J. Am. Chem. Soc. **1994,** *116,* 9577–9584 9577

Ab Initio Molecular Orbital Calculations of $C_6H_5O_2$ Isomers

A. M. Mebel and M. C. Lin*

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received May 6, 1994[⊛]

Abstract: The structures and energetics of 14 geometric isomers of $C_6H_5O_2$, including phenyl peroxy (C_6H_5OO), hydroperoxy phenyl (C_6H_4OOH), seven-membered ring $C_6(O)H_5O$ isomer, three isomers of hydroxyl phenoxy [C_6H_4O-(OH)], seven isomers of OC_6H_5O (including the three with epoxy structures), and a stable dual-ring $C_6H_5{\cdot}O_2$ π-complex have been calculated by ab initio molecular orbital methods. Geometries have been optimized at the UHF/6-31G* level, and their relative energies with respect to $C_6H_5 + O_2$ have been refined by the spin-projected UMP3(PUMP3) method with UHF/6-31G* zero-point energy corrections. All $C_6H_5O_2$ isomers identified except *m*-OC_6H_5O, which is not a local minimum, are more stable than the $C_6H_5 + O_2$ reactants. The most stable isomers are the three C_6H_4O-(OH) radicals, which are 105–110 kcal/mol below $C_6H_5 + O_2$. They are followed by the seven-membered ring C_6-(O)H_5O, the *m*-epoxy isomer, other OC_6H_5O radicals, and the initial adduct C_6H_5OO, which is 41 kcal/mol lower than $C_6H_5 + O_2$. The π-complex, formed by the association of C_6H_5 with O_2 at the center of the O=O bond, is 27 kcal/mol below the reactants. The C_6H_4OOH radical, which may be formed by intramolecular H-abstraction, is more stable than $C_6H_5 + O_2$ by 9 kcal/mol. The results suggest that several mechanisms may be involved in the $C_6H_5 + O_2$ reaction. Vibrational frequencies determined for each isomer at the UHF/6-31G* level of theory have been discussed.

Introduction

The reaction of the phenyl (C_6H_5) radical with O_2 is relevant not only to the chemistry of incipient soot formation but also to the combustion of aromatic hydrocarbons, which are important ingredients of lead-free gasoline.[1,2] At high temperatures, the $C_6H_5 + O_2$ reaction competes effectively with the polymerization process, $C_6H_5 + nC_2H_2 \rightarrow$ PAHs (polyaromatic hydrocarbons), which are believed to be the building blocks of soot particles in hydrocarbon combustion.[1,3]

The $C_6H_5 + O_2$ reaction at high temperatures ($T \geq 1000$ K) has been assumed to take place primarily via the metathetical process

$$C_6H_5 + O_2 \rightarrow C_6H_5O + O \qquad (1)$$

yielding a phenoxy radical which fragments to give C_5H_5 + CO above 900 K.[4,5] Other minor reaction channels producing H atoms and *o*- or *p*-benzoquinone have also been invoked:[6]

$$C_6H_5 + O_2 \rightarrow H + o/p\text{-}C_6H_4O_2 \qquad (2)$$

The validity of these reactions occurring presumably via ring-intermediates producing benzoquinones as indicated, albeit conceptually attractive, has not yet been confirmed theoretically.

In order to elucidate the mechanism of this important reaction, we have recently carried out extensive ab initio molecular orbital calculations for the structures and energetics of the geometric isomers of $C_6H_5O_2$. On account of the great stability of the aromatic ring structure, we centered our calculations on the aromatic isomers resulting from the migration of one of the two O atoms. Earlier, the C_6H_5OO isomer of this radical was calculated by Sakai, Yamada, and co-workers[7] by the HF/STO-3G method in connection with ROO• + RH → ROOH + R• hydrogen abstraction reactions. Ladik has studied the same isomer and its substituted derivatives to calculate hyperfine coupling constants for EPR spectra using UHF wave functions.[8] Recently, Carpenter calculated some intermediates and transition states for the oxidative cleavage of phenyl radical using the semiempirical PM3 method.[9] However, no study of different isomers of $C_6H_5O_2$ at higher levels of theory has been performed.

Calculation Methods

The geometries of different structures of $C_6H_5O_2$ have been optimized at the UHF/6-31G* level.[10] Vibrational frequencies have been calculated at the same level of theory for characterization of the nature of stationary points, for zero-point corrections and prediction of vibrational spectra. As has been shown recently, the UHF/6-31G* approximation gives the geometries for the phenoxy (C_6H_5O) radical as well as for intermediates and transition states of its decomposition in reasonable agreement with higher level UMP2 and CASSCF methods.[11] We expect that the geometric parameters of the $C_6H_5O_2$ structures obtained at the UHF level are of semiquantitative accuracy, and the more accurate geometries may be achieved with the use of the methods taking into account dynamic and nondynamic electron correlation. The UHF wave function can be subject to very serious spin contamination, one can see in Table 1 that $\langle S^2 \rangle$ values before projection reach 1.2–2.2 as compared to 0.75 for a pure doublet state. The UHF method may lead to artificially low relative energies for those isomers having large spin contamination. To obtain more reliable energies of the isomers of $C_6H_5O_2$, we carried out UMP4(SDQ)/6-31G* calculations[10] at the UHF optimized geometries. The spin projected PUMP2 and PUMP3 energies are expected to be more reliable than the energies calculated by the regular UMP2, UMP3, or UMP4(SDQ) methods. Therefore,

---

[⊛] Abstract published in *Advance ACS Abstracts*, September 15, 1994.

(1) Glassman, I. *Combustion*, 2nd ed.; Academic Press: New York, 1986.

(2) Brezinsky, K. *Prog. Energ. Combust. Sci.* **1986**, *12*, 1.

(3) Bittner, J. D.; Howard, J. B.; Palmer, H. B. *NATO Conference Series. 6: Materials Science*; Plenum Press: New York, 1983; Vol. 7, p 95.

(4) Colussi, A. J.; Zabel, F.; Benson, S. W. *Int. J. Chem. Kinet.* 1977, *9*, 161.

(5) Lin, C.-Y.; Lin, M. C. *J. Phys. Chem.* **1986**, *90*, 425.

(6) (a) Herzler, J.; Frank, P. *Third International Conference on Chemical Kinetics*; NIST, Gaithersburg, MD, July 12–16, 1993. (b) Frank, P.; Herzler, J.; Just, Th.; Wahl, C.; *25th Symposium (International) on Combustion*, submitted for publication.

(7) Tanaka, K.; Sakai, S; Tomiyama, S.; Nishiyama, T.; Yamada, F. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2677.

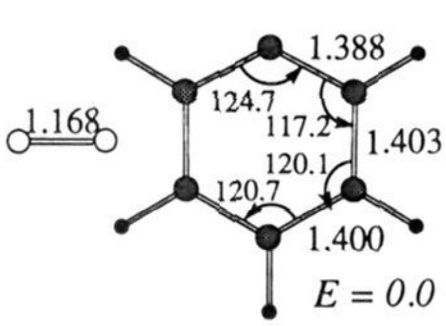
(8) Ladik, J.; Wendel, M.; Otto, P.; Liu, S. C. *J. Mol. Struct. (THEOCHEM)* **1987**, *37*, 1.

(9) Carpenter, B. K. *J. Am. Chem. Soc.* **1993**, *115*, 9806.

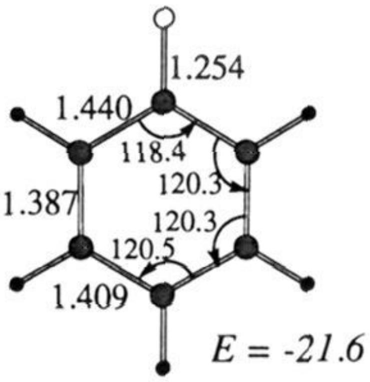
(10) Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(11) (a)Chipman, D. M.; Liu, R.; Zhou, X.; Pulay, P. *J. Chem. Phys.* **1994**, *100*, 5023. (b) Liu, R.; Morokuma, K. Ab Initio Study on the Mechanism of Thermal Decompostiion of the Phenoxy Radical, manuscript in preparation.

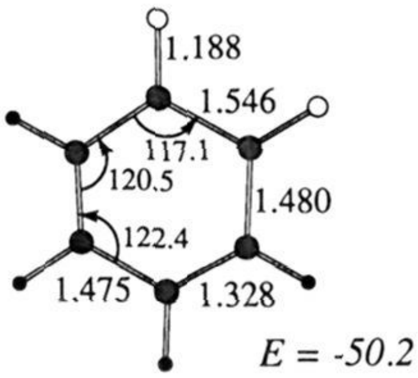
0002-7863/94/1516-9577$04.50/0



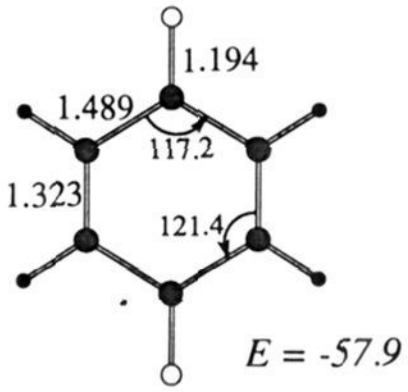
C_6H_5 (C_{2v}, $^2A_1$)
+ O_2



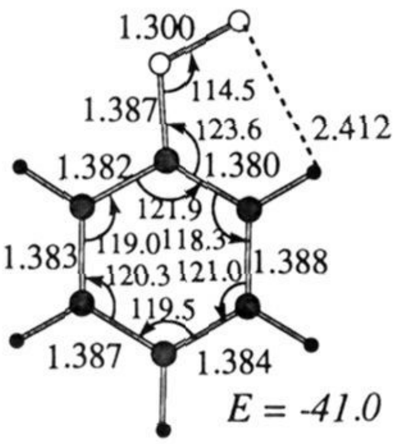
C_6H_5O (C_{2v}, $^2B_1$)
+ O



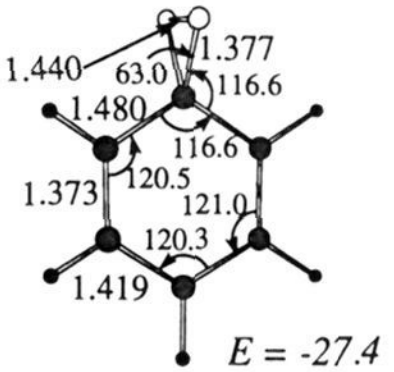
$C_6H_4O_2$ (ortho, C_{2v}, $^1A_1$)
+ H



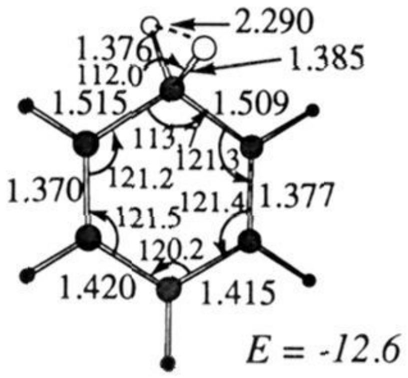
$C_6H_4O_2$ (para, D_{2h}, ^1A_g)
+ H



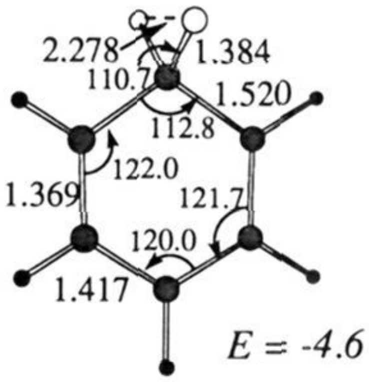
(**1**), C_6H_5OO, C_s, $^2A''$



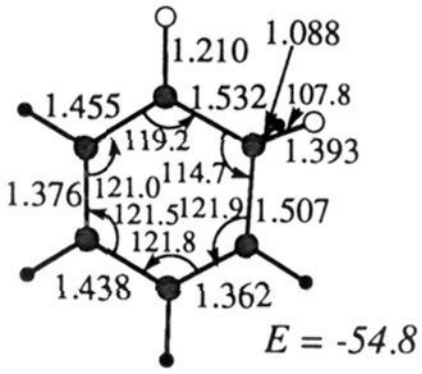
(**2**), $C_6H_5(O_2)$, C_{2v}, $^2B_1$



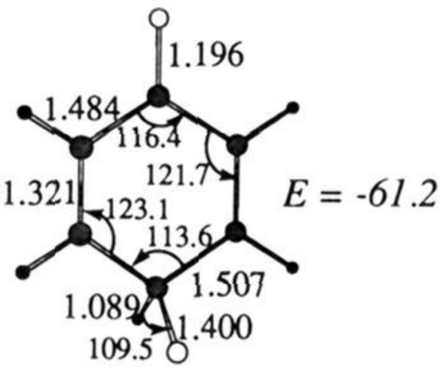
(**3d**), $C_6H_5(O)(O)$,
doublet, C_1



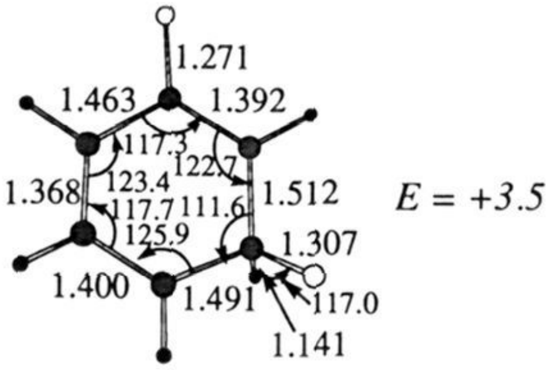
(**3q**), $C_6H_5(O)(O)$,
quartet, C_{2v}, $^4A_1$



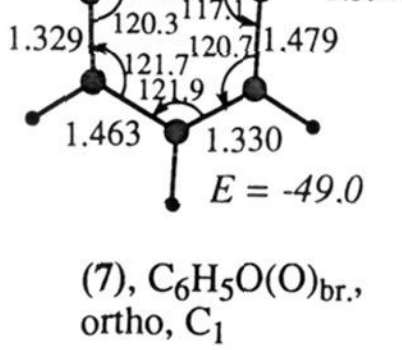
(**4**), $C_6H_4O(O)(H)$,
ortho, C_1



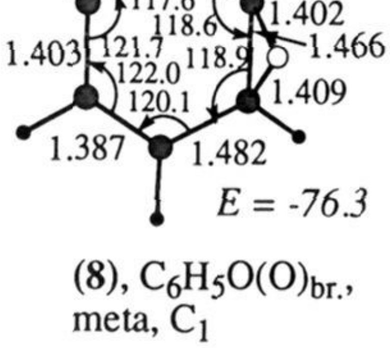
(**5**), $C_6H_4O(O)(H)$,
para, C_s, $^2A''$



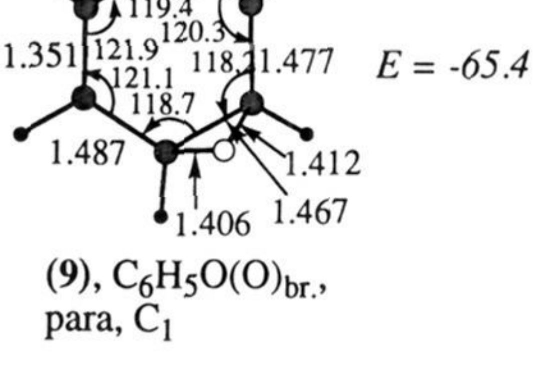
(**6**), $C_6H_4O(O)(H)$,
meta, TS, C_1



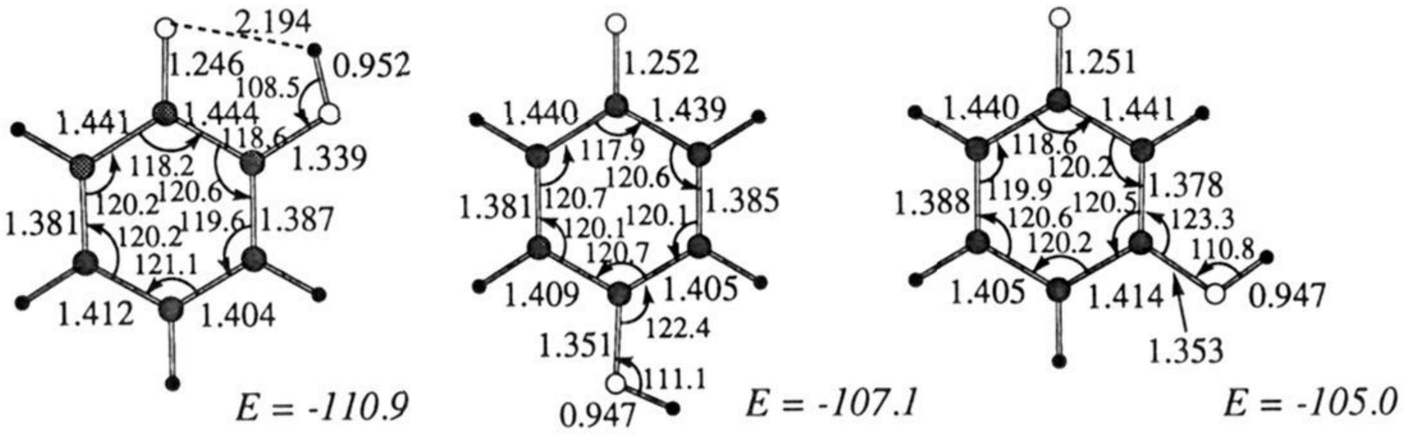
(**7**), $C_6H_5O(O)_{br.}$,
ortho, C_1



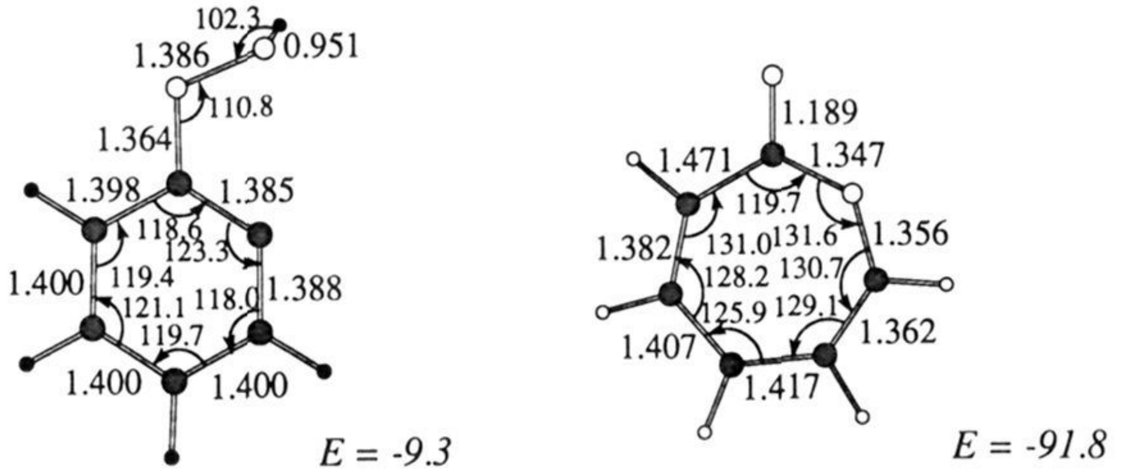
(**8**), $C_6H_5O(O)_{br.}$,
meta, C_1



(**9**), $C_6H_5O(O)_{br.}$,
para, C_1



(**10**), $C_6H_4O(OH)$, ortho, C_s, $^2A''$ (**11**), $C_6H_4O(OH)$, para, C_s, $^2A''$, (**12**), $C_6H_4O(OH)$, meta, C_s, $^2A''$



(**13**), $C_6H_4(OOH)$, C_1 (**14**), C_6OH_5O, C_s, $^2A''$

Figure 1. UHF/6-31G* optimized geometries and PUMP3/6-31G*+ZPE relative energies (in kcal/mol, with respect to $C_6H_5 + O_2$).

we consider the PUMP3/6-31G*//UHF/6-31G* + ZPE(UHF/6-31G*) method as the best one in the present study. The calculated ZPE were scaled by 0.893 to account for anharmonicity.[10] The calculations have been performed using the GAUSSIAN 92 program.[12]

Geometries and Relative Energies of the Isomers

The different isomers of the $C_6H_5O_2$ radical can be divided in six groups as shown in Figure 1:

1. (**1–3**): Two oxygen atoms are connected with each other and/or with the same carbon atom of the ring.
2. (**4–6**): One of the oxygen atoms forms a double bond with the C atom, and another one is bound to the other C in the ortho, meta, or para position forming a C(H)(O) group.
3. The (**7–9**) group contains epoxy isomers where in addition to a C=O double bond, the second O atom occupies some bridging position with respect to the C_6 ring.
4. The structures (**10–12**) include a C=O double bond and a terminal OH group in the ortho, para, or meta location relative to the C=O.
5. One isomer, **13**, has a hydroperoxy OOH ligand with one C atom and no ligand with the adjacent carbon.
6. The structure **14**, recently proposed by Carpenter,[9] contains six carbon atoms and one oxygen atom forming a seven-membered ring, with the second O attached to one of the two C atoms connected with the O atom in the ring, giving rise to the —C=O-(O)— group.

The relative energies of the various geometric isomers shown in Figure 1, with respect to $C_6H_5 + O_2$ calculated at different levels of theory, are presented in Table 1. Figure 2 shows the characters of bonds in C_6H_5, C_6H_5O, $C_6H_4O_2$, and $C_6H_5O_2$.

The phenyl peroxy radical, C_6H_5OO (**1**), is formed in the reaction of the phenyl radical, C_6H_5, with molecular oxygen. The calculated exothermicity of these biradical reactions is 41.0 kcal/mol at the PUMP3//UHF/6-31G* + ZPE(UHF/6-31G*), at which level all the energies will be reported hereafter unless otherwise indicated, in good agreement with an experimental estimate of 37 kcal/mol[13] and the value calculated by the BAC-MP4 method (40 kcal/mol).[14] **1** has a planar structure of C_s symmetry and $^2A''$ ground electronic state. The unpaired electron in this radical is located on the terminal oxygen atom perpendicularly to the molecular plane. In going from $C_6H_5 + O_2$ to C_6H_5OO (**1**) the O–O bond is stretched by as much as 0.13 Å, and a new single C–O bond is created. The aromaticity of the phenyl radical is preserved in **1**; all C–C bond lengths in the ring are similar, 1.38–1.39 Å. The $C^6C^1C^2$ angle with the carbon atom interacting with O_2 slightly reduces as compared with the corresponding angle in C_6H_5 but remains somewhat higher than 120°. The distance between the terminal oxygen and hydrogen atoms in the ortho position is 2.41 Å, implying only very weak hydrogen bond type interaction.

The isomer **2** is the π-complex of O_2 with the C_6H_5 radical. **2** is an analog of the H_2CO_2 dioxirane[15] and the $C_2H_3O_2$ dioxiranylvinyl radical.[9] This structure is about 14 kcal/mol less stable than the initial adduct **1** but still more favorable than $C_6H_5 + O_2$ by 27.4 kcal/mol at our best PUMP3 level. The energy difference between vinylperoxy and dioxiranylvinyl $C_2H_3O_2$ isomers is 6.3 kcal/mol at the PMP4(SDTQ)//UMP2/

---

(12) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Reglogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. GAUSSIAN 92; Gaussian, Inc.; Pittsburgh, PA, 1992.

(13) Lin, C.-Y. Ph.D. Dissertation, The Catholic University of America, 1986.

(14) Melius, C. F., private communication.

(15) (a) Murray, R. W.; Feyaraman, R. *J. Org. Chem.* **1985**, *50*, 2874. (b) Curci, R.; Fiorentino, M.; Troisi, L.; Edwards, J. O.; Pater, R. H. *J. Org. Chem.* **1980**, *45*, 4758. (c) Bunnelle, W. H. *Chem. Rev.* **1991**, *91*, 335.

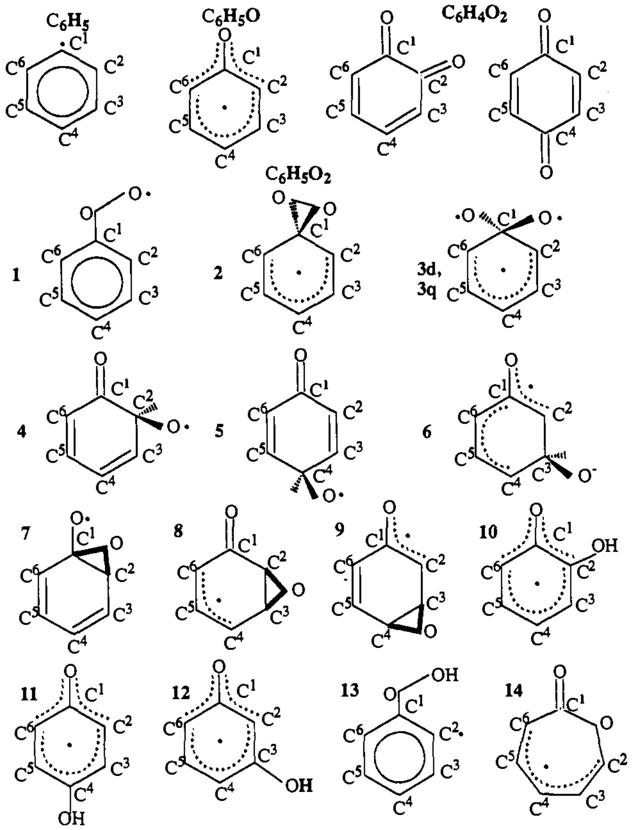


Figure 2. Characters of bonding in C_6H_5, C_6H_5O, C_6H_4OO, and various isomers of $C_6H_5O_2$.

6-311G(d) level.[9] Meanwhile, dioxirane is well established to be more stable than its dioxygen ylide H_2COO.[16] The calculated energy difference between the two is 32.9 kcal/mol at the MP4//HF/3-21G level and 22.1 kcal/mol at the QCISD(T)//QCISD/3-21G level.[16] The lesser stability of **2** relative to **1** can be attributed to the loss of aromaticity of the ring in the π-complex. We found a clear bond alternation in **2**: ortho C^1C^2 and C^6C^1 bonds become single (1.48 Å), meta C^2C^3 and C^5C^6 turn to double bonds (1.37 Å), and para C^3C^4 and C^4C^5 bonds have an intermediate length of 1.42 Å. The CCC angle with the C^1 atom connecting to O_2 sharpens to 116.6°. The bond alternation in **2** is more pronounced than that in C_6H_5O with a double C=O bond. The σ-bond in O is conjugated with π electronic orbitals of the C_6 ring. While the O–O distance in $C_6H_5O_2$ **2**, 1.44 Å, is strained by 0.14 Å, as compared to that in **1**, it is significantly shorter than the O–O bond length in the dioxirane, 1.52 Å, at the similar UHF levels of theory. It is worth noting that the geometry of dioxirane does not change much from the UHF/3-21G to QCISD/6-31G* levels of theory.[16] Therefore, UHF/6-31G* optimized geometry of **2** seems to be quite reliable. **2** has C_{2v} symmetry. Two oxygen atoms and the carbon atom C^1 form an almost equilateral triangle. The ground electronic state of **2** is $^2B_1$, and the unpaired electron is spread out between the carbon atoms in the plane perpendicular to the C_6 plane and is involved in the π electronic system of the ring. As far as we know, no such stable alkyl·O_2 complexes have been reported before except the alkenyl analog, $C_2H_3O_2$.[9]

In the isomers **3d** and **3q**, the O–O bond is broken, and the C^1 atom is connected with the two oxygens by single bonds. As a result, both O atoms have one unpaired electron. The structure is akin to that of OCH_2O dioxymethane biradical which has a triplet ground electronic state.[16] For $C_6H_5O_2$, however, the lower spin doublet structure **3d** is more preferable than the **3q** quartet by 8 kcal/mol. The optimized geometries of **3d** and **3q** are similar, but the latter is symmetric (C_{2v}), while the former has no symmetry. The structure of **3d** is close to C_{2v} but slightly distorted. The doublet electronic state for the symmetric **3q** geometry is still lower than the quartet state and higher than the energy of **3d** by only 0.4 kcal/mol at the UHF/6-31G* level. The lowest doublet state of **3q**, which has similar electronic structure with **3d**, is $^2A_1$. An unpaired electron of one of the oxygen atoms is coupled with the unpaired one of the C_6 ring. This coupling leads to distortion of geometry of **3d** from the C_{2v} symmetry. The ground quartet state of **3q** is $^4A_1$, and three unpaired electrons are located on the two oxygens and in the π-system of the ring. **3d** and **3q** have close geometries with an OO distance about 2.30 Å and an OCO angle of 111–112°. The CO bond lengths do not change almost as compared to that in **2**. The CC bond alternation in **3d** and **3q** is stronger than that in **2**, single ortho CC bonds are 0.03–0.04 Å longer. The critical $C^6C^1C^2$ angle in **3d** and **3q** becomes closer to the tetrahedral angle showing sp^3 hybridization for the "active" carbon atom. **3d** is 14.8 kcal/mol less stable than the π-complex **2**, in the PUMP3//UHF/6-31G* approximation, that is compatible with the energy difference of 11.2 or 12.4 kcal/mol between the dioxirane and dioxymethane biradical at the PUMP4//UMP2/6-31G* and QCISD(T)//QCISD/6-31G* levels of theory.[16] Note, for the OCH_2O biradical, on going from the UHF/3-21G to the QCISD/6-31G* level the CO bond length is shortened by 0.1 Å, while the OO distance change is less significant.[16] Similar changes of the geometry at higher levels of theory can be expected for **3d** and **3q**.

The isomers **4** and **5** contain C=O double bonds and C(H)(O) groups in the ortho and para position, respectively. Both structures are significantly more stable than **1**, and the energy gain with respect to $C_6H_5 + O_2$ is 54.8 for **4** and 61.2 kcal/mol for **5**. The unpaired electron in both structures is located on the oxygen atom having a single bond with the carbon of the ring. **5** has C_s symmetry, and the symmetry plane is perpendicular to the plane of the ring. The ground electronic state of **5** is $^2A''$; the single occupied orbital is parallel to the C_6 plane. This is also the case for the structure **4**. In the same manner as in **2** and **3**, the ring in **4** and **5** structures includes two long single C–C bonds (1.51–1.53 Å) and two short C=C double bonds (1.36–1.38 Å) in **5** as well as two CC bonds of an intermediate length (1.44–1.48 Å). The smallest CCC angle is found for the carbon of the HCO group (114–115°); it is followed by the angle with the C atom of the C=O double bond (119° and 116°). The HCO angle is close to the tetrahedral value. CH bonds in the HCO groups are slightly elongated as compared to the regular CH distance of 1.074–1.075 Å. The CO single bond is also found to be longer than those in **1–3**.

It is well known that there is no meta isomer for $C_6H_4O_2$ benzoquinone.[17] We were also unable to find any local minimum for the meta configuration of $C_6H_4O(O)(H)$. The meta structure **6** is determined to have one imaginary frequency and to be a transition state on the potential energy surface of the $C_6H_5O_2$ species. The energy of **6** is 3.5 kcal/mol higher than that of $C_6H_5 + O_2$. The instability of **6** can be explained by considering the bond character for this structure. To maintain the valence for all carbon atoms to be equal to four, the unpaired electron has to be delocalized between C^1, C^3, C^4, C^5, C^6 and oxygen connecting with C^1 (see Figure 2). As a result, the C^1O distance, 1.27 Å, is longer than a regular double CO bond but shorter than a regular single CO bond. The second oxygen atom connecting with C^3 by a shortened single bond (1.31 Å) has to be negatively charged O^-, which was confirmed by the data of Mulliken population analysis. Akin to the $H_2C{=}O^+{-}O^-$ carbonyl ylide,[16] this electronic structure is unfavorable.

The isomers **7–9** form the epoxy group of structures. Although they differ geometrically only by the position of the bridging oxygen, their electronic structures are distinct. **7** is the least stable isomer of the three. It lies 49.0 kcal/mol below the

---

(16) Bach, R. D.; Andrés, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207, and references therein.

Table 1. Relative Energies (kcal/mol) and Zero-Point Energy Corrections of Various Isomers of $C_6H_5O_2$

species	$\langle S^2\rangle$[a]	ZPE(NIMAG)[b]	E_{rel}[c]					
			HF	UMP2	PUMP2	UMP3	PUMP3	UMP4(SDQ)
C_6H_5 (C_{2v}, $^2A_1$) + O_2[d]	1.43	53.6(0)	−379.68298	−380.68400	−380.71751	−380.72411	−380.74920	−390.74558
C_6H_5O (C_{2v}, $^2B_1$) + O	1.39	53.6(0)	−47.7	−10.0	−10.4	−20.6	−21.6	−19.6
$C_6H_4O_2$ (ortho, C_{2v}, $^1A_1$) + H	0.0	51.6(0)	−25.0	−78.4	−57.3	−66.0	−50.2	−64.5
$C_6H_4O_2$ (para, D_{2h}, ^2A_g) + H	0.0	51.6(0)	−33.9	−85.5	−62.4	−73.6	−57.9	−79.7
1, C_s, $^2A''$	0.77	57.7(0)	−16.2	−63.3	−44.5	−55.4	−41.0	−51.6
2, C_{2v}, $^2B_1$	1.21	55.7(0)	−0.5	−34.9	−28.9	−31.3	−27.4	−30.9
3d, C_1, ^2A	2.23	54.4(0)	−25.5	−1.5	+3.6	−13.1	−12.6	−11.4
3q, C_{2v}, $^4A_1$	4.23	54.3(0)	−24.9	0.0	+9.9	−11.8	−4.6	−9.8
4, C_1, ^2A	1.57	55.9(0)	−52.1	−49.9	−46.7	−54.9	−54.8	−54.7
5, C_s, $^2A''$	0.76	58.3(0)	−46.9	−77.6	−57.8	−76.3	−61.2	−73.2
6, C_1, ^2A	1.05	54.3(1)	+19.2	−7.3	+3.3	−4.2	+3.5	−6.0
7, C_1, ^2A	0.78	57.8(0)	−25.4	−67.0	−48.3	−62.2	−49.0	−59.2
8, C_1, ^2A	1.11	57.0(0)	−54.1	−85.5	−78.0	−81.8	−76.3	−81.1
9, C_1, ^2A	1.23	56.6(0)	−45.3	−70.5	−64.5	−69.1	−65.4	−68.3
10, C_s, $^2A''$	1.31	56.8(0)	−92.5	−113.1	−110.5	−112.3	−110.9	−111.4
11, C_s, $^2A''$	1.33	56.3(0)	−89.1	−106.3	−104.5	−106.6	−107.1	−105.6
12, C_s, ^2A	1.35	56.2(0)	−88.9	−104.6	−103.4	−105.2	−105.0	−104.3
13, C_1, ^2A	1.41	56.1(0)	+10.5	−11.5	−7.7	−11.0	−9.3	−9.6
14, C_s, $^2A''$	1.25	56.5(0)	−75.7	−98.1	−93.0	−94.9	−91.8	−95.3

[a] $\langle S^2\rangle$ before projection. Values after projection are 0.75 for doublet states and 3.75 for quartets. [b] ZPE are calculated at the UHF/6-31G* level and scaled by 0.893. [c] The relative energies are calculated with ZPE (scaled UHF/6-31G*) corrections with respect to $C_6H_5O_2$. [d] The total energies (in hartree).

reactants. The bridging oxygen is located in the ortho position with respect to the terminal CO bond. The latter is more like a single bond, and the unpaired electron is located on the terminal oxygen, while the corresponding molecular orbital is perpendicular to the ring plane. In the ring we can see two double C=C bonds (C^3C^4 and C^5C^6, 1.33 Å) and four single C–C bonds (1.46–1.50 Å). The bridged CC bond is the longest one. CO distances for the bridging oxygen are close to the regular single CO bonds. The geometry of the C–O–C bridge is the common feature of the structures **7**–**9**. The CCC angles with the carbon atoms involved in the CO or COC bonds are reduced to 117–119°.

The meta isomer **8** is the most stable epoxy structure, 76.3 kcal/mol below $C_6H_5 + O_2$. As shown in Figure 2, the unpaired electron is distributed between C^4, C^5, and C^6 atoms at the MO perpendicular to the ring plane. The terminal CO bond is a typical double bond (1.22 Å). C^4C^5 (1.39 Å) and C^5C^6 (1.40 Å) are closer to double bonds; the other CC are single bonds (1.45–1.50 Å). The bridged CC bond (C^2C^3, 1.47 Å) is slightly shorter than that in **7** but close to that in **9**.

The *p*-epoxy isomer **9** lies 65.4 kcal/mol below $C_6H_5 + O_2$. It has the unpaired electron spread out mostly between the terminal oxygen atom and C^1 and C^2 perpendicularly to the ring plane. Therefore, the C^1O bond (1.25 Å) is longer than a regular double bond, and C^1C^2 (1.43 Å) is shorter than a regular CC single bond. C^5C^6 (1.35 Å) is rather a double bond, and the rest are single bonds.

The ortho, para, and meta hydroxyl isomers **10**–**12** form the group of the most stable structures lying 110.9, 107.1, and 105.0 kcal/mol below the reactants, respectively. **10**–**12** are geometric and electronic analogs of C_6H_5O with one of the hydrogens replaced by the OH group. In all three radicals, the unpaired electron is distributed between six carbons and terminal oxygen. The corresponding single occupied MO includes contributions of π p-atomic orbitals of these atoms. The C_6H_5O phenoxy radical has C_{2v} symmetry, and its ground electronic state is $^2B_1$. **10**–**12** have a plane of symmetry coinciding with the ring plane (C_s symmetry), and their ground electronic state is $^2A''$. The terminal C^1O bond (1.25 Å) in all four radicals is slightly elongated as compared to a regular C=O double bond; the $C^6C^1C^2$ angle is 118–119°. The bond alternation in the C_6 ring is not very strong; ortho C^1C^2 and C^1C^6 bonds are somewhat longer (1.44 Å), meta C^2C^3 and C^5C^6 are shorter (1.38–1.39 Å), and para C^3C^4 and C^4C^5 are in the middle (1.40–1.41 Å). The geometry of the ring does not depend on the position of the OH group.

The most stable isomer in this group is the ortho structure **10**. This may be attributed to the weak hydrogen bond-like interaction between the terminal oxygen and hydrogen of the OH group. Such bonding is possible only in ortho **10** but is absent in **11** and **12**. The hydrogen atom of the OH group is attracted by the O atom, the distance between them is 2.19 Å. The C^1C^2O, 118.6°, and C^2OH, 108.5°, angles in **10** are noticeably smaller than the corresponding C^3C^4O and C^4OH angles in **11** and C^2C^3O and C^3OH angles in **12**.

We speculate also the existence of another conformer of **10** where the OH group would be rotated around the C^2O axis by 180° and H would be in an *anti* position to the other O atom. Its energy would be close to those of **11** or **12**, since O···H hydrogen bond would be impossible. For **12**, the existence of the second conformer with a close energy is also expected. For **11**, as well as for each conformer of **10** and **12** another enantiomer can exist.

The structure **13**, hydroperoxyl phenyl radical, is a direct analog of C_6H_5 where one of the hydrogens is replaced by the hydroperoxy group (OOH). The isomer is only 9.3 kcal/mol more stable than $C_6H_5 + O_2$. In a similar manner as in C_6H_5 (C_{2v}, $^2A_1$), the unpaired electron in **13** is located on the "bare" C^2 atom in the plane of the ring. The ring aromaticity is preserved; all CC bonds have similar lengths of 1.39–1.40 Å. The $C^1C^2C^3$ angle is somewhat larger at 120° similar to the corresponding $C^6C^1C^2$, and $C^2C^3C^4$ angles are about 118°. The H atom of the OOH group is turned out of the ring plane, and **13** therefore possesses only C_1 symmetry. Other isomers of the $C_6H_4(OOH)$ radical with different mutual disposition of the "bare" C atom and the OOH group are also possible. However, we expect them to have similar energies, geometric, and electronic structures as **13**. Moreover, the other forms of the hydroperoxyl phenyl radical do not seem to be relevant to the kinetics of the $C_6H_5 + O_2$ reaction, and we did not investigate them.

In the structure **14**, six carbon atoms and one oxygen atom form a seven-membered ring. The second O atom is attached to one of the two C atoms connected with the oxygen in the ring, forming a C=O double bond. **14** lies 91.8 kcal/mol below the reactants. Interestingly, the $H_2COC(O)(H)$ structure with the COC chain and C=O double bond is 97.5 kcal/mol lower than $C_2H_3 + O_2$ at the PMP4(SDTQ)//UMP2/6-311G(d) level.[9] $C_6(O)H_5O$ **14** has a planar structure and $^2A''$ ground electronic state. The unpaired electron is distributed between C^2, C^3, C^4, C^5, and C^6 atoms at the π MO. The CO bond in the ring has a single character (1.35–1.36 Å), while the out-of-ring CO bond is a regular double bond (1.19 Å). We can expect also existence of the para isomer of $C_6(O)H_5O$, with the oxygen atom in the ring between C^3 and C^4, and single C^1C^2, C^1C^6, C^3O, and OC^4 bonds, double C^2C^3 bond, and an unpaired electron on the π orbital distributed between C^4, C^5 and C^6. The meta isomer, on the other hand, is unlikely to be stable for the same reasons as *m*-benzoquinone or *m*-$C_6H_4O(O)(H)$ **6**.

Vibration Frequencies

The calculated UHF/6-31G* vibrational frequencies for C_6H_5, C_6H_5O, $C_6H_4O_2$, benzoquinones, and different isomers of $C_6H_5O_2$ are presented in Table 2. They were scaled by 0.893 for anharmonicity correction. The vibrational spectrum of C_6H_5 radical contains the most intensive vibration B_1 at 675 cm^{-1}. It corresponds to out-of-plane deformation of the C_6 ring coupled with out-of-plane bending of CH bonds. Only this frequency has been observed experimentally, and the measured value is 710 cm^{-1}.[18] Similar vibrational modes are present in the spectra of all of the C_6H_5O, $C_6H_4O_2$, and $C_6H_5O_2$ species. The stretching vibrations for the CH bonds have regular values of about 3000 cm^{-1}. A peculiar feature of the spectrum of C_6H_5O is an A_1 vibration at 1262 cm^{-1} corresponding to the stretch of the CO bond strongly coupled with symmetric C^2H and C^6H bending. The UHF method tends to underestimate this frequency,[11a] the experimental value is 1505 cm^{-1}.[19]

In the spectrum of *o*-benzoquinone, the following vibrations are the most intensive: B_1 out-of-plane ring deformation at 738 cm^{-1}, A_1 CC bond stretch at 1258 cm^{-1}, and symmetric A_1 and asymmetric B_2 stretching vibrations of the double CO bonds at 1806 and 1810 cm^{-1}, respectively. The calculated IR spectrum of *p*-benzoquinone is quite different. The theoretical frequencies can be verified by comparing to those gleaned from experiments.[20] Among the most intense peaks, the spectrum contains the ring torsion B_{3u} vibration at 88 cm^{-1} (the experimental value is 108 cm^{-1}),[20a] in-plane CO bending B_{2u} at 401 cm^{-1} (409 cm^{-1}—experiment),[20a] out-of-plane CH bending B_{3u} at 888 cm^{-1} (884 cm^{-1}—experiment),[20a] CC stretching vibration at 1284 cm^{-1} (1302 cm^{-1}—experiment),[20a] and asymmetric B and symmetric Ag stretch of CO bonds at 1787 cm^{-1} (1660 cm^{-1}—experiment)[20a] and 1804 cm^{-1} (1688 cm^{-1}—experiment),[20a] respectively. The agreement between the theoretical and experimental data is good for qualitative estimates. The greatest disagreement with experiment, about 125 cm^{-1}, at the RHF/6-31G* level, is found for the CO stretch vibrations, and it has been shown that the agreement is better when the multireference UNO-CAS/6-31G* method with the optimized scaled ab initio force field is employed.[11a,21]

The isomer **1** of $C_6H_5O_2$ contains a COO fragment which is reflected in the vibrational spectrum by A′ OO stretch at 919 cm^{-1} and A′ CO stretch at 1220 cm^{-1}. The OO stretching vibration for the π-isomer **2** has the value of 946 cm^{-1}. The CO stretch in **2** is coupled with in-plane CH bending and its frequency (1286 cm^{-1}) shifts toward higher values as compared with that in **1**. There is another intense vibration involving the CO_2 fragment, the bending CO_2 triangle in the plane, perpendicular to the C_6 ring, with the frequency of 827 cm^{-1}.

In the spectra of **3d** and **3q**, where the OO bond is broken, the OO stretch is replaced by CO bending vibration with the frequency of 1064 cm^{-1} for **3d** and 1047 cm^{-1} for **3q**. The bending of CO_2 triangle with respect to C plane occurs at 1092 cm^{-1} for **3d** and at 1064 cm^{-1} for **3q**. The CO stretching vibrations have lower frequencies than that in **2**, 1108 and 1118 cm^{-1} for the doublet and quartet structures, respectively.

The most pronounced feature of IR spectra for **4** and **5** is an upfield shift of one of the CH stretching vibrations. The CH bond in the C(H)(O) fragment is slightly elongated, and the corresponding frequency shifts to the band around 2850 cm^{-1}. The CO single bond stretch vibrations have the frequencies of 1056 cm^{-1} in **4** and 1069 cm^{-1} in **5**. The stretching vibrations of CO double bonds are strongly coupled with the vibrations of C=C bonds, and their frequencies are 1467 and 1495 cm^{-1} for **4** and 1679 and 1788 cm^{-1} for **5**.

The calculated vibrational spectra of the epoxy isomers **7–9** include a lot of vibrations of medium intensities without any strong peaks. The stretching vibrations of bridged C–O–C bonds take place at 821 and 959 cm^{-1} for **7** and 872 and 933 cm^{-1} for **8** as well as at 813 and 991 cm^{-1} for **9**. The vibrations corresponding to the stretching of terminal CO bond have distinct frequencies in the three isomers. In **8**, the bond is a double C=O, and the frequency is high, 1471 cm^{-1}. In **7**, the bond is closer to a single one, and the frequency, 1196 cm^{-1}, is much lower. In **9**, the CO bond has an intermediate length and an intermediate vibrational frequency, 1274 cm^{-1}.

The structures **10–13** have OH bonds which are reflected in the vibrational spectra by peaks at the 3600–3700 cm^{-1} band. **10** has several peculiar frequencies. The vibration A′ at 315 cm^{-1} corresponds to the stretch of the weak O···H hydrogen bond. Rotations of the OH group around the C^2O paired with out-of-plane ring deformation (A″) have the frequencies of 467 and 479 cm^{-1}. Bending vibrations of the OH group (A′) occurs at 1189 and 1402 cm^{-1}. The frequency of the single CO bond stretch (A′) is 1210 cm^{-1}, while for the double ("one and a half") CO bond, the stretching vibrations (A′) are strongly coupled with that for C=C with the frequencies of 1310 and 1311 cm^{-1}. $C_6H_4(O)OH$ is an analog of C_6H_5O, and the latter frequencies are close to the corresponding frequencies of C_6H_5O.

The spectra of **11** and **12** are quite similar to that of **10**. The common features are the following: CO single bond stretching vibrations at 1244 cm^{-1} for **11** and 1193 cm^{-1} for **12**; OH bendings with the frequencies of 1127 and 1293 cm^{-1} in **11** and 1123 and 1376 cm^{-1} in **12**; and the stretch of C=O bonds at 1272 cm^{-1} for **11** and 1252 and 1276 cm^{-1} for **12**. The vibration, which belongs to the stretching of the O···H hydrogen bond in **10**, corresponds to bending of the OH group in **11** and **12**. But the frequency does not differ much: 349 cm^{-1} in **11** and 329 cm^{-1} in **12**. The difference in the IR spectra of **11** and **12** from that of in **10** is the lowering of the frequency for OH rotation by about 200 cm^{-1}, to 263 cm^{-1} for **11** and 279 cm^{-1} for **12**. This is caused by the absence of the O···H hydrogen bond in the meta and para isomers of C_6H_4OOH. Also, the frequency of the OH bend in **11** and **12** shifts by about 50 cm^{-1} toward higher values, as compared to that of **10**.

The calculated vibrational spectrum of **13** includes intense torsional vibrations of the OH bond with the frequencies of 193, 212, and 246 cm^{-1}. $C_6H_4(OOH)$ **13** is an analog of the C_6H_5 radical, and the frequency of out-of-plane ring deformation, 696 cm^{-1}, is close to that in C_6H_5 (675 cm^{-1}). The other characteristic vibrations of **13** are as follows: CO bending at 760 cm^{-1}; OO stretch at 1035 cm^{-1}; CO stretch at 1223 cm^{-1}; and the bending vibrations of the OH group at 1401 and 1429 cm^{-1}. The most prominent features of the vibrational spectrum of **14** are the CO double bond stretching mode A′ at 1694 cm^{-1}, the stretching mode of the ring single CO bond A′ at 1310 cm^{-1}, and the bending vibration of the COC fragment A′ with the frequency of 976 cm^{-1}.

Speculation on Possible Mechanisms of the $C_6H_5 + O_2$ Reaction

The reaction of C_6H_5 with O_2 initiates by formation of C_6H_5OO and at high temperatures gives various products including

---

(17) Patai, S., Ed. *The Chemistry of the Quinonoid Compounds*; Wiley: New York, 1974.

(18) Jacox, M. E. *J. Phys. Chem. Ref. Data* **1984**, *13*, 945.

(19) Tripathi, G. N. R.; Schuler, R. H. *J. Chem. Phys.* **1984**, *81*, 113.

(20) (a) Davies, M.; Prichard, F. E. *Trans. Faraday Soc.* **1963**, *59*, 1248. (b) Stammereich, H.; Forneris, R. *Z. Naturforsch.* **1952**, *7A*, 756. (c) Anno, T.; Sado, A. *Bull. Chem. Soc. Jpn.* **1958**, *31*, 734. (d) Becker, E. D.; Charney, E.; Anno, T. *J. Chem. Phys.* **1965**, *42*, 942. (e) Dunn, T. M.; Francis, A. H. *Mol. Spectrosc.* **1974**, *50*, 1. (f) Stammreich, M.; Teixeira San, Th. *J. Chem. Phys.* **1965**, *42*, 920.

(21) Liu, R.; Zhou, X.; Pulay, P. *J. Phys. Chem.* **1992**, *96*, 4255.

Table 2. UHF/6-31G* Vibrational Frequencies (Scaled by 0.893, in cm^{-1}) and Intensities (in Brackets, in kM/mol) for Different Isomers of $C_6H_5O_2$

		$C_6H_5O_2$		$C_6H_5O_2$														
C_6H_5	C_6H_5O	*o*-	*p*-	**1**	**2**	**3d**	**3q**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
361[0.0]	191[3]	69[0.0]	88[18]	34[0.1]	107[2]	81[1]	68[1]	43[2]	76[9]	497i[11]	201[1]	128[5]	135[6]	160[1]	134[2]	190[4]	46[8]	76[0.0]
389[2]	350[0.0]	223[8]	228[0.0]	228[0.4]	273[0.0]	198[0.2]	230[0.0]	194[4]	218[2]	149[12]	248[1]	255[7]	232[4]	254[0.2]	263[153]	205[2]	193[40]	109[9]
569[0.3]	427[10]	344[6]	338[0.0]	261[1]	376[12]	333[6]	365[0.0]	261[5]	290[9]	213[3]	378[4]	310[2]	376[3]	315[20]	312[0.0]	279[151]	212[44]	335[1]
571[0.7]	449[1]	402[0.0]	401[38]	409[0.0]	400[1]	363[1]	367[7]	378[1]	411[1]	359[19]	413[5]	419[18]	411[10]	410[1]	349[14]	329[20]	246[83]	344[0.3]
613[14]	435[0.2]	418[4]	431[0.0]	433[3]	421[0.0]	369[9]	375[8]	439[7]	431[28]	393[27]	462[11]	449[3]	423[9]	432[0.1]	358[0.3]	390[1]	382[2]	398[3]
675[77]	558[0.1]	463[1]	437[0.0]	494[4]	423[3]	389[5]	378[5]	449[11]	455[1]	434[10]	507[1]	502[3]	482[5]	467[48]	434[1]	474[1]	416[2]	476[5]
759[0.0]	607[28]	529[0.1]	502[1]	598[1]	549[0.0]	536[12]	538[17]	501[7]	490[6]	452[7]	595[10]	528[11]	537[5]	479[104]	444[7]	483[4]	463[1]	495[10]
821[0.7]	715[61]	535[23]	579[0.0]	603[0.4]	554[21]	545[2]	543[1]	535[4]	571[2]	477[16]	635[4]	610[21]	612[24]	536[4]	474[6]	501[1]	573[2]	604[16]
884[0.2]	744[0.0]	661[3]	721[0.4]	680[11]	658[47]	563[4]	572[5]	642[5]	679[6]	523[20]	678[4]	660[15]	650[2]	542[1]	601[1]	542[2]	579[0.4]	676[48]
894[0.0]	765[1]	738[111]	734[0.0]	758[87]	692[1]	634[61]	634[55]	690[68]	729[1]	638[14]	735[39]	727[5]	734[14]	644[8]	643[3]	606[12]	624[1]	689[3]
920[0.0]	831[10]	771[0.0]	747[0.0]	788[15]	696[0.0]	650[0.5]	641[0.0]	717[13]	775[1]	743[17]	779[8]	770[46]	737[18]	708[20]	733[4]	700[5]	696[78]	722[19]
946[2]	894[0.0]	847[0.1]	771[0.0]	842[0.0]	762[0.0]	721[0.1]	716[0.2]	785[7]	823[15]	785[35]	821[76]	803[2]	793[15]	710[70]	736[22]	713[36]	760[19]	780[18]
972[1]	909[0.2]	877[0.0]	888[122]	919[12]	827[51]	743[1]	744[0.3]	871[0.2]	875[49]	841[11]	855[12]	872[26]	813[31]	787[0]	771[0.3]	771[43]	785[3]	781[29]
999[0.6]	922[0.1]	906[1]	918[16]	974[0.2]	884[2]	873[0.0]	885[0.0]	900[12]	921[36]	865[71]	908[12]	893[5]	911[6]	847[6]	779[84]	805[7]	869[3]	868[1]
1102[0.2]	945[1]	1111[1]	1012[0.0]	982[0.0]	888[0.0]	882[0.2]	891[0.4]	905[0.7]	996[12]	958[11]	959[19]	914[6]	915[8]	866[7]	866[0.2]	892[11]	910[0.2]	879[6]
1110[0.2]	1013[3]	1023[0.0]	1014[0.0]	1000[1]	896[4]	899[3]	896[4]	917[5]	1021[0.3]	1011[7]	979[4]	933[11]	931[18]	905[1]	889[0.1]	894[0.2]	920[1]	894[1]
1244[0.1]	1087[11]	1095[26]	1055[46]	1005[3]	915[0.2]	916[0.2]	919[0.3]	966[6]	1030[14]	1016[3]	985[3]	1017[16]	991[35]	944[5]	943[0.7]	931[1]	956[6]	904[0.5]
1251[1]	1106[0.0]	1125[17]	1134[0.0]	1053[4]	946[1]	980[4]	960[2]	1056[30]	1069[51]	1039[29]	998[0.0]	1059[19]	1062[15]	1047[0.2]	1043[12]	1013[9]	1035[4]	976[38]
1392[6]	1247[21]	1152[1]	1198[0.0]	1091[1]	1010[4]	1064[44]	1047[53]	1081[5]	1121[10]	1079[51]	1098[10]	1092[4]	1086[7]	1102[9]	1088[27]	1091[16]	1055[6]	1108[69]
1413[8]	1262[31]	1258[79]	1284[106]	1129[13]	1089[0.4]	1082[24]	1064[158]	1120[6]	1161[7]	1109[76]	1156[11]	1126[2]	1135[1]	1189[30]	1127[123]	1123[162]	1108[1]	1147[30]
1463[1]	1276[2]	1354[0.2]	1348[5]	1148[14]	1099[0.0]	1092[123]	1078[0.3]	1196[39]	1239[38]	1178[26]	1170[5]	1230[8]	1228[21]	1210[216]	1241[14]	1193[103]	1180[7]	1217[91]
1488[1]	1392[1]	1397[40]	1371[0.0]	1192[44]	1248[13]	1108[12]	1118[4]	1271[0.3]	1316[20]	1188[54]	1196[30]	1244[21]	1247[9]	1257[17]	1244[94]	1252[42]	1223[39]	1310[214]
2994[0.1]	1399[2]	1618[1]	1638[10]	1220[106]	1275[2]	1176[15]	1137[0.2]	1310[3]	1375[43]	1230[1]	1263[16]	1304[6]	1274[29]	1310[6]	1272[36]	1272[46]	1255[19]	1338[3]
3002[5]	1458[25]	1662[0.5]	1658[0.0]	1315[1]	1286[81]	1268[0.1]	1272[2]	1369[6]	1378[12]	1277[32]	1357[12]	1342[4]	1338[41]	1311[73]	1293[61]	1280[36]	1389[1]	1388[23]
3012[29]	1464[14]	1806[295]	1787[656]	1454[5]	1369[1]	1343[1]	1338[3]	1394[5]	1434[32]	1346[62]	1387[5]	1380[12]	1363[4]	1402[59]	1384[27]	1376[33]	1401[30]	1408[15]
3018[45]	3000[0.1]	1810[101]	1804[0.0]	1489[76]	1421[59]	1398[12]	1335[9]	1413[49]	1653[0.1]	1393[44]	1425[22]	1432[17]	1376[1]	1428[30]	1409[2]	1409[0.2]	1429[110]	1458[6]
3023[7]	3011[13]	3010[6]	3027[2]	1610[36]	1457[7]	1446[2]	1450[0.4]	1467[25]	1679[5]	1426[131]	1616[2]	1438[4]	1413[13]	1474[4]	1462[33]	1448[13]	1471[16]	1494[42]
	3020[26]	3021[11]	3027[0.0]	1611[19]	1479[3]	1457[1]	1461[3]	1495[12]	1788[394]	1477[89]	1665[0.1]	1471[3]	1452[8]	1506[93]	1510[184]	1513[139]	1505[81]	1693[241]
	3030[18]	3039[6]	3043[6]	3005[0.0]	3006[0.0]	3002[1]	3001[1]	2855[37]	2836[46]	2333[107]	2998[8]	2991[14]	2982[14]	3008[3]	2989[17]	3010[8]	3003[1]	2992[3]
	3032[2]	3042[4]	3044[0.0]	3015[16]	3012[14]	3007[8]	3005[5]	3004[5]	3008[5]	3022[0.2]	3005[6]	3004[5]	2995[42]	3020[15]	3023[3]	3013[6]	3013[13]	3002[13]
				3027[26]	3025[24]	3020[18]	3018[11]	3015[14]	3009[3]	3037[5]	3014[19]	3005[27]	3009[14]	3031[14]	3033[5]	3031[9]	3022[26]	3017[147]
				3035[8]	3036[10]	3027[20]	3022[28]	3026[18]	3034[10]	3051[1]	3025[24]	3022[21]	3030[12]	3036[7]	3038[5]	3038[9]	3029[13]	3037[4]
				3064[1]	3038[0.4]	3033[7]	3030[11]	3034[5]	3036[0.2]	3055[3]	3034[10]	3033[6]	3031[1]	3612[36]	3676[93]	3674[78]	3637[82]	3063[12]

atomic oxygen and hydrogen.[1,2,6,13] The result of our calculations of possible isomers of the $C_6H_5O_2$ radical lets us speculate the following reaction mechanisms producing H and O atoms.

Mechanism 1. C_6H_5OO can eliminate an oxygen atom to produce $C_6H_5O + O$. Interestingly, the reaction is symmetry-forbidden (within the C_s symmetry), and the reverse reaction of two radicals, C_6H_5O ($^2B_1$) and O (^3P), might have a barrier. When we consider the separated C_6H_5O ($^2B_1$) + O (^3P) system in the doublet state, the unpaired π-electron of the ring is formally paired with p π-electron of the oxygen atom, and the p σ-electron of O remains unpaired. Hence, the ground electronic state of the $C_6H_5O + O$ is $^2A'$, while that of $C_6H_5O_2$ **1** is $^2A''$. After the elimination, the oxygen atom could come back and attack C_6H_5O at the ortho, para, or some bridging position to produce $C_6H_4O(H)(O)$ **4** or **5** or some of the epoxy isomers **7–9**. **7–9** could rearrange to form **4** and **5**. Elimination of hydrogen atom from *o*- and *p*-$C_6H_4O(O)(H)$ would give *o*- or *p*-benzoquinone, i.e., *o*/*p*-$C_6H_4O_2$ + H. If the reaction occurs by this mechanism, one would observe a delay in the appearance of hydrogen atoms with respect to the appearance of O atoms.

Mechanism 2. At first step C_6H_5OO **1** rearranges to give the π-complex **2**, which can also be formed directly from the $C_6H_5 + O_2$ reaction. Then, the O–O bond breaks to form **3d**. One of the oxygen atoms either dissociates or starts to migrate around the carbon ring. The sequence of its migration can give ortho **4** by **3d** → **7** → **4** or, further, para **5** by **4** → **8** → **6** → **9** → **5**. **4** or **5** would eliminate either hydrogen or oxygen atom. In this case, they would appear without delay. Our calculations did not show any intermediate or transition state of dioxetane species such as the

structure[6] between **2** and **5**. Moreover, the **2** → **5** transformation is forbidden by symmetry: The singly occupied B_1 orbital of **2** belongs to the A′ irreducible representation if only one plane of symmetry, perpendicular to the ring plane, remains in the system. Therefore, the electronic state of **2** corresponds to $^2A'$, while for **5**, it is $^2A''$, and no C_s symmetric transition state can exist between **2** and **5**.

Mechanism 3 involves the abstraction of the hydrogen atom by the terminal oxygen in C_6H_5OO from the adjacent C atom with the formation of $C_6H_4(OOH)$ **13**. The latter would then rearrange to *o*-hydroxyl phenoxy radical $C_6H_4O(OH)$ **10** by intramolecular migration of the OH group. Elimination of hydrogen from the OH group in **10** would give the *o*-benzoquinone. In addition, the $C_6H_4(OOH)$ radical may dissociate to produce C_6H_4O and OH; the latter can react with C_6H_5 to form C_6H_5OH. The dissociation of the latter would produce a hydrogen atom and the phenoxy radical, C_6H_5O.

Recently, Carpenter proposed another mechanism for the decomposition of the phenylperoxy radical.[9] It involves the **1** → **2** → **7** → **14** pathway followed by the dissociation of the seven-member ring isomer into $C_5H_5^\bullet + CO_2$. However, this mechanism does not lead directly to the appearance of oxygen or hydrogen atoms in the system.

In our laboratory, an extensive effort is underway to calculate the energies and structures of the transition states of the rate-controlling steps in the reaction paths identified above. We hope to provide a more realistic interpretation of high-temperature $C_6H_5 + O_2$ kinetic data, which are gradually becoming available in the literature.[6,13]

Conclusions

The *o*-hydroxyl phenoxy radical $C_6H_4O(OH)$ **10** was found to be the most stable isomer of the $C_6H_5O_2$ species; the exothermicity of the $C_6H_5 + O_2 \rightarrow C_6H_4O(OH)$ **10** reaction was calculated to be 111 kcal/mol. *p*- and *m*-$C_6H_4O(OH)$, **11** and **12**, lie by 4 and 6 kcal/mol above **10**. The seven-membered ring isomer **14** is 19 kcal/mol higher than **10**. The *m*-epoxy $C_6H_5O(O)_{br}$ isomer **8** is next on the stability scale, 35 kcal/mol above **10**. It is followed by the *p*-epoxy structure **9**, *p*-$C_6H_4O(O)(H)$ **5**, *o*-$C_6H_4O(O)(H)$ **4**, and the *o*-epoxy isomer **7**, with energies 46, 50, 56, and 62 kcal/mol higher than **10**, respectively. The phenyl peroxy radical C_6H_5OO **1**, the initial adduct of the $C_6H_5 + O_2$ reaction, is 70 kcal/mol less stable than **10**. The π-complex **2** and the doublet $C_6H_5(O)O$ structure **3d** have the relative energies of 84 and 98 kcal/mol, respectively. **13** is the least stable isomer in doublet electronic state (102 kcal/mol above **10**), while the quartet structure **3q** is 106 kcal/mol higher than the global minimum.

It should be mentioned that the PUMP3//UHF/6-31G* method may not be quantitatively accurate for description of relative energies of various isomers of $C_6H_5O_2$. For instance, it is very difficult with the MP perturbation theory to get a balanced treatment of the relative energies of systems having different numbers of rings, so the stabilities of the double-ring structures **2**, **7**, **8**, and **9** might change when configuration interaction methods would be employed. However, the present numerical results have provided us a sound theoretical basis for the future elucidation of the mechanism of the $C_6H_5O_2$ reaction.

The most stable product of the $C_6H_5 + O_2$ reaction, **10**, cannot be formed directly from the reactants. The conceivable mechanisms for its formation at higher temperatures are the following: $C_6H_5 + O_2 \rightarrow$ **1** → ··· → **4** → **10** and $C_6H_5 + O_2 \rightarrow$ **1** → **13** → **10**. *o*-Benzoquinone can be produced from **4** or **10** by hydrogen elimination. The elimination of the H atom from **5** can give *p*-benzoquinone. However, **5** cannot be formed directly via a highly symmetric

transition state, but it might be formed by a stepwise process involving the initial insertion of the carbon atom into the O=O bond, followed by the migration of one oxygen around the ring.

The relatively high stability of **1**, with $D(C_6H_5\text{-}O_2) = 41$ kcal/mol, is fully consistent with the result of our recent successful kinetic measurement for the $C_6H_5 + O_2$ reaction in the gas phase using the cavity-ring-down technique (see previous paper in this issue).[22] In this study, carried out under the conditions of 297 K ≤ T ≤ 473 K and 20 Torr ≤ P ≤ 80 Torr, the formation of C_6H_5OO was found to have negligible temperature and pressure dependence. This finding is in full agreement with the result of an RRKM calculation based on the calculated energetics and molecular parameters of C_6H_5 and C_6H_5OO.[22]

Acknowledgment. The authors gratefully acknowledge the support of this work by the Division of Chemical Sciences, Office of Energy Sciences, DOE (contract no. DE-FG05-91ER14192) and to the Cherry L. Emerson Center for Scientific Computation for the use of various programs and computing facilities. A fruitful discussion with Dr. C. F. Melius of Sandia National laboratories, Livermore, CA is much appreciated.

---

(22) Yu, T.; Lin, M. C. *J. Am. Chem. Soc.*, previous paper in this issue.