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Methyl- and *tert*-Butyl-Substituted Hydroquinones and Semiquinone Radicals: Bond Strength Estimates, Enthalpy of Formation, and the Rate Constants of Their Reactions with Peroxy Radicals

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Abstract—The strength of the O–H bonds (D) in hydroquinone (HQH) and its alkyl derivatives has been estimated by the intersecting parabolas method using rate constants known for the reactions of these compounds with the styrene peroxy radical. For unsubstituted HQH, $D = 352.6$ kJ/mol; for substituted HQH derivatives, $D = 349.9$ (Me), 346.9 (2,5-Me_2), 343.0 (Me_3), 347.6 (CMe_3), and 340.2 (2,5-$(CMe_3)_2$) kJ/mol. The enthalpies of formation of these HQH derivatives have been calculated. The O–H bond strengths in the semiquinone radicals ($HQ^\bullet$) resulting from the above HQH derivatives have been calculated using a thermochemical equation to be $D_{HQ^\cdot} = 236.7$, 237.4, 239.8, 244.7, 240.1, and 247.5 kJ/mol, respectively. Rate constants have been determined for the reactions of the hydroquinones with tertiary and secondary peroxy radicals and $HOO^\bullet$ at 323 K. The rate constants of the reactions between $HOO^\bullet$ and benzoquinones and the relative reactivities of the $HQ^\bullet$ radicals in their reactions with $ROO^\bullet$ have been estimated.

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The inhibited oxidation of organic compounds with hydroquinone (1,4-dihydroxybenzene, HQH) and its derivatives is a multistep composite reaction. Its specific feature is the nonstoichiometric consumption of the inhibitor [1–3]. For substituted HQHs, the inhibition coefficient is <1 because of the interaction between the semiquinone radical ($HQ^\bullet$) and oxygen [2]:

$$ROO^\bullet + HQH \xrightarrow{k_1} ROOH + HQ^\bullet, \quad \text{(I)}$$

$$ROO^\bullet + HQ^\bullet \xrightarrow{k_2} ROOH + Q, \quad \text{(II)}$$

$$HQ^\bullet + O_2 \longrightarrow HOO^\bullet + Q.$$

Here, the ultimate oxidation product is benzoquinone (Q). The $HOO^\bullet$ radical is active not only in chain propagation reactions but also in reactions with HQH and its oxidized forms. In this process, which involves both the $ROO^\bullet$ radical of the substrate being oxidized and the $HOO^\bullet$ radical, the oxidation rate shows a very complicated dependence on reactant concentrations. This makes it impossible to derive, from experimental data, the relative and, therefore, absolute values of reaction rate constants. Computer simulation of this oxidation process is also impossible, because the rate constants of several steps are unknown.

Here, we use the intersecting parabolas model (IPM) [4, 5] to calculate bond strengths for alkyl-substituted hydroquinones and for the corresponding semiquinone radicals, as well as the rate constants of their reactions with peroxy radicals with various structures.

The bond strength (D) in the molecules and radicals, their enthalpy of formation ($\Delta_f H^0$,g), and activation energy (E) will be expressed in kJ/mol; bimolecular rate constants (k), in l mol^{-1} s^{-1}. Hereafter, the dimensions of these quantities are omitted.

COMPUTATIONAL PROCEDURE

The bond dissociation energy D_i in HQH was calculated in terms of IPM using the known rate constant k_1 [4, 5] as follows.

The activation energy of reaction (I) was derived from experimental data using the Arrhenius formula

$$E = RT\ln(nA_0/k_1), \quad (1)$$

where n is the number of equivalent reacting atoms (n = 2 for HQH) and A_0 is the preexponential factor specific to a group of similar reactions.

Table 1. Strength of the O–H bonds (D) in hydroquinones (HQH) and semiquinone radicals (HQ$^\bullet$) and the enthalpies of formation of these species in the gas phase (ΔH) in kJ/mol

Entry	Substituent in HQH	D_i		$-\Delta H_{HQH}$	$-\Delta H_Q$	$D_{HO^\bullet}$	
		calculated data	reference data			calculated data	reference data
1	–	352.6	352.0 [4]	274*	121.3 [9]	236.7	226.3 [5]
2	Me	349.9	349.8 [4]	306.4	155.2 [9]	237.4	229.8 [5]
3	2.5-Me$_2$	346.9	–	339.0	188.3 [9]	239.8	229.5 [5]
4	Me$_3$	343.0	344.7 [4]	371.6	219.9**	244.7	–
5	CMe$_3$	347.6	–	375.2	223.5**	240.1	–
6	2.5-(CMe$_3$)$_2$	340.2	337.3 [6]	476.6	324.9**	247.5	–

*According to [10], $\Delta H = 277$.

**Data calculated using the increment $\Delta H = \Delta H_{HQH} - \Delta H_Q = -151.7$.

The true activation energy E_e, which includes the zero-point vibration energy for the O–H bond in the molecule, is related to E by the expression

$$E_e = E + 0.5hL\nu_i - 0.5RT, \quad (2)$$

where h is Planck's constant, L is Avogadro's number, and ν_i is the vibrational frequency of the breaking bond.

The enthalpy of a reaction (ΔH_e) depends on the heat of the reaction ($\Delta H = D_i - D_f$) and on the difference between the zero-point vibration energies of the breaking (i) and forming (f) bonds:

$$\Delta H_e = D_i - D_f + 0.5hL(\nu_i - \nu_f). \quad (3)$$

For the tertiary and secondary hydroperoxides and H_2O_2, the strengths of the ROO–H bonds forming in reaction (I) are $D_f = 358.6$, 365.5, and 369.0, respectively [4, 5]. Knowing D_i and k_1 for HQH, one can determine E_e (Eq. (2)), ΔH_e (Eq. (3)), and the parameter br_e:

$$br_e = \alpha(E_e - \Delta H_e)^{1/2} + E_e^{1/2}. \quad (4)$$

Here, $b \equiv b_i$ ($2b^2$ is the force constant of the Q–H bond), r_e is the distance between the minima of the parabolas, and $\alpha = b_i/b_f$.

The necessary calculated parameters (A_0, $0.5hL\nu_i$, α, and br_e) are known for this group of reactions [4, 5]. Furthermore, br_e = const. Therefore, using Eqs. (1), (2), and (4), it is possible to derive ΔH_e from k_1. The D_i value can be determined from relationship (3).

If D_i and D_f are known and k_1 is unknown, then, knowing ΔH_e (Eq. (3)), one can find E_e from the formula [4, 5]

$$\sqrt{E_e} = \frac{br_e}{1-\alpha^2}\left\{1-\alpha\left[1-\frac{1-\alpha^2}{(br_e)^2}\Delta H_e\right]^{1/2}\right\} \quad (5)$$

and calculate k_1 using relationships (2) and (1).

RESULTS AND DISCUSSION

Strength of the H–O bonds in alkyl-substituted hydroquinones. The values of k_1 for reaction (I) were determined experimentally by oxidizing styrene. The styrene peroxy radical has a secondary structure; therefore, $D_f = 365.5$ for the forming ROO–H bond. For hydroquinone (HQH) at 323 K, $k_1 = 4.85 \times 10^5$ [2]. For 310 K, the following k_1 data are known [3]: HQH, 5.54×10^5; mono-*tert*-butylHQH, 1.2×10^6; MeHQH, 7.13×10^5; 2,5-Me$_2$HQH, 1.19×10^6; Me$_3$HQH, 2.32×10^6.

The parameters calculated for reaction (I) are the following: $\alpha = 1.014$, $A_1 = 6.4 \times 10^7$ 1 mol^{-1} s^{-1}, $0.5hL\nu_i = 21.5$ kJ/mol, and $0.5hL(\nu_i - \nu_f) = 0.3$ kJ/mol [4]. The k_1 values are given above, and reference D_i data for hydroquinones are listed in Table 1. The E_e, ΔH_e, and br_e values were determined using Eqs. (1)–(4). The br_e value of (12.6 ± 0.1) (kJ/mol)$^{1/2}$, which was used in further calculations, is nearly equal to 12.5 ± 0.4 [7], the value reported for the interaction between ethylbenzene $ROO^\bullet$ and HQH, and differs markedly from 13.16 [4], the value reported for reaction (I) involving a sterically unhindered phenol (Ar$_1$OH). The calculated D_i values are listed in Table 1. They are in good agreement with the literature. A ±0.1 deviation of the parameter br_e corresponds to a calculation error of ±1.4 kJ/mol in D_i.

Enthalpy of formation of substituted hydroquinones. The enthalpy of formation was estimated by the increment method [8]. For two compounds differing by one group X, such as phenol and benzene, the difference between the enthalpies of the increments $C_B(X)$ and $C_B(H)$ is equal to the difference between the enthalpies of the molecules. An examination of pairs of compounds for which ΔH [9, 10] is known yielded the following data:

$$\Delta H(C_B(OH) - C_B(H)) = -178.3 \pm 2.7\ (n = 11),$$

$$\Delta \overline{H}\,(C_B(OH)) = -164.5,$$

Table 2. Rate constants ($k_1 \times 10^6$ l mol^{-1} s^{-1}) of the reactions of peroxy radicals with various structures with hydroquinones at 323 K

Peroxy radical	Substituent in HQH					
	no substituent	Me	2.5-Me$_2$	Me$_3$	CMe$_3$	2.5-(CMe$_3$)$_2$
HOO$^•$	0.96	1.5	2.5	4.6	2.2	7.0
sec-ROO$^•$	0.53	0.84	1.4	2.6	1.2	4.1
tert-ROO$^•$	0.16	0.25	0.43	0.84	0.38	1.3

$$\Delta H(\mathrm{C_B(Me)} - \mathrm{C_B(H)}) = -32.6 \pm 2.0\ (n = 11),$$

$$\Delta \overline{H}\,(\mathrm{C_B(Me)}) = -18.8,$$

$$\Delta H(\mathrm{C_B(CMe_3)} - \mathrm{C_B(H)}) = -101.6 \pm 2.3\ (n = 4),$$

$$\Delta \overline{H}\,(\mathrm{C_B(CMe_3)}) = -87.5.$$

Here, n is the number of pairs of compounds, $\Delta H(\mathrm{C_B(H)}) = 13.8$, and $\mathrm{C_B}$ is a carbon atom in the benzene ring. Table 1 lists the average enthalpies of the HQH compounds derived from these data along with the enthalpies of the corresponding benzoquinones. For HQH, MeHQH, and 2,5-Me$_2$HQH versus the corresponding quinones, $\Delta H_{\mathrm{HQH}} - \Delta H_{\mathrm{Q}} = -152.7$, -151.2, and -150.7, respectively, and the average is -151.7 ± 1.0. There is no reason to think that this difference will be different for other hydroquinone–quinone pairs (see entries 4–6 in Table 1). Therefore, it is possible to determine the enthalpy of formation for these pairs: $\Delta H_{\mathrm{Q}} = \Delta H_{\mathrm{HQH}} + 151.7$.

Using the thermochemical equations

$$D_{\mathrm{HQH}} + \Delta H_{\mathrm{HQH}} = \Delta H_{\mathrm{HQ^\cdot}} + \Delta H_{\mathrm{H^\cdot}},$$

$$D_{\mathrm{HQ^\cdot}} + \Delta H_{\mathrm{HQ^\cdot}} = \Delta H_{\mathrm{Q}} + \Delta H_{\mathrm{H^\cdot}}$$

and data presented in Table 1, we calculated the strengths of the O–H bonds in the semiquinone radicals ($D_{\mathrm{HQ^\cdot}}$), assuming $\Delta H_{\mathrm{H^\cdot}} = 218$. The significant discrepancy between our calculated data and the corresponding values known from the literature (Table 1) arises from the fact that Denisov et al. [5] took the enthalpy of formation of HQH to be $\Delta H = -263.6$ [9], while we determined ΔH to be -274. Use of one particular ΔH_{HQH} value would lead to similar $D_{\mathrm{HQ^\cdot}}$ values.

Calculating the rate constants for the reactions between ROO$^•$ and HQH and between HQ$^•$ and Q. Knowing D_{i} for HQH (Table 1) and D_{f} for ROOH, it is possible to calculate k_1 using Eqs. (5) and (1)–(3) if the following inequality is satisfied [4]:

$$\Delta H_{\mathrm{e,\,min}} < \Delta H_{\mathrm{e}} < \Delta H_{\mathrm{e,\,max}}, \quad (6)$$

where

$$\Delta H_{\mathrm{e,\,min}} = -\left(\frac{br_{\mathrm{e}}}{\alpha}\right)^2 + \frac{2br_{\mathrm{e}}(0.5hL\nu_{\mathrm{i}})^{1/2}}{\alpha^2} + \frac{0.5hL\nu_{\mathrm{i}}(\delta^2 - 1)}{\alpha^2}, \quad (7)$$

$$\Delta H_{\mathrm{e,\,max}} = br_{\mathrm{e}}^2 - 2\alpha br_{\mathrm{e}}(0.5hL\nu_{\mathrm{f}})^{1/2} + 0.5hL\nu_{\mathrm{f}}(\alpha^2 - 1). \quad (8)$$

The calculated parameters of reaction (I) are given above. It follows from these parameters that $\Delta H_{\mathrm{e,\,min}} = -40.2$, $\Delta H_{\mathrm{e,\,max}} = 40.5$, and ΔH_{e} for HQH and 2,5-di-*tert*-butylhydroquinone ranges between -5.7 and -25.7; that is, inequality (6) is satisfied. Both for the reactions of a given ROO$^•$ radical with different hydroquinones and for the reactions of a given hydroquinone with different ROO$^•$ radicals, the calculated k_1 values (Table 2) differ by a factor of 6–7.

Unlike reaction (I), reaction (II) is fast owing to its high exothermicity. For such processes, $\Delta H_{\mathrm{e}} < \Delta H_{\mathrm{e,\,min}}$, the activation energy is $E = 0.5RT$, and Eqs. (7)–(10) are used in calculations [4, 5]:

$$A_2 = A_{0,\,2}[1 + 1.3(|\Delta H_{\mathrm{e}}|^{1/2} - |\Delta H_{\mathrm{e,\,min}}|^{1/2})]^2, \quad (9)$$

$$k_2 = A_2 \mathrm{e}^{-0.5}. \quad (10)$$

For reaction (II), $n = 1$, $A_{0,\,2}$ is unknown, and the other parameters are the same as for reaction (I). ΔH_{e} ranges between -132.0 and -110.8, and $\Delta H_{\mathrm{e,\,min}} = -40.2$. The $k_2/A_{0,\,2}$ values calculated from $D_{\mathrm{HQ^\cdot}}$ data (Table 1) are listed in Table 3. These values, as distinct from their counterparts for reaction (I), are virtually independent of the reactant structure: in all cases, $k_2/A_{0,\,2} = 50.4 \pm 8.9$. The noticeable outliers are only trimethylhydroquinone and 2,5-di-*tert*-butylhydroquinone, for which $k_2/A_{0,\,2}$ deviates from the same parameter for unsubstituted HQH by 13 and 18%, respectively.

The reactivity of phenoxyl (PhO$^•$) radicals also depends only slightly on their structure. The average rate constant of their reactions with R$^•$, RO$^•$, and ROO$^•$ is ~3×10^8 [11]. For the reaction HQ$^•$ + HQ$^•$, $k \approx (3 \pm 2) \times 10^8$ [11, 12]. Hence, for these two reac-

Table 3. $k_2/A_{0,2}$ ratios for the reactions between ROO$^\bullet$ and HQ$^\bullet$ and the relative reactivities of substituted semiquinone radicals (β_2)

Peroxy radical	Parameter	Substituent in HQ$^\bullet$					
		no substituent	Me	2.5-Me$_2$	Me$_3$	CMe$_3$	2.5-(CMe$_3$)$_2$
HOO$^\bullet$	$k_2/A_{0,2}$	59.2	58.6	56.5	52.3	56.2	50.0
	β_2	1.00	0.99	0.95	0.88	0.95	0.84
sec-ROO$^\bullet$	$k_2/A_{0,2}$	56.2	55.6	53.5	49.4	53.3	47.1
	β_2	1.00	0.99	0.95	0.88	0.95	0.84
tert-ROO$^\bullet$	$k_2/A_{0,2}$	50.3	49.7	47.7	43.7	47.5	41.5
	β_2	1.00	0.99	0.95	0.87	0.94	0.82

Table 4. Parameters of the reactions between HOO$^\bullet$ and benzoquinones at 323 K

Substituent in HQH	$-\Delta H_e$	E_e	E	$k_3 \times 10^{-6}$
–	17.0	31.04	11.18	5.0
Me	17.7	30.73	10.87	5.6
2.6-Me$_2$	20.1	29.67	9.81	8.3
Me$_3$	25.0	27.55	7.69	18.3
CMe$_3$	20.4	29.53	9.67	8.8
2.5-(CMe$_3$)$_2$	27.8	26.38	6.52	28.3

tions, $A \approx 5 \times 10^8$ l mol^{-1} s^{-1}. Under the assumption that $A_{0,2} \approx A$, we obtain $\bar{k}_2 \approx 2.5 \times 10^{10}$. This value is obviously overestimated, since the liquid-phase reactions between free radicals are diffusion-controlled and their actual rate constants are much smaller [11, 12]. Therefore, the IPM method enables one to calculate only the relative reactivities of interacting radicals (Table 3).

The HOO$^\bullet$ radical can be not only an oxidizer, abstracting an H atom from a molecule according to reactions (I) and (II), but also a reducer. By donating an H atom to an oxidized species, they regenerate the original compound:

$$\mathrm{HOO^\bullet + Q \xrightarrow{k_3} HQ^\bullet + O_2}, \qquad \text{(III)}$$

$$\mathrm{HOO^\bullet + HQ^\bullet \xrightarrow{k_4} HQH + O_2}. \qquad \text{(IV)}$$

For reaction (III), the set of calculated parameters is known from the literature [5]: $\alpha = 0.986$, $0.5\,hL\nu_i = 21.2$, $0.5\,hL(\nu_i - \nu_f) = -0.3$, $n = 2$, and $A_{0,3} = 1.6 \times 10^8$; $br_e = 12.6/1.014 = 12.43$ (not 12.98 [5]). Here, $\Delta H_{e,\min} = -41.8$, $\Delta H_{e,\max} = 41.0$, and ΔH_e ranges between -17.0 and -27.8. Therefore, inequality (6) is satisfied, so the calculation is carried out in the same way as for reaction (I). The strength of the H–OO$^\bullet$ bond is 220 kJ/mol [5], and $D_{\mathrm{HQ^\cdot}}$ data are listed in Table 1. The results of this calculation are presented in Table 4. Depending on the structure of the substituents in benzoquinone, k_3 varies rather widely (by a factor of up to 5).

The calculated parameters of reaction (IV) are equal to those of reaction (III), but $n = 1$ and $A_{0,4}$ is unknown. Reaction (IV) is very exothermic: in passing from hydroquinone to 2,5-di-*tert*-butylhydroquinone, ΔH_e changes from -132.9 to -120.5. Since $\Delta H_e < \Delta H_{e,\min} = -41.8$, the calculation is carried out in the same way as for reaction (II). For the HQ$^\bullet$ radicals appearing in Table 3, the $k_4/A_{0,4}$ ratio decreases from 57.5 to 47.1 and the relative reactivity β_4 decreases from 1.00 to 0.82 in going from left to right. These values are nearly equal to the $k_2/A_{0,2}$ and β_2 values in Table 3 because of the similarity of the $\Delta H_{e,2}$ and $\Delta H_{e,4}$ values. The competing reactions (II) and (IV) are two pathways of the same interaction between the hydroperoxyl and semiquinone radicals:

$$\begin{tikzcd} & \mathrm{HOOH + Q} \quad \text{(II)} \\ \mathrm{HOO^\bullet + HQ^\bullet} \arrow[ur] \arrow[dr] & \\ & \mathrm{O_2 + HQH.} \quad \text{(IV)} \end{tikzcd}$$

These pathways are energetically equivalent; therefore, it is possible to assume that $A_{0,2} \approx A_{0,4}$. This implies that the constants k_2 and k_4 are similar.

Thus, the comparison of the reactivities of peroxy radicals with various structures has led us to the following conclusions:

(1) In passing from HOO$^\bullet$ to tertiary ROO$^\bullet$ radicals, the rate constant of the radical–hydroquinone reactions decreases by a factor of up to 7. The same difference is observed between the reactions of a given

$ROO^{\bullet}$ radical with 2,5-di-*tert*-butylhydroquinone and hydroquinone.

(2) The rates of the reactions between peroxy and semiquinone radicals are very similar, irrespective of the structure of these radicals, the difference being <20%.

(3) The reactions between the $HOO^{\bullet}$ and $HQ^{\bullet}$ radicals, in which an H atom is abstracted from $HQ^{\bullet}$ or $HOO^{\bullet}$, are energetically equivalent, and their rate constants are similar.

(4) The rate constants of the reactions of $HOO^{\bullet}$ and benzoquinones containing various substituents are $(0.5–2.8) \times 10^7$ l mol^{-1} s^{-1}.

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