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Quinones, monoradicals and diradicals from 3- and 4-mercaptocatechol and 3,4-bismercaptocatechol: a computational study of a plausibly biomimetic reaction

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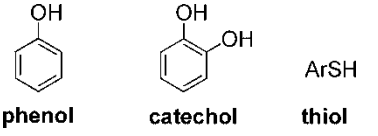
Little attention has been focused on radical and diradical formations from compounds that contain both phenol and thiol groups. Computational studies were conducted on radicals and diradicals from mercapto- and bismercaptocatechols to provide insight into their relative stability. The loss of a hydrogen atom from mercapto- or -bismercaptocatechol produces S- and O-centered radicals of similar energy. The loss of two hydrogen atoms from 3,4-bismercaptocatechol (**3**) is an example where a number of quinone and diradical structures become possible. However, the energetics are consistent with a 4-membered ring dithiete playing an important role in the two electron oxidation reaction of **3**.

Keywords: catechol; semiquinone; quinone; thioquinone; diradicals

1. Introduction

A number of studies have focused on the antioxidant properties of phenols, catechols, and thiols (*1*). Phenols can form the corresponding phenoxyl radical. Catechols can form O-centered radicals ($HOC_6H_4O^{\cdot}$ or $C_6H_4O_2^{\cdot-}$), *o*-quinones, or triplet diradicals. Thiols can form an S-centered thiyl radical. However, the literature appears to be devoid of studies that address antioxidant compounds that contain *both* aromatic alcohol and thiol groups, to compare radical-forming properties with compounds that contain either aromatic alcohol or thiol groups. An earlier study on phenols and aromatic thiols noted differences on the polymerization of methyl methacrylate (*2*). As part of a biomimetic study, sulfur-containing catechols have been recently observed.



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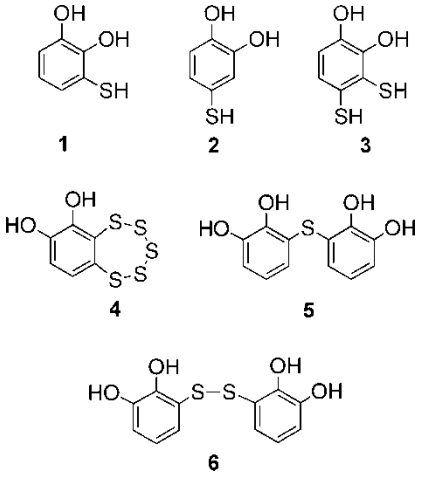
We recently reported the formation of 3-mercaptocatechol (**1**), 4-mercaptocatechol (**2**), and 3,4-bismercaptocatechol (**3**) among other products (*e.g.*, **4–6**) from the reaction of *o*-benzoquinone with reduced elemental sulfur (hydrogen polysulfides), H_2S_x (*3*). Thus, **1–3** have been characterized (*3-5*). However, no spectroscopic evidence or otherwise exists for semiquinone and quinone structures corresponding to **1–3**. We wished to study possible radical and diradical intermediates that may arise from oxidations of **1–3**. Reports neither exist for the oxidation of mercapto- and bismercaptocatechols **1-3** nor of other sulfur-containing catechols. Little is known about the relative energetics of forming a thiocarbonyl group ($R_2C{=}S$) (*6*) versus a carbonyl group ($R_2C{=}O$) from such precursors.



It would be a challenging task to determine the assignment of intermediates in one and two electron oxidations of **1–3**. Thus, computational theory has been applied here, in which the objective of the study was to compare stabilities of free radical, quinone, and thioquinone compounds and to predict the preferred structures. Spin distributions were also assessed theoretically to aid in determining relative stabilities of open-shell diradicals. The stabilities of singlet and triplet diradicals from the loss of two hydrogen atoms from **3** have been predicted. Information on the loss of hydrogen atoms from **1–3** may also reveal factors related to antioxidant activity.

2. Computational section

Standard computational protocols were used (*7*). Gas-phase density function theoretical (DFT) calculations were determined with B3LYP (*8,9*) and Pople's 6-31G(d) and 6-311+G(d,p) basis sets (*10*). Geometry optimizations were carried out at the B3LYP/6-31G(d) level. Closed-shell calculations gave the lowest energies for **1–3**, quinones, and dithiete **3k**, whereas open-shell calculations gave the lowest energies for radicals and diradicals. Triplet UB3LYP/6-311+G(d, p) energies were obtained using the singlet-diradical optimized geometry (*11,12*). Spin corrected values are reported for UB3LYP/6-311+G(d, p) energies when the open-shell singlet is contaminated with a triplet by means of the spin correction procedure of Yamaguchi and co-workers (*13,14*), in which the energy of the lower spin state is corrected by the following formula:

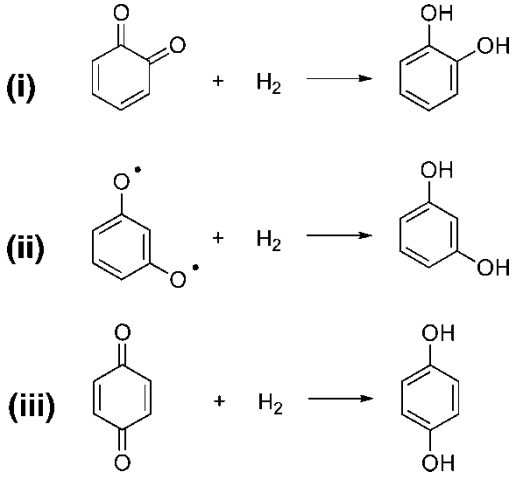
$$^{1}E \approx {}^{1}E + \frac{^{1}\langle S^2\rangle}{^{h}\langle S^2\rangle - {}^{1}\langle S^2\rangle}\left({}^{l}E - {}^{h}E\right)$$

where l and the h refer to low and high spin states, respectively, which provides the energy of the corrected singlet state.

Table 1. Hydrogenation energies [ΔH_{hyd} (kcal/mol)] of a series of benzoquinones to form the corresponding benzendiols.

Entry	Method	*o*-Benzoquinone†	*m*-Benzoquinone†	*p*-Benzoquinone†
1	Experiment‡	42.8 ± 4.1	74.8 ± 4.1	38.5 ± 3.0
2	G3‡	44.6	72.2	34.1
3	B3LYP/6-311+G(d,p)//B3LYP/6-31(d)	42.0	64.6	32.8

† Computed values obtained from Reactions (i)–(iii), which include the sum of electronic and thermal enthalpies.
‡ Ref 17.



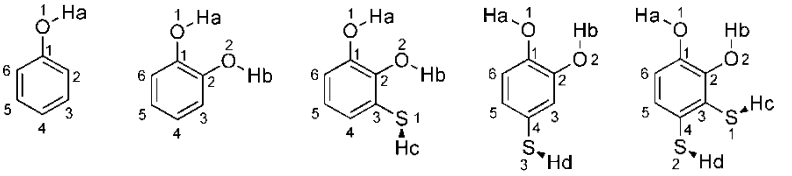
Computations of radical and diradicals derived from **1–3** using the more rigorous G3 would be desirable, but were not possible due to limitations on computational resources (*15,16*). B3LYP/6-311+G(d, p)//B3LYP/6-31G(d) calculations yielded hydrogenation energies of *ortho*-, *meta*-, and *para*-benzoquinone to form the corresponding benzenediol that are correlated reasonably well with G3 theory and with experimental values (cf. entries 1–3, Table 1) (*17*). Getting heat of formation phenols and catechols has proven to be difficult, the experimental error bars are large (3–4 kcal/mol) (entry 1, Table 1) (*18*). The energetics obtained were corrected for zero-point energies and thermochemical corrections to enthalpies (298.15 K and 1 atm) (*19*).

Previous B3LYP/6-31+G(d,p) studies have been successful in predicting redox potentials of quinones (*20*). We (*21*) and others (*22–26*) have used B3LYP/6-31G(d) or B3LYP/6-31+G(d) computations, which performed well in predicting the relative energetics of 1,2-dithiacyclobutene (dithiete, *c*-$C_2H_2S_2$) and dithioethanedial (S=CHCH=S). Contini *et al.* conducted B3LYP/TZVP//B3LYP/6-31G(d) calculations showing that *o*-thioquinones react with electron rich-alkenes by forming benzoxathiin cycloadducts, which were consistent with the product outcome observed in experimental studies (*27, 28*). Cramer *et al.* (*29, 30*) and Houk *et al.* (*31*) report that energetics of diradicals calculated with unrestricted DFT are in reasonable agreement with methods, such as CCSD(T), which account for long-range correlation effects.

3. Results and discussion

We report the results of a DFT study on sulfur-substituted catechols **1–3**, their corresponding quinones, monoradicals, diradicals, and a dithiete. First, we describe the computed structural

Table 2. Calculated bond lengths of phenol, catechol, and 1–3 (in Å).



phenol **catechol** **1** **2** **3**

Compound	C1−O1	C2−O2	C3−S1	C4−S2	O2−S1
Phenol	1.37	–	–	–	–
Catechol	1.38	1.36	–	–	–
1	1.36	1.37	1.80	–	3.06
2	1.38	1.36	–	1.80	–
3	1.38	1.37	1.78	1.79	3.01

Compound	Ha–O2	Hb–S1	Hb–O1	Hc–O2	Hd–S1
Phenol	–	–	–	–	–
Catechol	2.12	–	3.64	–	–
1	2.12	2.45	–	–	–
2	–	–	2.12	–	–
3	–	–	2.09	2.23	2.95

Structures optimized at the B3LYP/6-31(d) level.

features of **1–3**. Second, we describe the computed heats of formation (ΔH_f^0) of quinone, monoradical, diradical, and dithiete structures, which could theoretically arise from oxidations of **1–3**.

3.1. *Computed structures*

Compounds **1–3** optimized to minima at the B3LYP/6-31G(d) level of theory (Table 2). Phenol and catechol have C_S symmetry. Compounds **1–3** have C_1 symmetry. Bismercaptocatechol **3** favors three intramolecular hydrogen bonds, an OHO hydrogen bond, an OHS hydrogen bond, and an SHS hydrogen bond. Low-energy conformers of catechol and **1–3** show H–O bonds [*e.g.*, the H–O bond distances of 2.12 Å (Ha–O2 catechol), 2.12 Å (Ha–O2 **1**), 2.12 Å (Hb–O1 **2**), 2.09 Å (Hb–O2 **3**)] and H–S bond distances somewhat similar to each other [2.45 Å (Hb–S1 **1**) and 2.95 Å (Hd–S1 **3**)]. The structures predict that the O−H–O bonds possess a planar structure. The dihedral angles of catechol (Ha−O1−C1−C2), **1** (Ha−01−C1−C2), and **3** (Hb−O2−C2−C1) are equal to 0.0°. On the other hand, the S−H–O and S−H–S bonds are out of plane. The dihedral angle of **1** (Hc−S1−C3−C4) is equal to 91.7°, that of **2** (Hd−S3−C4−C3) is equal to 47.6°, and that of **3** (Hd−S2−C4−C3) is equal to 55.5°. The B3LYP/6-31G(d) computations adequately reproduce the experimental X-ray data of phenol (*32*) and thiophenol (*33*). The computed heats of formation of the mono- and diradicals, and quinones are the subjects of the following sections.

3.2. *Heats of formation,* ΔH_f^0

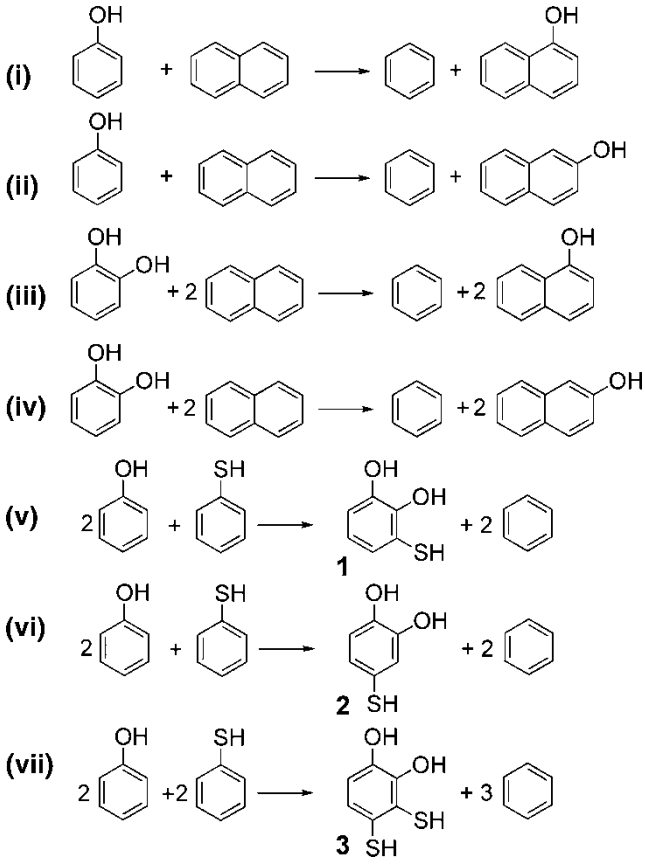
Experimental heats of formation (ΔH_f^0) have been reported for phenol and catechol (*18,34*). Phenol is predicted to have a value of $\Delta H^0_{f(gas)} = -22.8$ kcal/mol obtained by ring conserving isodesmic reactions from Reaction (i), and a value of −23.1 kcal/mol from Reaction (ii), which compare well with the experimental value (−23.0 kcal/mol) (Table 3) (*35*). Catechol is predicted

to have a value of $\Delta H^0_{f(gas)} = -67.6$ kcal/mol from Reaction (iii), a value of -66.5 from Reaction (iv), which compare well with the experimental value of about -65.7 kcal/mol (*36, 37*). Compound **1** is predicted to have a value of $\Delta H^0_{f(gas)} = -61.8$ kcal/mol obtained isodesmically from Reaction (v). Compound **2** is predicted to have a value of $\Delta H^0_{f(gas)} = -58.7$ kcal/mol from Reaction (vi). Compound **3** is predicted to have a value of $\Delta H^0_{f(gas)} = -51.9$ kcal/mol from Reaction (vii). The above analysis suggests that our computed gas-phase heats of formation compare well with the experiment data. Few experimental heats of formation (ΔH^0_f) of aryl oxygen- or sulfur-radicals are described in the literature (*34*). DiLabio and Mulder reported an experimental $\Delta H^0_{f(gas)}$ value for hyroxyphenoxy radical is 79.7 kcal/mol (*38*). Described next are computations of monoradicals from hydrogen atom loss of **1**–**3**.

Table 3. Calculated $\Delta H^0_{f(gas)}$ of phenol, catechol, and 1–3 (kcal/mol).

Compound	Calculated $\Delta H^0_{f(gas)}$	Experimental $\Delta H^0_{f(gas)}$
Phenol	$-23.2 \pm 0.4^{\dagger}$	$-23.0 \pm 0.2^{\ddagger}$
Catechol	$-67.1 \pm 0.8^{\S}$	$-65.7 \pm 0.3^{\P}$
1	$-61.8^{\|}$	–
2	$-58.7^{\#}$	–
3	-51.9^{**}	–

†Reactions (i) and (ii). ‡Ref. (*35*). ¶ Ref. (*36, 37*). §Reactions (iii) and (iv). ‖ Reaction (v). #Reaction (vi). ** Reaction (vii).

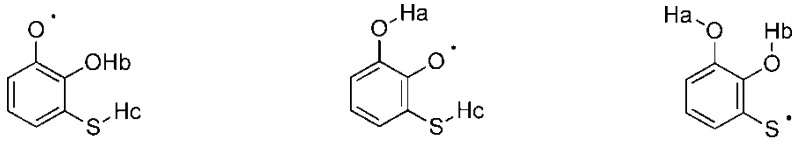


3.3. *Monoradicals*

We report computed $\Delta H^0_{f(gas)}$ for monoradicals **1a**–**1c**,**2a**–**2c**,**3a**–**3d** (Tables 4–6). Calculations were performed at the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level, and the isogyric reactions used to arrive at the relative energetics are described in the footnotes of Tables 4–6. For example, hydroxymercaptophenoxy radical **1a** and two benzene molecules were compared isogyrically with benzenethiol, phenoxy radical, and phenol (Reaction (i), Table 4). Compounds **1a**–**1c**,**2a**–**2c**, and **3a**–**3d** possess computed $<S^2>$ values of 0.75.

The S-centered radical **1c** is predicted to be of greater stability compared with the O-centered radicals **1a** and **1b** (Table 4). However, the monoradicals **2a**–**2c** reveal a different stability pattern, in which the O-centered radical **2a** is of greater stability compared with S-centered radical **2c** and O-centered radicals **2b** (Table 5). Compound **2b** is destabilized by 4.1 kcal/mol compared with **2a**. Our computed data show that monoradicals derived from the hydrogen atom abstraction of **3** can yield four different radical structures, **3a**–**3d** (Table 6). S-centered radicals **3c** and **3d** are slightly lower in energy compared with the O-centered radicals **3a** and **3b**. However, there is no one energetic low-lying isomer. The energetics of **3a**–**3d** are similar and thus appear to be isoenergetic. It appears that the stability of the monoradicals **1a**–**1c**,**2a**–**2c**,**3a**–**3d** is not limited to the single variable of radical localization on sulfur versus oxygen.

Table 4. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) Calculated $\Delta H^0_{f(gas)}$ for **1a–c**.



1a **1b** **1c**

Compound	Calculated $\Delta H^0_{f(gas)}$ (kcal/mol)	Relative $\Delta H^0_{f(gas)}$ (kcal/mol)	$<S^2>$
1a	−55.0	8.5	0.75
1b	−59.6	3.9	0.75
1c	−63.5	(0.0)	0.75

Values obtained from isogyric reactions (i)–(iii). Values include the sum of electronic and thermal enthalpies. The calculated $\Delta H^0_{f(gas)}$ for 3-mercaptocatechol **1** is −61.8 kcal/mol (Table 3).

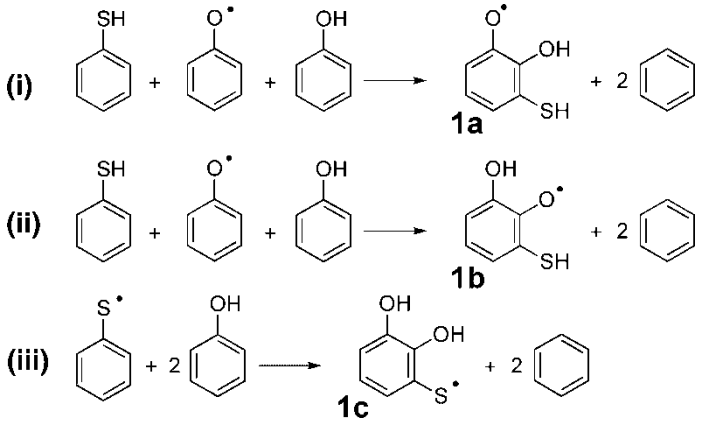
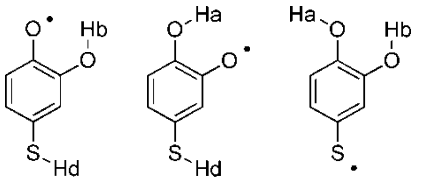


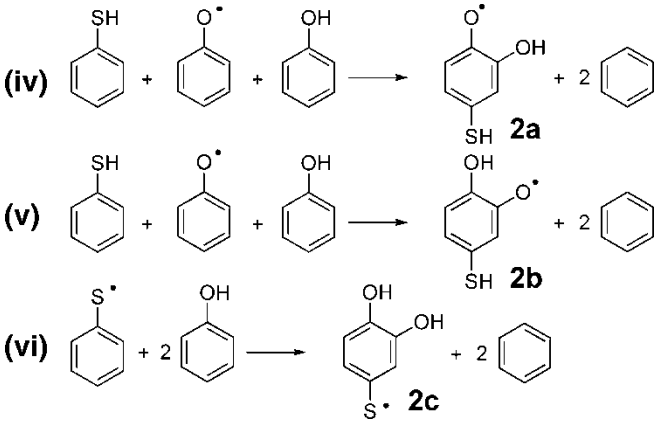
Table 5. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) Calculated $\Delta H^0_{f(gas)}$ for **2a–c**.



2a **2b** **2c**

Compound	Calculated $\Delta H^0_{f(gas)}$ (kcal/mol)	Relative $\Delta H^0_{f(gas)}$ (kcal/mol)	$< S^2 >$
2a	−59.8	(0.0)	0.75
2b	−55.7	4.1	0.75
2c	−57.8	2.0	0.75

Values obtained from isogyric reactions (iv)–(vi). Values include the sum of electronic and thermal enthalpies. The calculated $\Delta H^0_{f(gas)}$ for 4-mercaptocatechol **2** is −58.7 kcal/mol (Table 3).

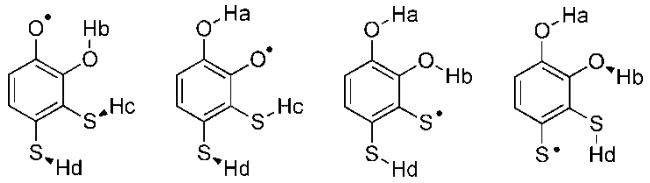


Calculations predict that monoradicals **1a–1c**, **2a–2c**, and **3a–3d** can form by a one-electron process; namely, hydrogen atom loss from the corresponding neutral compounds, **1–3**. There is a fairly small energy difference between the radicals within each series. How neutral **1–3** may lose two electrons, namely, the loss of two hydrogen atoms from **1–3** to access diradicals, quinones, thioquinones, dithioquinones, and a benzodithiete is the focus of the next section.

3.4. *Diradicals*

Calculated $\Delta H^0_{f(gas)}$ of quinones and diradicals **1d–1f**, **2d–2f**, **3a–3j**, and a dithiete **3k** are reported (Tables 7–9). The isogyric reactions used to arrive at the predicted energetics are described in the footnotes of Tables 7–9. For example, 3-mercapto-*o*-benzoquinone **1d** and benzene are compared isogyrically with benzenethiol and *o*-benzoquinone (Reaction (xi), Table 7). The $<S^2>$ values of **1d**, **1e**, **2d**, **2e**, **3e**, **3h**, **3j**, and **3k** are about equal to zero. Compounds **1f**, **2f**, **3f**, **3g**, and **3i** possess $<S^2>$ values of about 2.0. Triplet energies were obtained using the singlet–diradical optimized geometries of **1f**, **2c**, **3f**, and **3i** to determine whether the ground states were singlet or triplet. The singlet–triplet gap (ΔE_{ST}) of **2f** was estimated using the triplet-diradical optimized geometry since the singlet-state geometry did not converge under default convergence criteria.

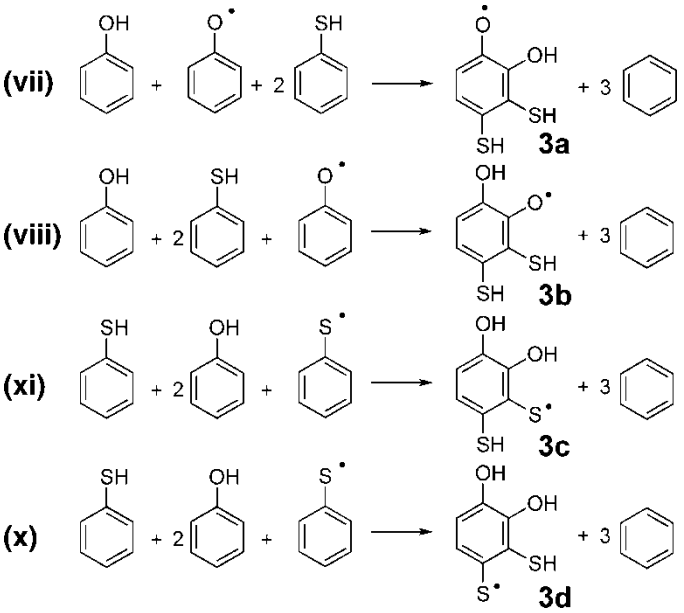
Table 6. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) Calculated $\Delta H^0_{f(gas)}$ for **3a–d**.



3a **3b** **3c** **3d**

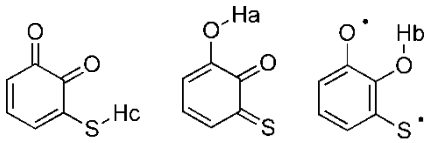
Compound	Calculated $\Delta H^0_{f(gas)}$ (kcal/mol)	Relative $\Delta H^0_{f(gas)}$ (kcal/mol)	$<S^2>$
3a	−50.2	1.5	0.75
3b	−50.6	1.1	0.75
3c	−51.7	(0.0)	0.75
3d	−51.1	0.6	0.75

Values obtained from isogyric reactions (vii)–(x). Values include the sum of electronic and thermal enthalpies. The calculated $\Delta H^0_{f(gas)}$ for 3,4-bismercaptocatechol **3** is −51.9 kcal/mol (Table 3).



o-Benzoquinone **1d** is more stable than the *o*-thiobenzoquinone **1e** and the non-Kekulé diradical **1f**. Triplet **1f** is lower in energy than singlet **1f**. The energetics of triplet **1f** is nonetheless quite high (endothermic by 21.1 kcal/mol) compared to **1d**. A triplet diradical is also observed in **2f** when considering the series **2d–2f** (Table 8). The *p*-thioquinone **2e** is more stable than the *o*-thioquinone **2d** and the O- and S-centered triplet diradical **2f**. Compound **2d** lies 5.0 kcal/mol above **2e**. A greater number of possible radical and quinone intermediates arise from the abstraction of two hydrogen atoms from **3**, namely **3e–3k** (Table 9). The energetics favor the formation of dithiete **3k**, which is pronounced, compared with **3e–3i**, although the formation of **3j** may be competitive since it is only destabilized by 4.9 kcal/mol. Dithietes are known in a number of experimental systems (*39, 40*). Dithiobenzoquinone **3e** is destabilized by 15.5 kcal/mol compared with the

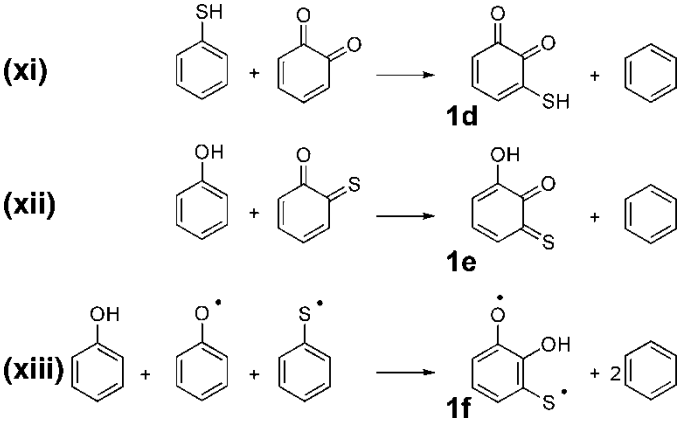
Table 7. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) Calculated $\Delta H^0_{f(gas)}$ for **1d-f**.



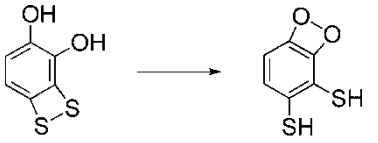
1d **1e** **1f**

Compound	Calculated $\Delta H^0_{f(gas)}$ (kcal/mol)	Relative $\Delta H^0_{f(gas)}$ (kcal/mol)	$<S^2>$
1d	−14.0	(0.0)	0.00
1e	−10.2	3.8	0.00
1f	7.1	21.1†	2.04‡

Values obtained from isogyric reactions (xi)–(xiii), which include the sum of electronic and thermal enthalpies.
†Triplet ground state. ‡$\Delta E_{ST} = 9.8$ kcal/mol. The $<S^2>$ value of singlet **1f** singlet is 0.10.



most stable isomer dithiete **3k**. The equivalent 4-membered ring peroxide, benzo[c][1, 2]dioxete (**3l**) is a high-energy isomer, endothermic by 81.5 kcal/mol relative to the corresponding dithiete **3k** [Equation (1)].



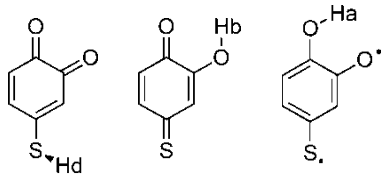
3k **3l**

0 kcal/mol 81.5 kcal/mol

(1)

In all cases, the non-Kekulé diradicals are high-energy species compared with the closed-shell species. This is not surprise to see the diradicals are much higher in energy; for example, *m*-quinones are known to be far less stable than *o*- and *p*-quinones (*41, 42*). The above singlet–triplet energy gaps appear to be reasonably predicted even though a relatively low level of theory was used. For comparison, the ΔE_{ST} of *m*-xylylene diradical (**7**) is predicted to be 13.4 kcal/mol [B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) with spin projection],

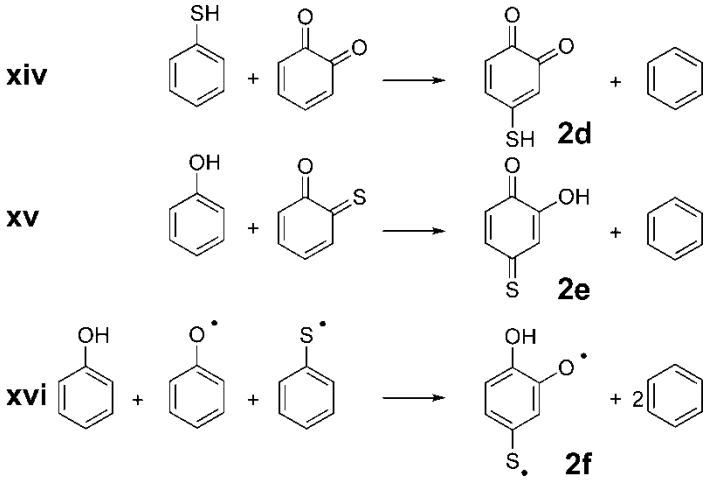
Table 8. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) Calculated $\Delta H^0_{f(gas)}$ for 2**d–f**.



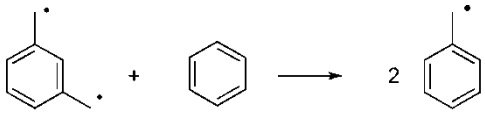
2d **2e** **2f**

Compound	Calculated $\Delta H^0_{f(gas)}$ (kcal/mol)	Relative $\Delta H^0_{f(gas)}$ (kcal/mol)	$<S^2>$
2d	−14.0	5.0	0.00
2e	−19.0	(0.0)	0.00
2f	7.1	26.1†	2.04‡

Values obtained from isogyric reactions (xiv)–(xvi), which include the sum of electronic and thermal enthalpies.
†Triplet ground state. ‡$\Delta E_{ST} = 7.1$ kcal/mol. It was determined using a single point calculation of the singlet compound on the triplet-diradical optimized geometry.



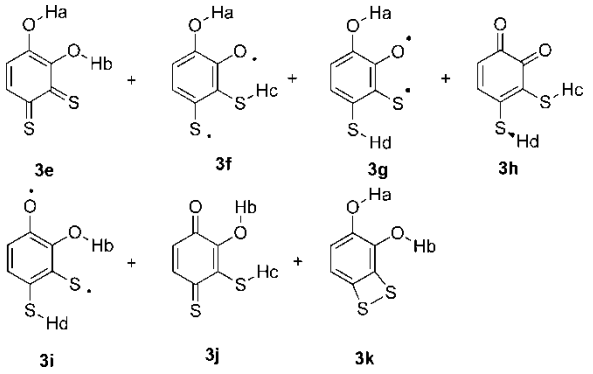
13.2 kcal/mol [B3LYP/6-31G(d) with spin projection] (*43, 44*), 7.1 kcal/mol [UCCSD(T)/4-31G] (*45*), ∼10 kcal/mol (π-CI) (*46, 47*), and 11.0 kcal/mol [CASPT2N/6-31G(d)] (*48*), compared well with the experimental value of 9.6 kcal/mol measured by photoelectron spectroscopy (*49*). The isogyric B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) $\Delta H^0_{f(gas)}$ of triplet ground-state diradical **7** is 77.2 kcal/mol, which is similar to the experimental value of 80 ± 3 kcal/mol [Equation (2)] (*50*).



(2)

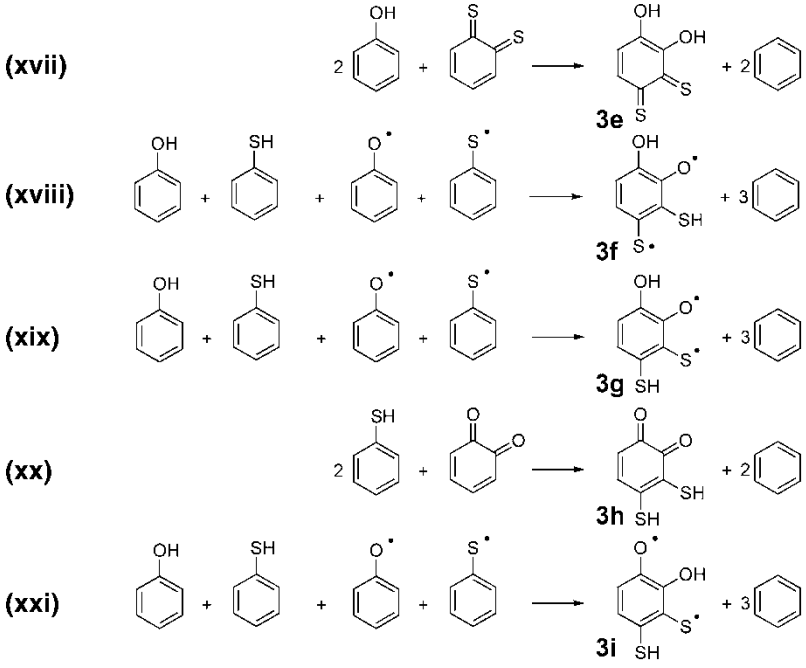
7

Table 9. B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) Calculated $\Delta H^0_{f(gas)}$ for **3e–k**.

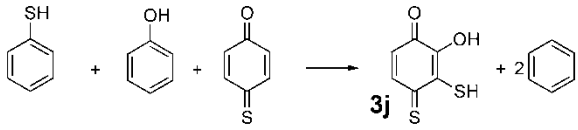


Compound	Calculated $\Delta H^0_{f(gas)}$ (kcal/mol)	Relative $\Delta H^0_{f(gas)}$ (kcal/mol)	$<S^2>$
3e	−9.1	15.5	0.00
3f	−2.7	21.9[†,‡]	2.02
3g	−2.0	22.6[§,¶]	2.04
3h	−12.8	11.8	0.00
3i	−0.9	23.7[‡,‖]	2.03
3j	−19.7	4.9	0.00
3k	−24.6	0.0	0.00

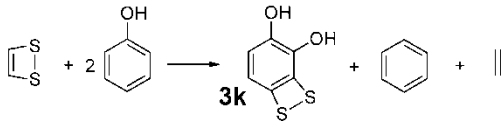
Values obtained from isogyric reactions (xvii)–(xxiii), which include the sum of electronic and thermal enthalpies.
[†]Triplet ground state. [‡]ΔE_{ST} gap is equal to 7.1 kcal/mol. The $<S^2>$ value of singlet **3f** is 0.09. [§] Singlet ground state. [¶]ΔE_{ST} gap is equal to about 1 kcal/mol. The $<S^2>$ value of singlet **3g** is 0.05. [‖]ΔE_{ST} gap is equal to 3.9 kcal/mol. The $< S^2 >$ value singlet **3g** is 0.14. The calculated $\Delta H^0_{f(gas)}$ for **3** is −51.9 kcal/mol (Table 3).



(xxii)



(xxiii)



4. Conclusion

This study has discovered a new aspect to 3,4-bismercaptocatechol chemistry. The calculations predict the formation of dithiete **3k** from the loss of two hydrogen atoms in **3** instead of the formation of quinone or diradical intermediates. Non-Kekulé diradicals are destabilized compared with their *o*- or *p*-quinone counterparts, which may be intuitively obvious, but allowed us to predict the structures likely to emerge when two H atoms are removed from **1**–**3**. Our theoretical study also provides evidence that monoradical stability is not determined solely by whether the radical is centered on the sulfur or oxygen center (cf., **1a** with **2c**, and **3b** with **3d**). We do not ascribe a trend in radical stability due to intramolecular hydrogen bonding or loss thereof, in which one could imagine stronger OHO type hydrogen bonds compared with SHO and SHS hydrogen bonds (cf., **1c** with **1a**, and **3d** with **3a**). For **1**–**3**, the SHO and SHS hydrogen bonds are twisted out-of-plane, but the OHO hydrogen bonds are in-plane. Our study cannot discriminate whether a pathway is favored in a simultaneous two-electron process or by two sequential one-electron processes from **1**–**3**. Aside from the interest in products formed from the loss of hydrogen atoms from **1**–**3**, it is of special significance that the factors related to hydrogen atom loss are coupled with chain termination in dimer or oligomer structures.

Supporting Information Available. Contains the total energies and Cartesian coordinates of the calculated structures.

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Supporting information available

This material is available free of charge via the internet at www.informaworld.com

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