH), entropy (as $-T\Delta S$), and free energy (ΔG) in solution for reactions 1 and 2.

energies, the redox potential for one-proton-two-electron reduction, reaction 1, has been calculated as 0.65 V vs SHE. This value is in good agreement with the experimental value of 0.67 V vs SHE obtained in this work. The redox potential for the two-proton-two-electron reduction, reaction 2, has been calculated as 0.81 V, which shows a deviation of just 0.02 V when compared with the experimental value of 0.79 V. Using the CBS-QB3 energies, the calculated redox potentials are 0.69 and 0.83 V for reactions 1 and 2, respectively, in good agreement with G3 results and experimental values.

While the free energy change of reaction 1 is considerably less than that of reaction 2 in the gas phase, the difference is much smaller in solution, implying that solvation energies play a major role. Indeed, the change of the Gibbs energies of solvation, as calculated at the CPCM RHF/6-31+G(d,p) level of theory, are -307.7 and 0.9 kcal mol⁻¹ for reactions 1 and 2, respectively. The significant difference between these two values is due to the fact that the products of reaction 1 are charged, whereas reaction 2 involves only neutral species.

The components of Gibbs free energy of solvation, $\Delta H^\circ(\text{solv})$ and $\Delta S^\circ(\text{solv})$, can be calculated from the differences between

the solution-phase experimental values and the gas-phase theoretical values, which can be obtained with a high degree of accuracy.

$$\Delta H_i(\text{solv}) = \Delta H_i(\text{tot expt}) - \Delta H_i(\text{gas theory}) \quad (11)$$

$$\Delta S_i(\text{solv}) = \Delta S_i(\text{tot expt}) - \Delta S_i(\text{gas theory}) \quad (12)$$

Using the G3 results from Table 2 for the gaseous thermodynamic quantities, $\Delta H^\circ(\text{solv})$ and $\Delta S^\circ(\text{solv})$ are thus calculated as -328.8 kcal mol⁻¹ and -75.4 cal mol⁻¹ K⁻¹ for reaction 1 and -5.0 kcal mol⁻¹ and -22.3 cal mol⁻¹ K⁻¹ for reaction 2, respectively. These data are plotted in Figure 4 for each reaction.

From Figure 4, it is clear that solvation has a favorable enthalpic effect and an unfavorable entropic effect on both reactions; however, these effects are much more significant for reaction 1 as this reaction involves charged species. Indeed, the solvation effects in this case are so significant as to render this reaction marginally *more* enthalpically favorable than reaction 2, despite being approximately 300 kcal mol⁻¹ more endothermic in the gas phase. These solvation effects also render reaction 1 *less* entropically favorable in solution despite the fact it is *more* entropically favorable in the gas phase as, in contrast to

reaction 2, there is no loss of translational degrees of freedom upon reaction. The net effect of these solvation energies is to bring the overall free energies for reactions 1 and 2 much closer to one another than they are in the gas phase; however, reaction 2 is still favored in solution (at the standard state of pH 0) due to entropic factors.

OCAH₂ is an acidic species and we have determined its pK_a value using cyclic voltammetry as 5.05 in aqueous solution. In the present work, we have also calculated the value of pK_a for this species based on an accurate method reported previously.^{46,47}

Briefly, pK_a of OCAH₂ is related to the total change of Gibbs energy of dissociation of OCAH₂ based on the following equation:⁴⁷

$$\text{p}K_{\text{a}} = \Delta G^{\circ}/(2.303RT) \quad (13)$$

where ΔG° is the total change of Gibbs energy of dissociation. As mentioned earlier, the total Gibbs energies of studied reactions are sums of gas-phase Gibbs energies and corresponding total change of Gibbs energies of solvation for the studied reaction.^{46,47} Using the energies presented in Table 2, the theoretical pK_a value of OCAH₂ has been calculated as 5.2 in pK_a units based on G3 results. The theoretical value is in good agreement with the experimental value of 5.0.

4. Conclusions and Implications

In this work a combination of experimental and theoretical procedures was used to study the electrochemical behavior of *o*-chloranil, OCA, in aqueous solution. OCA is reduced to the corresponding hydroquinone by a one-step, two-electron redox reaction including protonation, and has a formal potential that shifts to increasingly negative values as the pH is increased. The competition between the alternative two-electron—one-proton and two-electron—two-proton processes is pH dependent, with the two-proton process favored at pH < pK_{a1} and the one-proton process favored at pK_{a1} < pH < pK_{a2}. The standard redox potentials (i.e., at pH 0) for the one- and two-proton processes are 0.67 and 0.79 V, respectively. The first acidic dissociation constant of the reduced form of OCA (K_{a1}) was also measured as 5.0 at 298 K.

A key finding of this work was the important contribution of solvation energies to the overall reaction energetics, and to the competition between the one- and two-proton processes. For the one-proton process, which involves charged species, the effects of solvation are so significant as to render it marginally more enthalpically favorable than the two-proton process, despite being approximately 300 kcal mol⁻¹ more endothermic in the gas phase. At the same time, solvation effects render the two-proton process more entropically favorable, despite being less entropically in the gas phase due to the resulting translational degrees of freedom. It is this difference in reaction entropy that ultimately governs the competition between the one- and two-proton reduction processes at standard conditions.

This significant role of solvation energies and pH in governing not only the reduction potential but also the reduction mechanism of OCA is likely to be applicable to the reduction of other catechol derivatives. It also seems reasonable to suppose that the competition between two-electron and deleterious one-electron reduction of quinones, of key importance in biological systems, will also be strongly dependent on pH and solvation effects. This has important implications for the applicability of aqueous solution studies to biological systems, with care needed to match the experimental conditions to those in the interior of the enzyme. With this caveat, the present results tentatively support the hypothesis⁴⁸ that, at biological pH, the two-electron

reduction of quinones is a one-proton process, at least for OCA (since the crossover point, pK_{a1}, was measured to be 5.0).

As part of this work, high-level ab initio molecular orbital calculations were used to calculate the standard redox potentials and first acidic constant of OCAH₂. All theoretical calculations were in excellent agreement with experiment (within 0.02 V and 0.2 pK_a units, respectively), mutually verifying the experimental and theoretical studies. Since most quinone derivatives possess one-proton—two-electron and two-proton—two-electron redox reactions in aqueous solution, the theoretical methodology benchmarked here should be widely applicable to other quinone derivatives.

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Supporting Information Available: Cyclic voltammetric responses as a function of pH and temperature; temperature dependence of the equilibrium constants for the two redox processes studied; van't Hoff analysis of the experimental data; complete optimized geometries of all species and corresponding total energies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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