Biradical Intermediates

Generation of the Elusive *meta*-Benzoquinone in the Gas Phase**

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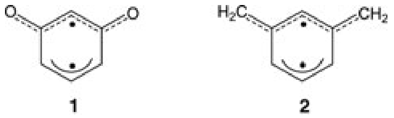
Dedicated to Professor Josef Michl on the occasion of his 65th birthday

meta-Benzoquinone (**1**) is a challenging molecule that belongs to the family of biradicaloid *meta*-disubstituted benzenes.[1] While numerous experimental and theoretical studies have been devoted to the closely related *meta*-xylylene (**2**),[2–4] *meta*-benzoquinone has been studied only theoretically.[4–6] Extensive (σ-S, π-SD)QCI calculations con-



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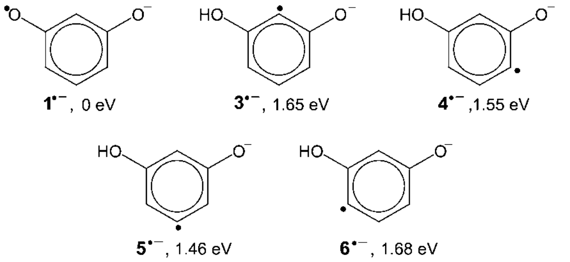
ducted by Fort et al.[4] predict a $^3B_2$ ground state of neutral **1**. The first excited singlet state ($^1B_2$) also has a biradicaloid structure and has been calculated to be 0.4 eV higher in energy.[7] There have been attempts to prepare derivatives of *meta*-benzoquinone, but probably due to the suggested rapid decarbonylation, none of the substituted *meta*-benzoquinones has been isolated so far.[8–10] This work reports the generation of *meta*-benzoquinone by means of neutralization–reionization (NR) mass spectrometry, a technique proved efficient for the generation and characterization of elusive molecules.[11,12]

Neutralization–reionization mass spectrometry consists of three steps. First, an ion of the desired structure is generated in the gas phase. Next, the mass-selected ion is neutralized in high-energy collision with an appropriate gas and all remaining charged species are deflected. In the third step, the beam of neutral species—the parent molecule and its fragments—is reionized in a second time-delayed collision to facilitate mass analysis, detection, and structural characterization based on the fragmentation pattern. As amply demonstrated,[11,12] in an ideal case an NR experiment is a convenient means for the generation and detection of otherwise hardly accessible neutral molecules. However, a conventional NR spectrum contains not only signals indicative for the neutral target molecule, rather it constitutes a superposition of fragmentations of neutral and ionic species involved in the sequential collision events. The problem of extracting the desired information specific to the neutral molecule in question has been addressed by several approaches,[11,13] of which the neutral and ion decomposition difference (NIDD) method[14] is applied here.

The first step towards *meta*-benzoquinone concerns the generation of a suitable ionic precursor.[15] The present study is confined to the corresponding anion, because experiments with the molecular cation $\mathbf{1}^{\bullet+}$ are considered ambiguous as far as the ion structure is concerned due to facile Wagner–Meerwein and other rearrangements in cationic species.[18] The anion $\mathbf{1}^{\bullet-}$ (Scheme 1) is generated by chemical ionization of resorcinol (1,3-dihydroxybenzene) using N_2O as reagent gas, where ionization of the latter provides $O^{\bullet-}$, which serves as the ionizing agent. Formation of $\mathbf{1}^{\bullet-}$ requires the elimination of both hydrogen atoms from the hydroxy groups of the precursor; of course, the singly deprotonated ion $C_6H_5O_2^-$ is observed as well. However, hydrogen may also be abstracted from the ring carbons, which would then lead to the putative anions $\mathbf{3}^{\bullet-}$–$\mathbf{6}^{\bullet-}$ (Scheme 1). According to B3LYP calculations,[19] these tautomers are about 1.5 eV higher in energy than $\mathbf{1}^{\bullet-}$. Therefore, the contribution of ring-deprotonated isomers is very likely to be small—if there is any—compared to $\mathbf{1}^{\bullet-}$. Abstraction of both hydrogen atoms from C–H bonds only as well as ring-opening would lead to anions with even considerably higher relative energies; these structures are therefore not considered any further in the discussion.



Scheme 1. Various isomers of $C_6H_4O_2^{\bullet-}$ and their energies $E_{0K} = E_{tot} + E_{ZPV}$ relative to $\mathbf{1}^{\bullet-}$; $E_{tot}(\mathbf{1}^{\bullet-}) = -381.628204$ Hartree, E_{ZPV} (zero-point vibration energy) $(\mathbf{1}^{\bullet-}) = 0.081688$ Hartree.

The connectivity of the $C_6H_4O_2^{\bullet-}$ anion generated from resorcinol was examined by recording its metastable ion (MI) and collisional activation (CA) mass spectra (Figure 1). The most dominant feature in both spectra corresponds to the loss of carbon monoxide with a characteristic peak shape that indicates a significant reverse activation barrier. The kinetic energy release associated with this process is estimated as 0.53 eV from the horn-to-horn distance of the composite peak in an energy-resolved experiment.[23] However, as the fragmentation pattern in the CA spectrum cannot be associated unambiguously with a particular connectivity of the parent ion, the CA and charge reversal ($^-CR^+$) spectra of $C_6H_4O_2^{\bullet-}$ generated by chemical ionization of $(O\text{-}D)_2$- resorcinol[24,25] and 1,3-bis(trimethylsilyloxy)benzene, respectively, were acquired as well; N_2O was used as reagent gas. If mixtures of isomers were formed, the relative populations of isomers should be precursor-dependent and hence lead to differences in the spectra. Experimentally, the CA and $^-CR^+$ spectra of $C_6H_4O_2^{\bullet-}$ generated from resorcinol, its $(O\text{-}D)_2$ analogue, and 1,3-bis(trimethylsilyloxy)benzene are identical within experimental uncertainty. Thus, we conclude that only the most stable isomer $\mathbf{1}^{\bullet-}$ is formed, irrespective of the precursor employed. Even if other isomers were generated initially,[26] the experimental findings imply that isomerization to $\mathbf{1}^{\bullet-}$ must have occurred either inside the ion source or within the time elapsed during mass selection (ca. 25 μs). The eventual isomerization to other benzoquinone isomers, that is, *ortho* and *para* isomers, is excluded on the basis of different CA as well as $^-CR^+$ spectra of the respective anions (see the

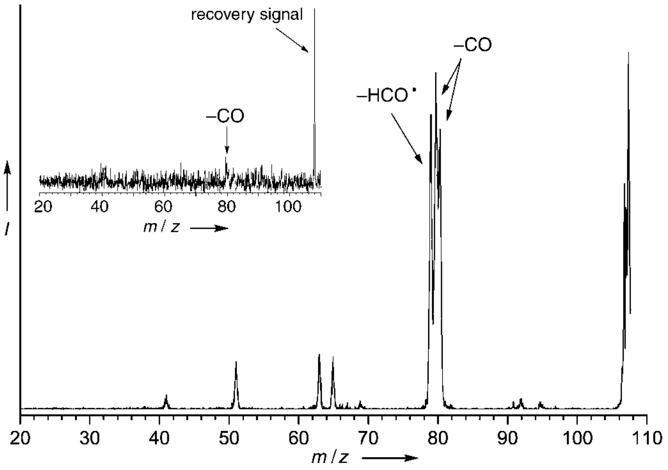
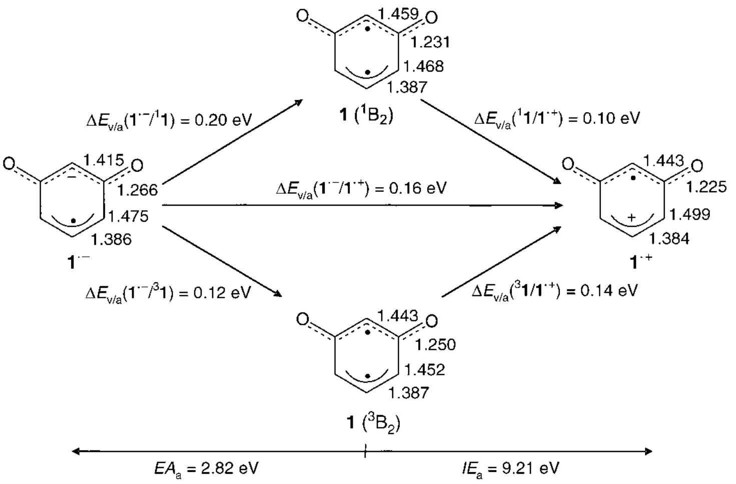


Figure 1. CA mass spectrum of $C_6H_4O_2^{\bullet-}$ generated by chemical ionization of resorcinol using N_2O as a reagent gas. The inset shows the $^-NR^-$ mass spectrum of $C_6H_4O_2^{\bullet-}$.

Supporting Information). Specifically, the base peak in the $^-$CR$^+$ spectrum of *para*-benzoquinone, the thermodynamically most stable isomer, corresponds to C_2H_2 elimination (*m*/*z* 82). This fragmentation is completely missing in the $^-$CR$^+$ spectra of either *ortho* or *meta* isomer. On the other hand, the $^-$CR$^+$ spectrum of *meta*-benzoquinone anion shows intense loss of $C_3H_3^{\bullet}$ (*m*/*z* 69), which is missing in the spectra of the two other isomers. Therefore, the occurrence of skeletal rearrangements leading to the formation of a mixture of benzoquinone isomers can certainly be ruled out.[27] Accordingly, the experimental results imply that $\mathbf{1}^{\bullet-}$ serves as the major, if not exclusive, contributor to the beam of mass-selected $C_6H_4O_2^{\bullet-}$ ions.

Collisional neutralization by electron transfer at keV energies is considered to occur on the femtosecond timescale as a vertical process and is thus governed by Franck–Condon factors.[11–13] The efficiency of the transition between an ion and the corresponding neutral counterpart together with the associated amount of internal excitation can be estimated from the difference of the vertical and adiabatic energies ($\Delta E_{v/a}$) of the corresponding transitions (Scheme 2). Generation of triplet ground state of *meta*-benzoquinone ($^3B_2$) from the anion $\mathbf{1}^{\bullet-}$ is associated with a calculated $\Delta E_{v/a}(\mathbf{1}^{\bullet-}/{}^3\mathbf{1})$ of 0.12 eV; likewise, $\Delta E_{v/a}(\mathbf{1}^{\bullet-}/{}^1\mathbf{1}) = 0.20$ eV results for the formation of singlet $^1B_2$ (Scheme 2).[28] These rather small values suggest favorable Franck–Condon factors for electron detachment from $\mathbf{1}^{\bullet-}$. The probability of $\mathbf{1}^{\bullet-}$ to survive an NR sequence has been probed by a $^-$NR$^-$ experiment.[17] Despite a rather poor signal-to-noise ratio, the $^-$NR$^-$ spectrum of $\mathbf{1}^{\bullet-}$ clearly shows the recovery ion as the major signal (inset in Figure 1). In agreement with the theoretical predictions, neutral *meta*-benzoquinone (**1**) can thus be generated from its anion without undergoing complete dissociation during the time interval of about 1 μs required for the passage from the neutralization to the reionization cell, which defines a minimum lifetime of **1**.



Scheme 2. Redox energies relevant in the neutralization–reionization and charge-reversal experiments. Relative energies and bond lengths [Å] were obtained from calculations.[19]

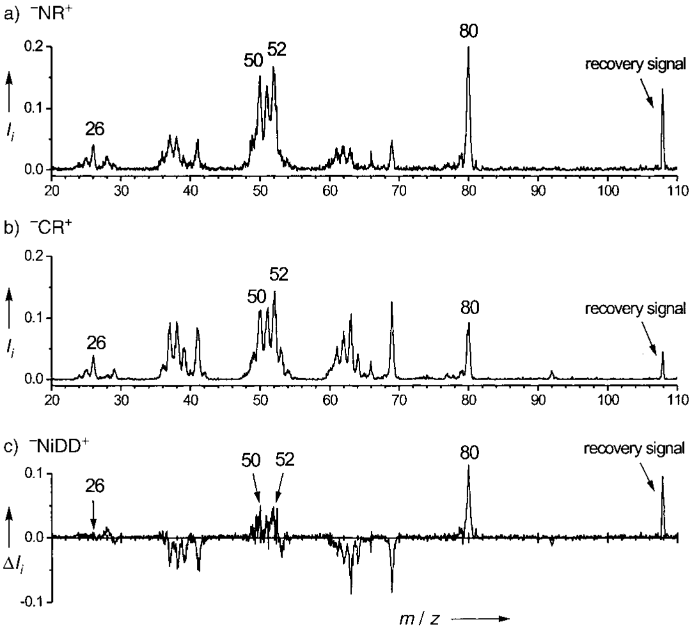
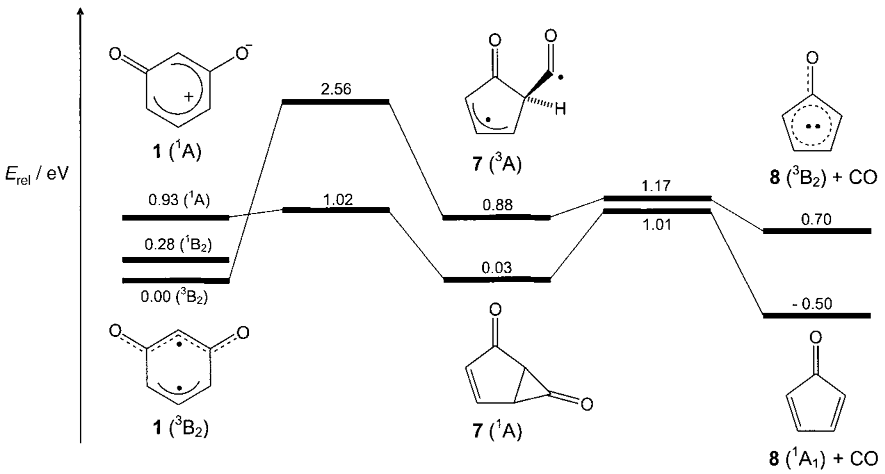


Figure 2. a) $^-$NR$^+$ ($\Sigma I_i = 1$), b) $^-$CR$^+$ ($\Sigma I_i = 1$), and c) $^-$NIDD$^+$ ($\Sigma I_i = 0$) mass spectra of $C_6H_4O_2^{\bullet-}$ ($\mathbf{1}^{\bullet-}$) generated by chemical ionization of resorcinol using N_2O as reagent gas.

The $^-$NR$^+$ spectrum (Figure 2a) differs largely from the $^-$NR$^-$ spectrum (Figure 1, inset) in that extensive fragmentation processes are observed, for which two explanations can be put forward. First, the ionization cross sections for fragments formed at the neutral stage differ substantially for reionization to anions and reionization to cations.[29] Secondly, excessive fragmentation often takes place at the cationic stage which is also reflected in the charge-reversal spectrum ($^-$CR$^+$, Figure 2b).[30] Information about fragmentations of the neutral molecules can be extracted from a comparison of the $^-$NR$^+$ signals, resulting as a superposition of fragmentations of both, ions and neutrals, with the $^-$CR$^+$ spectrum, in which mostly fragmentations of ionic species are sampled.[13,14] In the resulting $^-$NIDD$^+$ spectrum, positive signals are due to fragmentations occurring at the neutral stage, while negative signals originate from preferential decompositions of ionic species. According to Figure 2c, the most intense fragmentation of neutral **1** is associated with loss of carbon monoxide concomitant with generation of cyclopentadienone, which is then reionized (*m*/*z* 80). Formation of cyclopentadienone is further supported by the positive $^-$NIDD$^+$ signal of a subsequent CO loss, which implies the generation of C_4H_4 (*m*/*z* 52);[31] the latter can further lose molecular hydrogen under NR conditions (*m*/*z* 50).[32]

To corroborate the experimental findings, we also considered the reaction pathway for CO loss from *meta*-benzoquinone (**1**) computationally (Scheme 3). For the triplet ground state **1** ($^3B_2$), the rate-determining barrier is quite significant (2.56 eV), and decarbonylation to afford triplet cyclopentadienone is endothermic. On the singlet surface, however, the initial barrier is much lower ($E_{rel} = 1.02$ eV) and the asymptote **8** + CO is lower in energy than **1** ($^3B_2$).



Scheme 3. Calculated reaction pathways for the decarbonylation of the singlet and triplet states of *meta*-benzoquinone (**1**). Energies are given at 0 K and related to **1**(^{3}B$_2$); $E_{tot}(^3\mathbf{1}) = -381.524990$ Hartree, $E_{ZPV}(^3\mathbf{1}) = 0.0822234$ Hartree).

Accordingly, decarbonylation of **1** (^{3}B$_2$) can be assisted by a spin change along the reaction coordinate.[33]

In conclusion, the elusive *meta*-benzoquinone (**1**) has been generated in the gas phase by means of neutralization–reionization mass spectrometry. The main fragmentation channel of the neutral molecule leads to loss of carbon monoxide concomitant with cyclopentadienone as the most probable product. The present experimental and theoretical results pose no fundamental objections against the generation of *meta*-benzoquinone under different conditions. Matrix isolation of this molecule, which appears feasible, could then provide the ultimate spectroscopic characteristics of **1**.

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[15] The experiments were performed with a modified VG ZAB/HF/AMD four-sector mass spectrometer of BEBE configuration (B stands for magnetic and E for electric sector).[16] $\mathbf{1}^{\cdot-}$ was generated by negative-ion chemical ionization of resorcinol, 1,3-bis(trimethylsiloxy)benzene, and 1,3-dimethoxybenzene, using N_2O as reagent gas, accelerated to a kinetic energy of 8 keV and mass-selected by means of B(1)/E(1). The structure of the anion was probed by its metastable ion and collisional activation (CA) mass spectra. To this end, the unimolecular fragmentations of anions and their fragmentations upon collision with helium (80 % transmission, *T*), respectively, in the field-free region preceding the second magnet (3rd FFR) were recorded by scanning B(2). NR and charge reversal (CR) spectra were obtained by using a tandem of differentially pumped collision cells located in the 3rd FFR equipped with a deflector placed in between the cells. For NR experiments, both cells were filled (80 % *T*) by appropriate gases (O_2/Xe in $^-NR^-$ and O_2/O_2 in $^-NR^+$, respectively)[17] and the deflector was switched on. For $^-CR^+$ experiments, only the first cell was filled with O_2 (80 % *T*) and the deflector was grounded. Usually 10–50 scans were averaged to improve the signal-to-noise ratio, and the final data were derived from two to six independent measurements.

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[19] The calculations were performed using the density functional method B3LYP[20] in conjunction with 6-311 + G(2d,p) basis sets as implemented in Gaussian 98.[21] For all optimized structures, a frequency analysis was performed in order to assign them as genuine minima or transition structures and to determine the zero-point vibrational energies (E_{ZPV}). All transition structures were characterized by intrinsic reaction coordinate calculations.[22] The calculations of the anions $\mathbf{1}^{\cdot-}$ and $\mathbf{3}^{\cdot-}$–$\mathbf{6}^{\cdot-}$ were restricted to doublet states. The energies given in Schemes 1–3 are obtained as $E_{0K} = E_{tot} + E_{ZPV}$.

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[24] The hydrogen atoms of the hydroxy groups of resorcinol were exchanged by its reaction with CH_3OD at room temperature. Due to facile keto–enol tautomerization, the sample contains also a small amount of D_3-resorcinol ($<4\%$).

[25] The $^{-}CR^{+}$ spectra of O-deprotonated nonlabeled and O-bisdeuterated resorcinol (*m*/*z* 109 and 110, respectively) show characteristic losses of $O^{\bullet}$ atoms and $OH^{\bullet}$ and $OD^{\bullet}$ groups, respectively. Instead, the $^{-}CR^{+}$ spectrum of $C_6H_4O_2^{\bullet-}$ (Figure 2b) shows only the loss of $O^{\bullet}$ atom, which is yet further evidence for the suggested connectivity of $C_6H_4O_2^{\bullet-}$, rather than ring-deprotonated forms.

[26] In the studies of *meta*-xylylene, the radical anion $\mathbf{2}^{\bullet-}$ was generated by hydrogen abstraction from *meta*-xylene with $O^{\bullet-}$.[2] The authors claim generation of 75% of desired *meta*-xylylene and 25% of anions with one of the hydrogen atoms eliminated from the ring.

[27] In the context of a possible contribution of the ring-deprotonated isomers $\mathbf{3}^{\bullet-}$–$\mathbf{6}^{\bullet-}$, it is also worth mentioning that generation of *para*-benzoquinone anion by CI from either *para*-benzoquinone or hydroquinone leads to identical $C_6H_4O_2^{\bullet-}$ ions.

[28] The results for the $^1B_2$ state should be taken with some caution because the description of an open-shell singlet state with single reference methods, like B3LYP, inevitably encounters spin-contamination by the triplet state.

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