

Substituent effects on the activation parameters of the reaction between 1,4-benzoquinones and hydrogen peroxide: A combined experimental and theoretical study

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ARTICLE INFO

Article history:

Received 28 December 2021

Revised 18 March 2022

Accepted 22 March 2022

Available online 23 March 2022

Keywords:

Rate equation

Oxidative degradation

Hydroxy-quinone

Density functional theory

Hammett correlation

ABSTRACT

Experimental and theoretical results on the aqueous reactions of various substituted 1,4-benzoquinone derivatives (2-*tert*-butyl-, 2-methyl-, 2-chloro-, 2,6-dichloro- and the unsubstituted 1,4-benzoquinone) are reported. The rate law of the process was confirmed to be first order with respect to the quinone, first order with respect to hydrogen peroxide, and inverse first order with respect to hydrogen ion, which is interpreted by a rate controlling reaction between the quinone and the mononegative hydroperoxide ion. Activation parameters are reported for each substituted quinone except for the 2-*tert*-butyl derivative, where the influence of parallel and consecutive processes made it impossible to determine these kinetic parameters with satisfactory precision. The trend of the activation parameters was interpreted by Hammett correlation. In the quantum chemical studies, the M06-L functional along with the 6-311+G(d,p) basis set was used to optimize the relevant structures including the transition states of the rate controlling step. The results of the theoretical calculations were in reasonable agreement with the experimental findings.

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1. Introduction

1,4-Benzoquinone derivatives form a versatile family of compounds, which have notable significance in a number of (bio)chemistry-related fields. Ubiquinone plays a vital role in the respiration apparatus [1], plastoquinone and phyloquinone are important parts of the photosynthetic process [2,3]. Vitamin K, which is vital to humans, also refers to a group of compounds with the 1,4-benzoquinone structural motif [4,5]. Natural dyes lawsone [6] and alizarin [7] also have quinoidal structures. In the chemical industry, millions of tons of hydrogen peroxide are produced each year through a refined process relying on anthraquinone [8]. Chloro-

ranil (tetrachloro-1,4-benzoquinone) is a commonly used oxidizing agent in organic chemistry [9], whereas water suitable anthraquinones are promising candidates for use in flow batteries because of their highly reversible redox transformations [10,11].

Quinones appear in the oxidative degradation pathway of most aromatic compounds; they are often accumulating intermediates [12]. They are also known to be sensitive to light [13,14,15,16,17,18,19,20,21,22,23,24,25], which contributes to their significance in photosynthesis, but also complicates non-photochemical degradation studies of pollutants. It was confirmed that kinetics of the oxidative removal of chlorinated phenols in water is highly sensitive to light, even ambient light alters the observations quite significantly [23]. It was also shown that this is caused by the photosensitivity of chlorinated quinones, which appear as high-concentration intermediates in the process [23]. Detailed studies showed that the aqueous photoreactions of quinones produce a mixture of hydroquinones and hydroxyquinones, so there is a competition between reduction and hydroxylation [24]. The overall quantum yield is close to 1, and the reduction pathway produces oxygen, so this system was identified as a potential candidate in the chemical storage of the energy of light [26,27].

Abbreviations: IRC, Intrinsic reaction coordinate; Q, 1,4-benzoquinone; QCl, 2-chloro-1,4-benzoquinone; Q-2,6-Cl₂, 2,6-dichloro-1,4-benzoquinone; QMe, 2-methyl-1,4-benzoquinone; Q-2,6-Me₂, 2,6-dimethyl-1,4-benzoquinone; Q-2,6-OMe₂, 2,6-dimethoxy-1,4-benzoquinone; Q-2,3-OMe₂-5-Me, 2,3-dimethoxy-5-methyl-1,4-benzoquinone; Q^tBu, 2-*tert*-butyl-1,4-benzoquinone; QR, 1,4-benzoquinone derivative; QR-OH, hydroxy-1,4-benzoquinone derivative; SMD, Solvation Model Based on Density.

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Table 1

Detection wavelength (λ), ϵ , temperature dependent k , k_b and activation parameter values for different substituted 1,4-benzoquinone derivatives.

Derivative		Q-2,6-Cl ₂	QCl	Q	QMe	Q _t Bu
λ (nm)		524	510	480	Details of the calculations are in Ref. 22	291
ϵ_{QR} (M ⁻¹ cm ⁻¹), ϵ_{QR-O^-} (M ⁻¹ cm ⁻¹)		0, 2530**	28, 823*	24, 1703*		15640, 0
$10^{-3} \times c(QR)$		0.50	0.99	0.99		Various
$c(H_2O_2)$		0.054	0.036	0.054		
pH		6.37	6.38	6.36		
$10^8 \times k$ (s ⁻¹), $10^{-4} \times k_b$ (M ⁻¹ s ⁻¹)	10 °C	6.93, 6.47	7.53, 7.02	0.631, 0.588	-	-
	15 °C	-	-	-	-	0.09, 0.06
	20 °C	12.4, 6.96	13.9, 7.81	1.21, 0.682	-	0.09, 0.051
	25 °C	16.0 , 7.15	19.0 , 8.48	1.78 , 0.794	0.346* , -	0.13 , 0.059
	30 °C	-	25.4, 9.00	2.38, 0.846	-	0.14, 0.051
	35 °C	-	-	3.34, 0.941	-	0.20, 0.057
	40 °C	35.3, 8.09	-	4.87, 1.12	-	0.30, 0.068
E_a (kJ mol ⁻¹)		5.5±0.3	8.9±0.6	15.3±0.4	18.4*	-
$\Delta H^\ddagger$ (kJ mol ⁻¹)		3.0±0.3	6.5±0.6	12.9±1.3	15.9*	-
$\Delta S^\ddagger$ (J mol ⁻¹ K ⁻¹)		-142±1	-128±2	-127±4	-129*	-
$\Delta G^\ddagger$ (kJ mol ⁻¹) at 25 °C		45.4±0.3	44.7±0.8	51±1	54.4*	-

*Data from [Ref. 22] **Data from [Ref. 28].

However, the hydroxylation pathway is a dead end in this process, which shortens the lifetime and decreases the efficiency. Therefore, methods to suppress the formation of hydroxyquinones must be sought.

Follow-up studies showed that hydroxyquinones are also formed from 1,4-benzoquinones in a non-photochemical reaction with hydrogen peroxide [22,28]. This process gave an important way of studying the properties of the hydroxylated products independently of the photochemistry of quinones. Initial results on the rate law of the process were published [28], and a later study connected the reactivities of various substituted quinone derivatives to the redox potential of the corresponding two-electron quinone-hydroquinone electron transfer process [22].

The present study aims to broaden the scope of earlier studies by reporting kinetic details of the reactions between hydrogen peroxide and a number of substituted quinones. The substituents were chosen so that both electron-withdrawing and electron-donating ones are included. Quantum chemical calculations are also reported to interpret the experimental findings.

2. Experimental

2.1. Materials

Solid 1,4-benzoquinone (Q) and its derivatives (QR) were purchased from Alfa Aesar and used as received. The substituents on the benzoquinone ring were selected such that they provided a reasonably large range of electron withdrawing and electron properties but still had an aqueous solubility sufficient for detailed studies. The concentrations of the aqueous stock solutions used for the kinetic experiments were typically 1×10^{-3} mol dm⁻³. 1,4-Benzoquinones are photosensitive compounds in aqueous solution. Therefore, fresh solutions in water were prepared for all experiments in brown glass volumetric flasks. As the aqueous solubility of these quinones is not very high, the dissolution of the solid Q and QRs was aided using an EMMY-40-HC-EMAG ultrasonic bath at room temperature. The concentrations of the solutions were calculated based on the mass of the solid and the volume of the solution prepared.

30% (w/w) hydrogen peroxide solution (analytical grade, purissimum) was purchased from VWR. The accurate concentrations of

the solutions used for the oxidation experiments were determined by permanganometric titrations.

The investigated oxidation reactions were proved to be sensitive to pH. Therefore, NaH₂PO₄/Na₂HPO₄ buffer solutions were prepared using sodium dihydrogen phosphate dihydrate (analytical grade, Normapur) and di-sodium hydrogen phosphate dodecahydrate (analytical grade, Normapur), both purchased from VWR. In the absence of any buffer, the pH of the solution becomes acidic during the measurements because of the acidic proton in the product hydroxyquinone. So, most kinetic curves were measured in aqueous buffered solutions at pH = 6.4.

2.2. Instruments and softwares used for temperature dependent kinetic measurements

The pH values of the buffered benzoquinone solutions were measured with a Metrohm hydrogen ion selective glass electrode connected to an ABU 93 Triburette.

A Shimadzu UV-1601 double beam spectrophotometer with a TCC-240A thermostat and UV-Probe software was used for the kinetic study on the formation of hydroxyquinones. For every quinone derivative, only one wavelength at the maximum absorbance of the product in the visible range was used to follow the reaction. These wavelength values are listed in Table 1.

The reactions were measured in 1.00-cm path length quartz cuvettes in the 10–40 °C temperature range. For the temperatures other than room temperature, a 10-min pre-thermostating period of the samples was used before the kinetic measurements.

The least squares fitting of the measured data was carried out using the general fitting software MicroMath SCIENTIST [29].

2.3. Spectrophotometric determination of pK_a for the tert-butyl derivative of hydroxy-1,4-benzoquinone

For the determination of the pK_a values of the hydroxyquinone derivative of 2-tert-butyl-1,4-benzoquinone, the solution was prepared by adding H₂O₂ to 1×10^{-4} mol dm⁻³ aqueous solutions of 2-tert-butyl-1,4-benzoquinone at different pH values. The pH (in the range 5.59–9.20) was set using phosphate buffers. Oxidation of these samples was followed by spectrophotometry. The MicroMath SCIENTIST program [29] was used to evaluate the data at 291 nm. It was found that at pH higher than 8, rapid polymerization reaction [24,30] of the hydroxyquinone derivative affects the spectra.

As a result, only the data points at $\text{pH} < 8$ were used for calculation of the pK_a .

2.4. NMR measurements

^1H NMR spectra were measured on a BRUKER DRX 400 instrument operating at 400 MHz and at 25 °C. As a solvent, 99.99% D_2O (for the 2-methyl-1,4-benzoquinone only) or $\text{H}_2\text{O}:\text{D}_2\text{O} = 70:15$ (after the addition of the oxidant) was used. The pH of the solution was kept constant using a 0.50 mol dm^{-3} phosphate buffer (pH 6.3). Chemical shifts were referenced to the water signal. For the evaluation of the spectra, the MestReNova NMR software was used.

2.5. Theoretical calculations

For all the calculations, the Gaussian 16 software package was employed [31]. All structures were fully optimized employing the M06-L functional developed by Truhlar and Zhao along with the 6-311+G(d,p) basis set [32,33]. The M06-L functional was found to be accurate for main group thermochemistry and it is especially accurate for systems with noncovalent interactions [34]. The stationary points were characterized by frequency calculations to verify that they have zero imaginary frequencies for equilibrium geometries and one imaginary frequency for transition states. Thermochemistry corrections were taken from frequency calculations at 298.15 K and 1 bar. Intrinsic reaction coordinate (IRC) analyses [35] were carried out throughout the reaction pathway to confirm that the stationary points are smoothly connected to each other. The effect of the solvent was taken into account utilizing the SMD solvation model, introduced by Marenich, Cramer, and Truhlar [36], with the dielectric constant of $\epsilon_r(\omega) = 78.3553$ for water. The SMD method is based on the charge density of a solute molecule interacting with the solvent represented as continuum. The full solute electron density is employed without the definition of partial atomic charges, therefore the “D” stands for “density” in the abbreviation of the model.

The choice of the computational model was based on our previous experience with water-phase systems. [37] For the prediction of the Hammett constant via proton transfer free energies, we studied several functionals, including M06, M062X, and B2PLYP (as well as several solvation models) and M06-L proved to be the most accurate one especially when combined with Pople basis sets.

3. Results and discussion

3.1. Kinetic measurements, determination of the activation parameters

The reaction between benzoquinone derivatives and hydrogen peroxide was measured for different substituted benzoquinones. The reaction itself together with the mechanisms is well-known [22,28]. The 2-*tert*-butyl-, 2-methyl-, 2-chloro-, 2,6-dichloro- and the unsubstituted 1,4-benzoquinone show the following reaction stoichiometry and rate law:



$$\nu = k \cdot \frac{[\text{QR}] \cdot [\text{H}_2\text{O}_2]}{[\text{H}^+]} = k_{\psi 1} \cdot [\text{QR}] \quad \text{where } k_{\psi 1} = k \cdot \frac{[\text{H}_2\text{O}_2]}{[\text{H}^+]} \quad (2)$$

In our experiments, the concentration of the oxidizing agent H_2O_2 was always much higher than that of the benzoquinone derivative, so the concentration of the oxidant was practically constant (i.e. the kinetic method of flooding was used). The pH of the

solutions was also kept constant with buffers. Consequently, the kinetic traces could be fitted with a single exponential function giving the pseudo-first order rate constant, $k_{\psi 1}$ as a parameter of the curve:

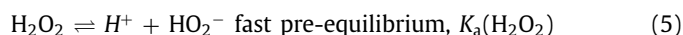
$$\nu = \frac{1}{\Delta \epsilon \cdot l} \cdot \frac{dA}{dt} = k_{\psi 1} \cdot [\text{QR}] \quad \text{or} \quad \frac{dA}{dt} = (\epsilon \cdot l \cdot [\text{QR}]_0 - A) \cdot k \cdot \frac{[\text{H}_2\text{O}_2]}{[\text{H}^+]} \quad (3)$$

where ϵ is the molar absorption coefficient of the hydroxyquinone at the wavelength of the measurement (see: Table 1) and at the pH of the kinetic run, $\Delta \epsilon$ is the difference between the molar absorption coefficients of QR-OH and QR at the wavelength of the measurement and the pH of the measurement, and l is the path length of the cuvette (1.000 cm). The solution of Eq. (3) is as follows:

$$A = \epsilon \cdot l \cdot [\text{QR}]_0 - \Delta \epsilon \cdot l \cdot [\text{QR}]_0 \cdot e^{-kt \frac{[\text{H}_2\text{O}_2]}{[\text{H}^+]}} \quad (4)$$

Based on the rate equation, k values for the different substituted derivatives were determined at different temperatures in the 10–40 °C range. The k values are collected in Table 1 together with some other measured parameters for the different derivatives.

The rate equation described in Eq. (2) is explained by the following two-step mechanism, in which reaction (5) is a rapid pre-equilibrium [22,28]:



Based on the mechanism, the rate constant of the rate determining step, k_b can be calculated as follows:

$$k_b = \frac{k}{K_a(\text{H}_2\text{O}_2)} \quad (7)$$

The k_b values for the different derivatives can be calculated using the temperature dependent k values from the exponential curve fitting and the temperature dependent $\text{pK}_a(\text{H}_2\text{O}_2)$ values [38]. The activation parameters for the rate determining step can be calculated from the Eyring and Arrhenius plots of the temperature dependent k_b values. These parameters are also listed in Table 1. The activation parameter values for another derivative, 2-methyl-1,4-benzoquinone published earlier are as follows: $E_a = 18.4 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 15.9 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -129 \text{ J mol}^{-1} \text{ K}^{-1}$ and $\Delta G^\ddagger$ (at 25 °C) = 54.4 kJ mol^{-1} [22].

The difficulty of these measurements is that the oxidation reaction does not stop when the original quinone is fully consumed. The excess of H_2O_2 oxidizes also the hydroxyquinone further [22].

In the case of the 2-*tert*-butyl-1,4-benzoquinone (QtBu), there are many experimental difficulties: (i) the oxidation reaction is slow compared to the same reaction of the other derivatives (see the k values at 25 °C in Table 1, with bold letters) and, since the substance is quite sensitive to light in aqueous solutions, the light-induced photoreaction should also be taken into correction during the evaluation of the kinetic traces. (ii) The reaction can be followed at a relatively short wavelengths (250 nm, the absorption maximum of QtBu, or 291 nm, the absorption maximum of QtBu-OH) where H_2O_2 also has a substantial absorbance, so, the increase of the H_2O_2 concentration is not a viable path to speed up the oxidation reaction. (iii) Increasing the pH is not a good way to accelerate the reaction, either, because at basic pH, a polymerization reaction of the hydroxy-1,4-benzoquinone derivatives occurs [24,30]. (iv) The increase of the 2-*tert*-butyl-1,4-benzoquinone concentration is limited by its relatively low solubility in water. (v) Since the reaction is slow and cannot be accelerated substantially (see

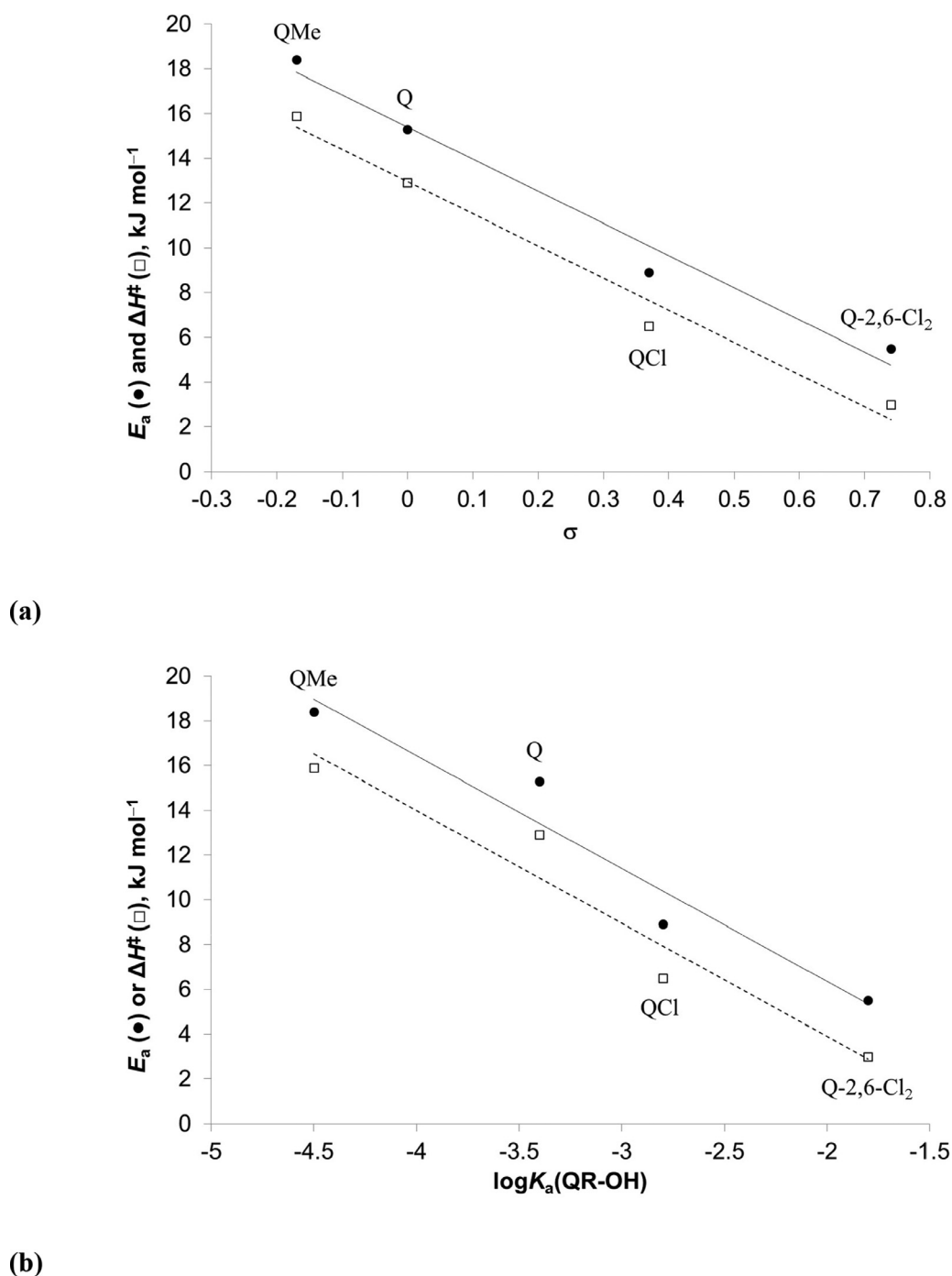


Fig. 1. Activation parameters in the 1,4-benzoquinone + H₂O₂ reaction plotted as a function of Hammett substituent constants (a), and as a function of $\log K_a(\text{QR-OH})$ (b).

the reasons listed before), the less accurate initial rate method had to be used instead of full kinetic curves. Because of all these experimental difficulties, although the rate constant of the reaction can be determined with an acceptable precision ($k = (1.3 \pm 0.1) \times 10^{-9} \text{ s}^{-1}$ at 25 °C), the error of the activation parameters is too high for a meaningful comparison.

Some other substituted 1,4-benzoquinone derivatives, namely: 2,6-dimethyl-1,4-benzoquinone (Q-2,6-Me₂), 2,6-dimethoxy-1,4-benzoquinone (Q-2,6-OMe₂) and 2,3-dimethoxy-5-methyl-1,4-benzoquinone (Q-2,3-OMe₂-5-Me) were also measured with H₂O₂. For these derivatives, however, the hydroxyquinone was not detectable either because its formation was too slow compared to its

decomposition (Q-2,6-Me₂), or, because the oxidation affected the OMe substituent instead of the benzoquinone ring (Q-2,6-OMe₂ and Q-2,3-OMe₂-5-Me).

3.2. Substituent effect on the activation parameters

Substituent effects have been evaluated primarily through electronic effects as described in Hammett correlations [39,40,41]. Hammett substituent constants (σ) for the investigated 1,4-benzoquinone derivatives were taken from [42] and these are as follows: $\sigma(\text{QtBu}) = -0.200$, $\sigma(\text{QMe}) = -0.170$, $\sigma(\text{QCl}) = 0.370$ and $\sigma(\text{Q-2,6-Cl}_2) = 0.740$. It is seen that these values span a range of

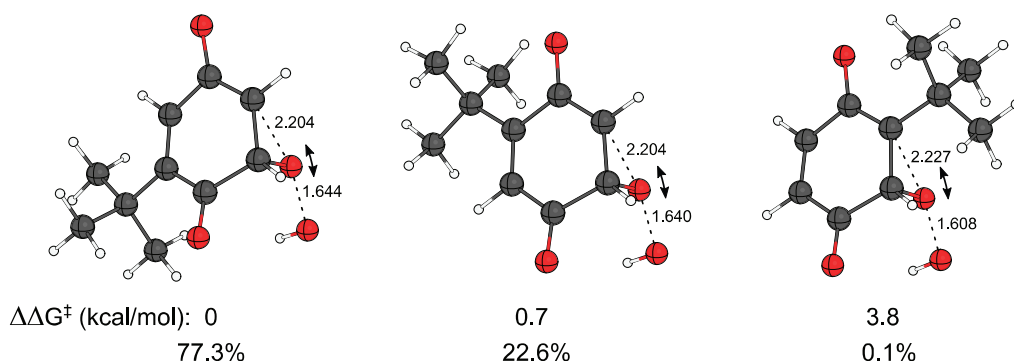


Fig. 2. Computed structures and their relative Gibbs free energies of the *tert*-butyl substituted transition states describing the nucleophilic attack of the hydroperoxyl anion. The bottom line shows the expected population ratios based on Boltzmann distribution. Bond distances are given in Å.

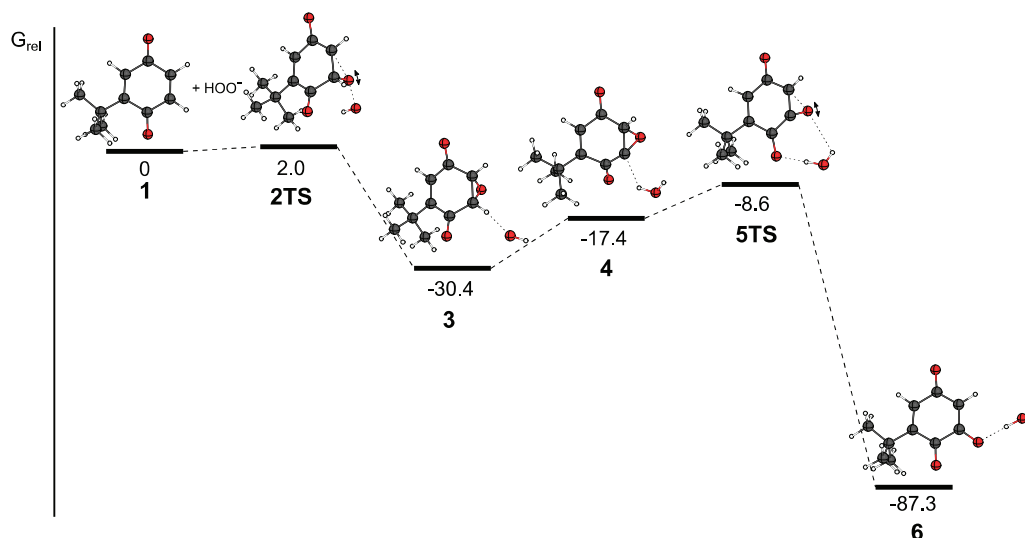


Fig. 3. Free energy profile for the formation of *tert*-butyl-hydroxyquinone (deprotonated, with one explicit water) from 2-*tert*-butyl-1,4-benzoquinone. Gibbs free energy values are given in kcal mol⁻¹.

about 1.0, which is usually sufficient to draw meaningful conclusions for the sensitivity of the studied reaction for electron withdrawing and donating effects. In Fig. 1(a), activation parameters are plotted *versus* the Hammett substituent constants. The other plot (Fig. 2(b)) demonstrates the correlation between the log K_a values of the hydroxy-1,4-benzoquinones (6.5(±0.1) for QtBu-OH, 4.5 for QMe-OH [22], 3.4 for Q-OH [22], 2.8 for QCl-OH [22] and 1.8 for Q-2,6-Cl₂-OH [22]) and the activation parameters determined in this work. It is important to note that for the temperature-dependent kinetic measurements, the pH value (pH 6.4) was set so that the hydroxy-1,4-benzoquinone product of the reaction is always overwhelmingly in the RQ-O⁻ (deprotonated) form (except for QtBu-OH, where the initial rate method was used instead of full kinetic traces, as explained earlier).

As we can see from the activation parameter data of Table 1, the activation entropy, $\Delta S^\ddagger$ depends on the number of substituents on the 1,4-benzoquinone ring (approx. -128 J mol⁻¹ K⁻¹ for mono- and -142 J mol⁻¹ K⁻¹ for disubstituted derivatives). The other activation parameters, however, depend on the electron donating or withdrawing effects of the substituents. When these parameters are plotted against σ , a fairly good linear correlation can be seen with E_a and $\Delta H^\ddagger$. Earlier studies with the peroxomonosulfate ion showed that the entropy of activation is typically slightly more negative than -100 J mol⁻¹ K⁻¹ when it oxidizes in an oxygen

atom transfer pathway; the data presented here seem to be in agreement with this finding [43].

3.3. Theoretical calculations

The reaction of benzoquinones and hydrogen peroxide can be interpreted as the nucleophilic attack of the hydroperoxyl anion on one of the methylene carbons which are somewhat activated by the electron withdrawing character of the carbonyl groups. For the unsubstituted benzoquinones, all the four methylene carbons are equivalent, however, the inclusion of the *tert*-butyl group provides three possible sites for the nucleophilic attack with three transition states for the individual reaction channels (see Fig. 2).

The activation free energy is 0.7 kcal mol⁻¹ (3.0 kJ mol⁻¹) larger when the HOO⁻ group is directed in the γ -position, instead of the β -position, and notably larger (3.8 kcal mol⁻¹, 15.9 kJ mol⁻¹) for the α -position. This is in contrast with the reactivity sequence for the methyl substituent where the γ -attack is preferred (by 1.7 kcal mol⁻¹, 7.1 kJ mol⁻¹) over the β -attack, in agreement with the previous experiments, followed by the barrier for the α -attack (3.6 kcal mol⁻¹, 15.1 kJ mol⁻¹). For 2-chloro-1,4-benzoquinone, the HOO⁻ anion prefers to react with the γ -carbon as well. Interestingly, the second most preferred position for the nucleophilic attack is the α -position, with a difference in free energy barrier of 0.3 kcal mol⁻¹ (1.3 kJ mol⁻¹) and the least preferred site is

the β -carbon ($1.4 \text{ kcal mol}^{-1}$, 5.9 kJ mol^{-1}). It should be noted that for the chloro-substituted 1,4-benzoquinone all the three pathways are feasible albeit to different extents. For 2-methyl-1,4-benzoquinone, the nucleophilic attack takes place on the γ -carbon, whereas for the *tert*-butyl derivative, the β -attack is preferred, but the route via the γ -attack cannot be excluded either.

The reaction mechanism was computed for the reaction of 2-*tert*-butyl-1,4-benzoquinone with the HOO^- group and the free energy diagram is depicted in Fig. 3. The free energy profile shows close resemblance with the unsubstituted case [22], with similarly overall (highly negative) reaction free energies.

As discussed above, the nucleophilic attack of the hydroperoxyl anion leads to the formation of the oxirane derivative **3** via transition state **2TS**. As this elementary step is highly exergonic and irreversible, it can be considered as the selectivity determining step. In basic environment, the oxirane reacts with the OH^- ion, losing the more weakly bound hydrogen in 6-position, affording the unstable intermediate **4**. Species **4** undergoes a ring opening reaction, assisted by the explicit water molecule via **5TS** leading to the deprotonated form of the *tert*-butyl-hydroxyquinone product in a highly exergonic step. The step **3** $\rightarrow$ **4** $\rightarrow$ **5TS** $\rightarrow$ **6** is the rate determining step with an overall barrier of $21.6 \text{ kcal mol}^{-1}$ (90.4 kJ mol^{-1}).

4. Conclusion

From both the experimental and theoretical results presented in this paper, it is clear that the rate controlling step of the reaction between hydrogen peroxide and 1,4-benzoquinones involves a nucleophilic attack of the hydroperoxide ion (HO_2^-) on the benzoquinone ring. This attack is only feasible on carbon atom that are bonded to a hydrogen atom. Electron withdrawing substituents decrease the activation energy, whereas electron donating ones increase it. The activation parameters and the pK_a values of the product hydroxy-quinones correlate quite nicely with the Hammett substituent constants, which implies that electronic effects dominate the mechanism.

A further interesting implication of the findings is relevant to the possible use of quinones in photochemical energy storage. Derivatives of 1,4-benzoquinone are known to undergo photochemical reduction in aqueous solution with the simultaneous formation of dioxygen. The overall efficiency and the quantum yield of the process is usually enhanced by the presence of electron withdrawing substituents on the quinone. In this process, the formation of the hydroxy-quinone in side reactions is a dead end and should be suppressed. However, the present study shows that the electron-withdrawing substituents also facilitate this side reaction. As a consequence, in a general strategy, attempts must be made to lower the losses to this side reaction by a suitable application of steric effects.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Éva Józsa: Investigation, Formal analysis. **Laura Barbara Jenei:** Investigation, Formal analysis. **Tamás Kégl:** Investigation, Formal analysis, Writing – original draft. **Katalin Ósz:** Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing, Funding acquisition.

Acknowledgements

The research work performed by Éva Józsa for this manuscript was supported by the European Union and the State of Hungary, co-financed by the European Social Fund in the framework of TÁ-MOP 4.2.4. A/2–11–1–2012–0001 ‘National Excellence Program’.

This work was supported by NTP-HHTDK-20–0056.

This work was supported by the Higher Education Institutional Excellence Programme of the Ministry of Human Capacities in Hungary, within the framework of the 1st thematic program of the University of Pécs (2020–4.1.1-TKP2020).

The authors wish to thank Gábor Lente for helpful discussions.

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