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An experimental and computational study of the ions formed by the reaction of cyclopentanone with $O^{\bullet -}$

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Dedicated to Professor Bill Hase on the occasion of his 60th birthday.

Abstract

The structures and reactivities of the ions formed by the reaction of cyclopentanone with $O^{\bullet -}$ have been studied using flowing afterglow-selected ion flow tube (FA-SIFT) experiments in conjunction with density functional theory (DFT) calculations. Three $C_5H_6O^{\bullet -}$ isomers were found to be generated – cyclopentanone-2,5-diyl radical anion ($\mathbf{4}^{\bullet -}$), 2-carbenacyclopentanone radical anion ($\mathbf{5}^{\bullet -}$), and cyclopentanone-2,4-diyl radical anion ($\mathbf{6}^{\bullet -}$). The large amount of signal loss observed in this reaction is attributed to formation of 2-cyclopentenone radical anion ($\mathbf{10}^{\bullet -}$), in which the electron is predicted to be unbound. DFT calculations predict $\mathbf{4}^{\bullet -}$ to be the most stable of the bound $C_5H_6O^{\bullet -}$ ions, and FA-SIFT experiments confirm $\mathbf{4}^{\bullet -}$ is the major ion formed in this reaction. Bracketing experiments found the proton affinity (PA) of $\mathbf{4}^{\bullet -}$ to be 362 ± 5 kcal/mol and the electron binding energy (EBE) to be ca. 0.5 eV. Although the PA of this species predicted by DFT calculations (363.2 kcal/mol) is consistent with the experimental value, both DFT and ab initio calculations predict an EBE of ca. 1.6 eV for this radical anion. The apparent conflict between the calculated and experimental EBE is resolved by proposing that, in the gas phase bracketing experiments, the electron transfer process leads adiabatically, not to cyclopentanone-2,5-diyl (**4**), but, by a retro-Nazarov reaction, to the more stable 1,4-pentadien-3-one (**18**). DFT calculations show that the difference between the computed and measured EBEs of $\mathbf{4}^{\bullet -}$ can be accounted for by the calculated difference between the energies of **18** and **4**.

Keywords: Cyclopentanone; Didehydro radical anion; Proton affinity; Electron affinity; Density functional theory

1. Introduction

Oxyallyl (**1**) has been postulated to be an intermediate in many reactions, such as the Favorskii rearrangement [1], the photochemical rearrangement of 2,5-cyclohexadienones [2], and the rearrangement of allene oxides to cyclopropanones [3]


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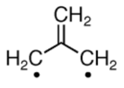
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Oxyallyl can be thought of as a heteroatom derivative of trimethylenemethane (**2**), one of the best-studied non-Kekulé hydrocarbon diradicals [4]. The nonbonding molecular orbitals of **2** are non-disjoint; therefore, **2** is expected to be a ground state triplet [4,5]. Electron paramagnetic resonance (EPR) [6] and negative ion photoelectron spectroscopy (NIPES) [7] experiments have both confirmed this prediction. The NIPES experiments found the energy difference between the singlet and triplet to be ΔE_{ST} = 16.1 kcal/mol [7], which is in good agreement with the results of the best calculations [5].

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If oxygen is substituted for a methylene group in **2**, the resulting diradical (**1**) is predicted to have nearly degenerate singlet and triplet states [5,8]. If alkyl substituents are added to **1** the singlet is calculated to be the ground state [5,8b,9].

Organic chemists typically think of **1** as having a zwitterionic structure, since this is an attractive way of explaining the stabilization of singlet **1**. However, electronic structure calculations have shown that singlet **1** is predominantly a diradical species, with a strong C=O bond [8a,9,10]. In addition, Lim et al. have shown that, in solution, oxyallyl does not appear to be significantly more polar than cyclopropanone [10]. Although experimental evidence suggests that oxyallyl derivatives have a singlet ground state [11], neither ΔE_{ST} nor $\nu_{C=O}$ have yet been measured in the parent oxyallyl (**1**) or in any derivative of **1**.

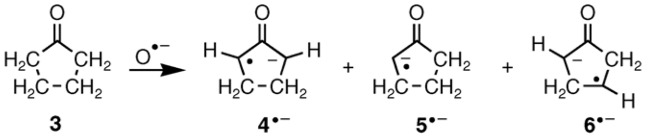
Perhaps the best way to measure the ΔE_{ST} in a diradical is to utilize NIPES [12]. Obtaining a NIPE spectrum requires a beam of radical anions, and one of the most common ways to generate this type of reactive intermediate in the gas phase is to allow a neutral compound to react with atomic oxygen radical anion ($O^{\bullet -}$). This reaction results in net $H_2^{\bullet +}$ abstraction from the neutral, thus producing a didehydro radical anion and H_2O [13].

Reaction with $O^{\bullet -}$ has been used to generate a variety of carbene and distonic radical anions [14]. However, $O^{\bullet -}$ is a highly reactive and, hence, unselective reagent. For example, Dawson et al. observed 1,1-$D_2^{\bullet +}$, 3,3-$H_2^{\bullet +}$, and 1,3-$HD^{\bullet +}$ abstraction products when acetone-1,1,1-d_3 was allowed to react with $O^{\bullet -}$, although a slight preference for 1,3-$HD^{\bullet +}$ abstraction (56%) was noted [15]. Presumably, both oxyallyl radical anion (**1**$^{\bullet -}$) and the isomeric carbene radical anion are formed in this reaction [15].

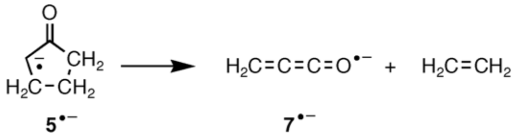
Cyclopentanone (**3**) is an ethano-bridged derivative of acetone, and it is likely that the reaction of **3** with $O^{\bullet -}$ would produce cyclopentanone-2,5-diyl radical anion (**4**$^{\bullet -}$). The singlet state of diradical **4** is calculated to be lower than the triplet by 7.0 kcal/mol [9b]. In addition, the C=O bond in **4** is predicted to be strong, with $\nu_{C=O} = 1736\,\mathrm{cm}^{-1}$ [9b]. This predicted value is very close to the experimental value of $\nu_{C=O} = 1740\,\mathrm{cm}^{-1}$ found for **3** [16].

Since $O^{\bullet -}$ is an unselective reagent, it is likely that the reaction of **3** with $O^{\bullet -}$ would produce more than one isomer. As in the case of acetone [15], a carbene radical anion (**5**$^{\bullet -}$) is expected to be formed when **3** is allowed to react with $O^{\bullet -}$ (Scheme 1). It is also possible that this reaction could form cyclopentanone-2,4-diyl radical anion (**6**$^{\bullet -}$).

In order to utilize NIPES to measure both ΔE_{ST} in **4** and the C–O stretching frequencies in the singlet and triplet states of this diradical, we sought to generate cyclopentanone-2,5-diyl radical anion (**4**$^{\bullet -}$). Therefore, we investigated whether reaction of cyclopentanone (**3**) with $O^{\bullet -}$ would provide a satisfactory method for producing **4**$^{\bullet -}$.



Scheme 1.



Scheme 2.

Relatively little is known about the gas phase ion chemistry that occurs when **3** is allowed to react with $O^{\bullet -}$. Using ion cyclotron resonance spectrometry (ICR), Harrison and Jennings have shown that $C_5H_7O^-$, $C_5H_6O^{\bullet -}$, and $C_3H_2O^{\bullet -}$ are produced, but these anions were not characterized [17]. However, the $C_3H_2O^{\bullet -}$ ion was shown to contain none of the hydrogens that are attached to the carbons that are α to the carbonyl group in **3**. On this basis it was suggested that this radical anion is most likely methylene ketene radical anion (**7**$^{\bullet -}$), formed, as shown in Scheme 2, by loss of ethylene from 2-carbenacyclopentanone radical anion (**5**$^{\bullet -}$).

We have carried out a detailed investigation of the radical anions formed from the reaction of **3** with $O^{\bullet -}$, using calculations to help interpret the experimental data. We find that the $C_5H_6O^{\bullet -}$ radical ions formed in this reaction actually consist of three isomers – **4**$^{\bullet -}$, **5**$^{\bullet -}$, and **6**$^{\bullet -}$. We have used bracketing experiments to measure the proton affinity (PA) and adiabatic electron binding energy (EBE)[1] of **4**$^{\bullet -}$. We present evidence that the apparent EBE measured for **4**$^{\bullet -}$ corresponds to the formation of 1,4-pentadien-3-one, rather than **4**.

After the research described in this manuscript had been completed, a paper by Lin and Grabowski appeared, which describes their studies of the reactions of ketones with $O^{\bullet -}$ in a flowing afterglow (FA) [18]. While their results for the reaction of $O^{\bullet -}$ with **3** generally agree with ours, there are several significant discrepancies that are important. These differences are discussed in this manuscript.

2. Experimental

2.1. Gas phase experiments

All experiments were carried out with a tandem flowing afterglow-selected ion flow tube (FA-SIFT) apparatus, which has been described previously [19]. The $O^{\bullet -}$ and HO^- ions were generated in the first flow tube by electron impact on N_2O and on a mixture of N_2O and CH_4, respectively. In a typical experiment, $O^{\bullet -}$ (or HO^-) was mass-selected with a quadrupole mass filter and injected through the SIFT injection orifice into the second flow tube containing helium.

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[1] The electron binding energy of an anion is equivalent to the electron affinity of the corresponding neutral.

Cyclopentanone was added through an inlet near the upstream end of the second flow tube. In other experiments, cyclopentanone and $O^{\bullet-}$ (or HO^-) were allowed to react in the first flow tube and mass-selected $C_5H_6O^{\bullet-}$ (or $C_5H_7O^-$) ions were injected into the second flow tube. In all experiments, injected ions were rapidly thermalized by collisions with helium (0.5 Torr, ~300 K) before the ions reacted with reagents that are added downstream. The SIFT injection energy (defined as the voltage difference between the source flow tube and the SIFT injection orifice, E_{inj}) was typically 16–20 eV. For collision induced dissociation (CID) experiments E_{inj} was increased up to 50 eV, to facilitate fragmentation of the reactant ions by collision with helium near the injection orifice.

$C_5H_6O^{\bullet-}$ and $C_5H_7O^-$ ions were allowed to react with neutral reagents that were added via fixed inlets downstream on the second flow tube. PA and electron affinity (EA) bracketing experiments were carried out by allowing neutrals, with known gas-phase acidities and EAs [20] to react with mass selected $C_5H_6O^{\bullet-}$ and $C_5H_7O^-$ ions. The reactivity of $C_5H_6O^{\bullet-}$, and of deuterated and methylated derivatives of this ion, was also explored with several other neutral reagents. The detection quadrupole mass filter was optimized for minimal mass discrimination; however, product branching ratios are reported without further correction for the differential detection sensitivities.

Reaction rate measurements were carried out by adding a constant amount of neutral reagent at different distances along the second flow tube, thereby effectively changing the reaction time. Semi-logarithmic plots of parent ion counts versus reaction time were found to be linear within the detection limits. Rate constants were derived from the slopes of signal decay, and these constants typically have absolute error bars of ±20%. Reaction efficiencies were obtained as the ratio of the measured rate constants to the theoretical collision-rate constant, calculated using the parameterized trajectory collision theory [21].

2.2. Materials

Cyclopentanone was obtained from Aldrich (99+%) and used as received. Cyclopentanone-2,2,5,5-d_4 was synthesized in 95% isotopic purity as described by Malloy [22]. Samples of 2,2-dimethylcyclopentanone were prepared by literature methods [23]. 2,2,5-Trimethylcyclopentanone was a major product (~20%) of the synthesis of 2,2-dimethylcyclopentanone. Since the chemistry of 2,2-dimethylcyclopentanone and 2,2,5-trimethylcyclopentanone could be studied on the 4:1 mixture of these two ketones, the mixture was not separated.

2.3. Calculations

Density functional theory (DFT) calculations were carried out with Becke's hybrid three-parameter exchange functional [24] and the correlation functional of Lee et al. [25] (B3LYP). Geometries were fully optimized, and a vibrational analysis was performed at each stationary point, in order to confirm its identity as a minimum energy structure (no vibrational modes with imaginary frequencies) or as a transition structure (one vibrational mode with an imaginary frequency). The vibrational analyses also provided the zero-point and thermal energy corrections that were necessary to convert the B3LYP electronic energies into enthalpies at 298 K. For this purpose the vibrational frequencies were used without scaling.

Geometry optimizations were also performed with (4/4)CASSCF for neutral structures and (5/4)CASSCF for radical anions. The active electrons were distributed among four π molecular orbitals. CASSCF vibrational analyses were carried out to establish the nature of each stationary point found and to obtain zero-point and thermal corrections to its energy. The CASSCF vibrational frequencies were used without scaling. In order to include the effects of dynamic electron correlation [26] CASPT2 [27] single-point calculations were performed at the CASSCF optimized geometries. The CASSCF zero-point and thermal corrections were used to convert the CASPT2 electronic energies to enthalpies.

All calculations were performed using the 6-31+G* basis set [28]. The (U)B3LYP and CASSCF calculations were carried out using the Gaussian 98 suite of programs [29], while all CASPT2 calculations were performed using the MOLCAS package of programs [30].

3. Results and discussion

3.1. Cyclopentanone + $O^{\bullet-}$

The reaction of **3** with $O^{\bullet-}$ was found to be facile ($k = 2.94 \times 10^{-9}\ cm^3\ molecule^{-1}\ s^{-1}$, efficiency = 63%) and to generate four primary anions: $C_5H_6O^{\bullet-}$, $C_5H_7O^-$, $C_3H_2O^{\bullet-}$, and HO^- (Eq. (1)). The values in parentheses are the primary branching fractions, derived by extrapolating the product yields to zero reactant concentration. The increase in the intensities of the peaks due to the products was only about 25% as large as the loss in intensity of the peak due to $O^{\bullet-}$. We attribute the 75% loss of product signal to detachment of an electron from the major product of the reaction of **3** with $O^{\bullet-}$ (vide infra).

$$
\begin{aligned}
&\mathbf{3} + O^{\bullet-}\\
&\longrightarrow C_5H_6O + H_2O + e^- \quad (75\%)\\
&\longrightarrow C_5H_6O^{\bullet-} + H_2O \quad (9\%)\\
&\longrightarrow C_3H_2O^{\bullet-} + C_2H_4 + H_2O \quad (4\%)\\
&\longrightarrow C_5H_7O^- + HO^{\bullet} \quad (3\%)\\
&\longrightarrow HO^- + C_5H_7O^{\bullet} \quad (9\%)
\end{aligned}
\tag{1}
$$

Lin and Grabowski observed only three primary products ($C_5H_6O^{\bullet-}$, $C_5H_7O^-$, and HO^-) and one secondary product

Scheme 3.

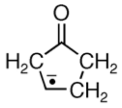
(m/z 97) from the reaction of **3** with $O^{\bullet-}$ [18]. In the present study, m/z 97 was not an observed product in the reaction of **3** with $O^{\bullet-}$. In addition, Lin and Grabowski noted that both the HO^- and $C_5H_6O^{\bullet-}$ products undergo a secondary proton abstraction reaction with **3** to give $C_5H_7O^-$ [18]. In the current experiments, these secondary reactions were also observed and become significant at higher concentrations of **3**. The former reaction is very exothermic; whereas, the latter is computed to be slightly endothermic.

(U)B3LYP/6-31+G* predicts the reaction of **4**$^{\bullet-}$ with **3** to yield $C_5H_7O^-$ and cyclopentanone-2-yl (**8**) to be endothermic by 3.6 kcal/mol (Scheme 3). However, there are exothermic proton transfer channels for **5**$^{\bullet-}$ and **6**$^{\bullet-}$. Carbene **5**$^{\bullet-}$ is predicted to react in an exothermic manner with **3** to give $C_5H_7O^-$ and **8** ($\Delta H_{\text{rxn}} = -19.6$ kcal/mol). While the reaction of **6**$^{\bullet-}$ with **3** to yield cyclopentanone-3-yl and $C_5H_7O^-$ is predicted to be endothermic by 2.2 kcal/mol, if **6**$^{\bullet-}$ reacts with **3** to generate the more stable radical (**8**) and $C_5H_7O^-$, the reaction is predicted to be exothermic by 5.6 kcal/mol.

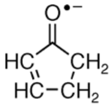
The $C_5H_7O^-$ ion was identified as the enolate anion of cyclopentanone by PA and EA bracketing experiments. Proton transfer to $C_5H_7O^-$ was observed with CHF_2CH_2OH ($\Delta H_{\text{acid}} = 366.4 \pm 2.2$ kcal/mol) and CH_3SH ($\Delta H_{\text{acid}} = 357.6 \pm 2.0$ kcal/mol); however, no proton transfer was observed with either PhCCH ($\Delta H_{\text{acid}} = 370.6 \pm 2.3$ kcal/mol) or *i*-PrOH ($\Delta H_{\text{acid}} = 375.1 \pm 1.0$ kcal/mol). Thus, we assign a PA of 368.5 ± 3.8 kcal/mol to the $C_5H_7O^-$ ion. This experimental PA is in good agreement with the value of PA = 366.6 kcal/mol predicted by B3LYP/6-31+G*. The EBE of the $C_5H_7O^-$ ion was found to be greater than 1.1 eV, as no electron transfer to SO_2 (EA = 1.107 ± 0.008 eV) was observed. These values are consistent with this anion being the enolate of cyclopentanone ($\Delta H_{\text{acid}} = 368.0 \pm 4.2$ kcal/mol, EA = 1.598 ± 0.007 eV) [20]. Confirmation that the $C_5H_7O^-$ ion is, in fact, the enolate of cyclopentanone was obtained by generating the enolate anion independently, from the reaction of **3** with HO^-. The $C_5H_7O^-$ ion that was formed showed the same reactivity as the $C_5H_7O^-$ ion generated in the reaction of **3** with $O^{\bullet-}$.

There are a number $C_5H_6O^{\bullet-}$ isomers that might be formed from the reaction of **3** with $O^{\bullet-}$. If $O^{\bullet-}$ abstracts a hydrogen atom from C-2 and a proton from C-5 of **3**, the desired radical anion (**4**$^{\bullet-}$) would be generated. However, net $H_2^{\bullet+}$ abstraction can also occur from C-2 and C-4 to generate distonic radical anion **6**$^{\bullet-}$ (Scheme 1).

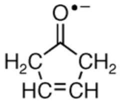
Formation of two carbene radical anions is also possible. If 2,2-$H_2^{\bullet+}$ abstraction occurred, carbene radical anion **5**$^{\bullet-}$ would be formed; whereas, 3,3-$H_2^{\bullet+}$ abstraction would lead to carbene radical anion **9**$^{\bullet-}$. In addition, 2,3-$H_2^{\bullet+}$ abstraction could also occur to produce the radical anion of 2-cyclopentenone (**10**$^{\bullet-}$), while 3,4-$H_2^{\bullet+}$ abstraction would lead to the radical anion of the unconjugated ketone, 3-cyclopentenone (**11**$^{\bullet-}$).



9$^{\bullet-}$



10$^{\bullet-}$



11$^{\bullet-}$

In addition, there are many other possible bicyclic or ring-opened $C_5H_6O^{\bullet-}$ isomers. (U)B3LYP/6-31+G* calculations have been found to compute accurately the EBEs and other thermodynamic properties of a wide range of radical anions [31]. Therefore, in order to aid in the structural assignments of the $C_5H_6O^{\bullet-}$ anion(s) formed in the reaction of **3** with $O^{\bullet-}$, (U)B3LYP/6-31+G* calculations were performed on many $C_5H_6O^{\bullet-}$ isomers. These calculations have shown that the most likely isomers formed in the reaction of $O^{\bullet-}$ with **3** are the six discussed in this article. The results of these calculations are summarized in Table 1 for the six most likely $C_5H_6O^{\bullet-}$ products and in Appendix A for all $C_5H_6O^{\bullet-}$ isomers.

Although isomer **10**$^{\bullet-}$ is computed to be the radical anion of lowest enthalpy, the unpaired electron in it is predicted to be unbound. Even if the (U)B3LYP calculations underestimated the EBE of **10**$^{\bullet-}$ by a few tenths of an eV, the large reaction exothermicity (−45.9 kcal/mol) could lead to autodetachment. This result is consistent with previous attempts to generate **10**$^{\bullet-}$ [32]. Therefore, our calculations predict that **10**$^{\bullet-}$ should not be observed and, since **11**$^{\bullet-}$ is predicted to be even less bound than **10**$^{\bullet-}$, **11**$^{\bullet-}$ is also unlikely to be observed.

Table 1
(U)B3LYP/6-31+G* predictions of relative enthalpies, PAs, and EBEs for six $C_5H_6O^{\bullet-}$ radical anions at 298 K

	Anion					
	4$^{\bullet-}$	**5**$^{\bullet-}$	**6**$^{\bullet-}$	**9**$^{\bullet-}$	**10**$^{\bullet-}$	**11**$^{\bullet-}$
Relative enthalpy (kcal/mol)	0[a]	23.4	9.0	40.4	−8.9	11.9
PA (kcal/mol)	363.2	386.6	372.2[b]	395.9	–	–
EBE (eV)	1.66[c]	1.63	1.56	0.91	−0.03	−0.72

[a] The enthalpy of **4**$^{\bullet-}$ + H_2O, relative to the reactants **3** + $O^{\bullet-}$, is computed to be −37.0 kcal/mol.

[b] PA for protonation at C-4. Protonation at C-2 gives PA = 364.4 kcal/mol and generates the less stable neutral.

[c] EBE = 1.48 eV is obtained by combining the UB3LYP/6-31+G* EA of the triplet with ΔE_{ST}, obtained from CASPT2 calculations (see Section 3.4).

However, **10**$^{\bullet-}$ is energetically accessible and is computed to be the thermodynamically most stable $C_5H_6O^{\bullet-}$ ion (Table 1); therefore, it is expected to be formed in the reaction of **3** with $O^{\bullet-}$. Formation of **10**$^{\bullet-}$, followed by prompt electron detachment, provides a very attractive explanation of the 75% ion loss that is observed in the reaction of **3** with $O^{\bullet-}$.

The extra electron in all four of the remaining $C_5H_6O^{\bullet-}$ isomers is computed to be strongly bound. Isomer **4**$^{\bullet-}$ is predicted to be lowest in enthalpy by 9.0 kcal/mol. Formation of **5**$^{\bullet-}$ and **6**$^{\bullet-}$ in the reaction of **3** with $O^{\bullet-}$ is also calculated to be thermodynamically favorable; but the reaction of **3** with $O^{\bullet-}$ to produce **9**$^{\bullet-}$ and H_2O is predicted at the (U)B3LYP/6-31+G* level of theory to be endothermic by 3.4 kcal/mol and is, therefore, much less likely to occur.

The $C_5H_6O^{\bullet-}$ radical anions that are likely to be formed in the reaction of **3** with $O^{\bullet-}$ and which are stable to electron loss, can thus be limited to three possible isomers – **4**$^{\bullet-}$, **5**$^{\bullet-}$, and **6**$^{\bullet-}$. As shown in Table 1, although these ions are predicted to have similar EBEs, their PAs are computed to be significantly different. Distonic radical anion **4**$^{\bullet-}$ (PA = 363.2 kcal/mol) is predicted to be the least basic by 9.0 kcal/mol, and distonic ion **6**$^{\bullet-}$ (PA = 372.2 kcal/mol) is computed to be less basic than **5**$^{\bullet-}$ (PA = 386.6 kcal/mol) by 14.4 kcal/mol.

There are many neutral compounds available in the acidity range predicted for **4**$^{\bullet-}$, **5**$^{\bullet-}$, and **6**$^{\bullet-}$ that can be used for PA bracketing experiments. Rapid and quantitative proton transfer to $C_5H_6O^{\bullet-}$ was observed upon reaction of the $C_5H_6O^{\bullet-}$ ion(s) with both *t*-BuSH ($\Delta H_{\text{acid}} = 352.5 \pm 2.2$ kcal/mol, $k = 1.18 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, efficiency = 68%) and CH_3SH ($\Delta H_{\text{acid}} = 357.6 \pm 2.0$ kcal/mol, $k = 1.01 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, efficiency = 60%). When $C_5H_6O^{\bullet-}$ was allowed to react with CF_3CH_2OH ($\Delta H_{\text{acid}} = 361.7 \pm 2.5$ kcal/mol), depletion of $C_5H_6O^{\bullet-}$ was also found to be rapid ($k = 1.47 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}, efficiency = 88%), but the increase observed in the $CF_3CH_2O^-$ signal accounted for less than 1% of the $C_5H_6O^{\bullet-}$ loss. The only other product observed was the cluster of $C_5H_6O^{\bullet-}$ with CF_3CH_2OH, the amount of which was also very small. The result with CF_3CH_2OH is thus deemed inconclusive. Therefore, a conservative lower limit for the PA of $C_5H_6O^{\bullet-}$ is 357.6 kcal/mol, the ΔH_{acid} of CH_3SH.

Reaction of $C_5H_6O^{\bullet-}$ with CHF_2CH_2OH ($\Delta H_{\text{acid}} = 366.4 \pm 2.2$ kcal/mol) resulted in rapid loss of the $C_5H_6O^{\bullet-}$ signal, with negligible adduct formation and no proton transfer products observed. Slow depletion of the parent signal was observed for the reaction of PhCCH ($\Delta H_{\text{acid}} = 370.6 \pm 2.3$ kcal/mol) with $C_5H_6O^{\bullet-}$. However, the products (mainly $PhCC^-$ along with a minor amount of adducts) accounted for only 3% of the parent loss. Likewise, the $C_5H_6O^{\bullet-}$ ion depleted moderately fast upon reaction with *i*-PrOH ($\Delta H_{\text{acid}} = 375.1 \pm 1.0$ kcal/mol). The only products observed in this reaction were due to adduct formation and accounted for ca. 10% of the parent ion loss. Inexplicable signal loss was commonly observed in the reaction of $C_5H_6O^{\bullet-}$ with these reagents. In addition, neither deuteron abstraction nor H/D exchange was observed when $C_5H_6O^{\bullet-}$ was allowed to react with CD_3OD or CH_3CH_2OD; instead, quantitative adduct formation was observed.

The results of the bracketing experiments place the PA of $C_5H_6O^{\bullet-}$ between those of CH_3SH and CHF_2CH_2OH and thus lead to $\Delta H_{\text{acid}} = 362 \pm 5$ kcal/mol for $C_5H_6O^{\bullet-}$.[2] This experimental PA is in good agreement with the UB3LYP/6-31+G* calculated value of PA = 363.2 kcal/mol for radical anion **4**$^{\bullet-}$.

It seems probable that the reaction of $O^{\bullet-}$ with **3** produces, in addition to **4**$^{\bullet-}$, other $C_5H_6O^{\bullet-}$ radical anions. Based on Dawson's observations of $H_2^{\bullet+}$ (and $D_2^{\bullet+}$) loss in the reaction of acetone-1,1,1-d$_3$ with $O^{\bullet-}$ [15], it seems likely that **3** (an ethano-bridged derivative of acetone) should also form carbene radical anion **5**$^{\bullet-}$.

As originally reported by Harrison and Jennings [17] and confirmed in the present study, formation of the $C_3H_2O^{\bullet-}$ ion (Eq. (1)) suggests that carbene radical anion **5**$^{\bullet-}$ is, in fact, also generated in the reaction of $O^{\bullet-}$ with **3** but that some or all of **5**$^{\bullet-}$ produced subsequently fragments to methylene ketene radical anion (**7**$^{\bullet-}$) and ethylene.

At the (U)B3LYP/6-31+G* level of theory the fragmentation of **5**$^{\bullet-}$ to form **7**$^{\bullet-}$ and ethylene is computed to be a stepwise reaction with a net activation barrier of 14.5 kcal/mol for passage over the second transition state (TS2, Fig. 1, dotted line). The exothermicity calculated for the reaction of **3** and $O^{\bullet-}$ to produce **5**$^{\bullet-}$ and H_2O ($\Delta H_{\text{rxn}} = -13.6$ kcal/mol, Table 1) is about 1 kcal/mol too small for nascent **5**$^{\bullet-}$ to surmount the activation barrier. However, if the fragmentation of **5**$^{\bullet-}$ occurs within the ion–dipole complex [**5**$^{\bullet-}\cdots H_2O$], the energy for passage over the transition state [TS2 $\cdots H_2O$] will be lowered relative to the reactants, **3** + $O^{\bullet-}$, by the ion–dipole stabilization energy (Fig. 1, solid lines). The energy available from complex formation between **5**$^{\bullet-}$ and water should facilitate the conversion of the [**5**$^{\bullet-}\cdots H_2O$] complex to [**7**$^{\bullet-}\cdots C_2H_4 \cdots H_2O$], leading to products **7**$^{\bullet-}$, C_2H_4, and H_2O ($\Delta H_{\text{rxn}} = -9.5$ kcal/mol). This reaction thus becomes competitive with the dissociation of the [**5**$^{\bullet-}\cdots H_2O$] complex to **5**$^{\bullet-}$ and water ($\Delta H_{\text{rxn}} = -13.6$ kcal/mol).

The EBE and PA of the $C_3H_2O^{\bullet-}$ radical anion formed in the reaction of **3** with $O^{\bullet-}$ were bracketed in order to compare them with the values computed for **7**$^{\bullet-}$. (U)B3LYP/6-31+G* predicts an EBE of 1.03 eV and PA = 351.1 kcal/mol to form the most stable neutral for **7**$^{\bullet-}$. Rapid loss of the $C_3H_2O^{\bullet-}$ signal was observed when this ion was allowed to react with SO_2 (EA = 1.107 ± 0.008 eV), but only a very slow depletion was observed with CS_2 (EA = 0.51 ± 0.10 eV). If the disappearance of the $C_3H_2O^{\bullet-}$ ion is due to electron transfer, the bracketed EA of 0.8 ± 0.3 eV is consistent with the calculated value of EA = 1.03 eV for **7**.

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[2] The maximum uncertainty limits for the proton affinity measurement is ±7 kcal/mol, based on the accuracy of the acidity values for the reference acids.

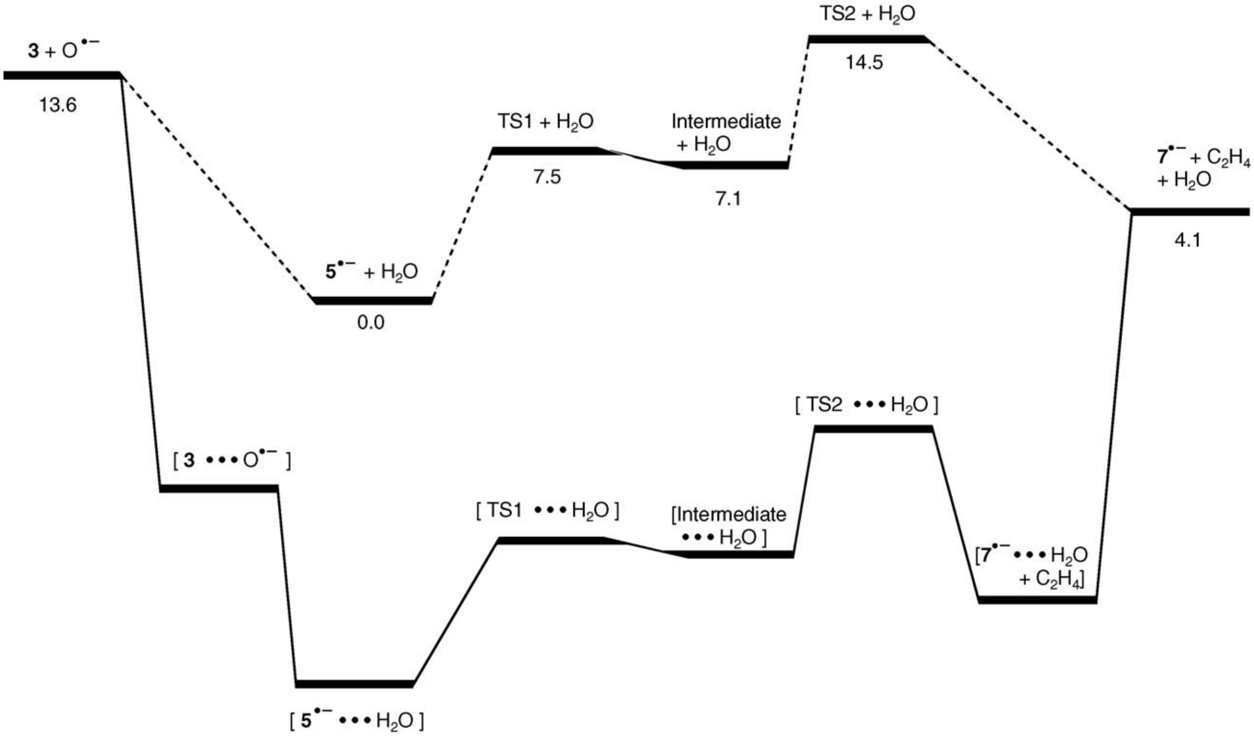


Fig. 1. (U)B3LYP/6-31+G* enthalpies (kcal/mol) for the reaction of **3** + $O^{\bullet-}$ to form $\mathbf{5}^{\bullet-}$ + H_2O and $\mathbf{7}^{\bullet-}$ + C_2H_4 + H_2O. The dotted lines connect stationary points, whose energies are computed with H_2O treated as a spectator, which does not form complexes with the ions. The solid lines connect the same stationary points, but with the stabilization energies of the ion–dipole complexes indicated schematically.

Lin and Grabowski suggested that the reason they failed to observe $\mathbf{7}^{\bullet-}$ in their experiments might be that "the EA of H_2C–C–C–O is too low to allow it to have a long enough lifetime to be observed in the high pressure flow tube" [18]. The EBE, both calculated and measured for $\mathbf{7}^{\bullet-}$ rules out this explanation. The sizable barrier (14.5 kcal/mol) that we compute for the fragmentation of $\mathbf{5}^{\bullet-}$ to $\mathbf{7}^{\bullet-}$ leads us to prefer the alternate explanation, proposed by Lin and Grabowski, that under their reaction conditions, "1,1-$H_2^{\bullet+}$ abstraction products are formed from the cyclic ketone, but they are [kinetically] stable against the fragmentation process" [18].

When $C_3H_2O^{\bullet-}$ was allowed to react with CH_3SH ($\Delta H_{\mathrm{acid}} = 357.6 \pm 2.0$), rapid loss of the $C_3H_2O^{\bullet-}$ signal was observed; however, only a very slow depletion was observed in the reaction of $C_3H_2O^{\bullet-}$ with CHF_2CH_2OH ($\Delta H_{\mathrm{acid}} = 366.4 \pm 2.2$ kcal/mol). If the rapid loss of $C_3H_2O^{\bullet-}$ is assigned to proton transfer, these observations lead to PA = 362 ± 5 kcal/mol being assigned to $\mathbf{7}^{\bullet-}$.

UB3LYP/6-31+G* predicts PA = 351.1 kcal/mol for $\mathbf{7}^{\bullet-}$, a value well below even the lower limit obtained from the bracketing experiments. B3LYP calculations are known to overestimate the stability of cumulenes [33], and this may be the reason that UB3LYP calculations underestimate the PA of $\mathbf{7}^{\bullet-}$.

The EA and PA experiments were feasible only in the copresence of $\mathbf{4}^{\bullet-}$ (and other ionic products) that react with SO_2 and CH_3SH to form SO_2^- and CH_3S^-, respectively. Thus, formation of SO_2^- or CH_3S^- from $C_3H_2O^{\bullet-}$ cannot be verified. Generation of $\mathbf{7}^{\bullet-}$ in the source flow tube followed by SIFT injection would allow direct observation of the reaction products from $\mathbf{7}^{\bullet-}$ as well as more precise depletion measurements. However, SIFT injection of $\mathbf{7}^{\bullet-}$ has been found to be technically difficult.

As shown in the top half of Fig. 1 (dotted lines), UB3LYP calculations predict the existence of an appreciable barrier to fragmentation of $\mathbf{5}^{\bullet-}$ to form $\mathbf{7}^{\bullet-}$. The question of whether a measurable amount of $\mathbf{5}^{\bullet-}$ remains intact, without fragmenting to $\mathbf{7}^{\bullet-}$, was addressed by CID experiments. The $C_5H_6O^{\bullet-}$ radical anion was generated in the source flow tube, mass selected, and injected into the second flow tube. When mass-selected $C_5H_6O^{\bullet-}$ (*m*/*z* 82) was injected with high E_{inj} (∼30–50 eV), CID products were observed at *m*/*z* 53 and *m*/*z* 54. At low E_{inj} (∼15 eV) the only observed CID product was that at *m*/*z* 54. This is direct evidence that the reaction of **3** and $O^{\bullet-}$ produces an *m*/*z* 82 radical anion (presumably $\mathbf{5}^{\bullet-}$) that lives long enough to be injected into the second flow tube, where it fragments to $\mathbf{7}^{\bullet-}$.

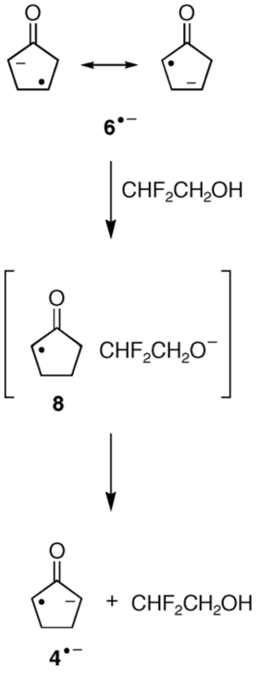
Interestingly, the amount of $\mathbf{7}^{\bullet-}$ formed in the CID experiments remains constant over all E_{inj}, suggesting that all of carbene radical anion $\mathbf{5}^{\bullet-}$, formed in the reaction of **3** with $O^{\bullet-}$, fragments to $\mathbf{7}^{\bullet-}$ in the second flow tube, even at the lowest injection energies. An alternative explanation is that at higher E_{inj}, some of the nascent $\mathbf{7}^{\bullet-}$ loses an electron. Establishing which of these two possibilities is correct would require investigations of the ion transmission efficiencies and other experimental parameters pertinent to SIFT injection, and such quantitative studies were beyond the scope of this project.

It is possible that $\mathbf{7}^{\bullet-}$ loses a hydrogen atom to form the *m*/*z* 53 anion at high E_{inj}. However, CID of the deuterium labeled radical anion, $C_5H_4D_2O^{\bullet-}$, produces the same *m*/*z* 54 anion as the all-protio species; however, at high injection energies *m*/*z* 55 was observed, instead of *m*/*z* 53. Therefore, the *m*/*z* 53 ion must be a primary CID product, formed from $\mathbf{4}^{\bullet-}$, $\mathbf{5}^{\bullet-}$, or $\mathbf{6}^{\bullet-}$.

It appears that the reaction of **3** with $O^{\bullet-}$ produces both distonic radical anion $\mathbf{4}^{\bullet-}$ and carbene radical anion $\mathbf{5}^{\bullet-}$. Since UB3LYP/6-31+G* calculations predict distonic ion $\mathbf{6}^{\bullet-}$ to be 14.4 kcal/mol lower in energy than $\mathbf{5}^{\bullet-}$ (Table 1), if $\mathbf{5}^{\bullet-}$ is generated in the reaction of **3** with $O^{\bullet-}$, it is reasonable to expect $\mathbf{6}^{\bullet-}$ to be generated as well. However, based on the measured PA of 362 ± 5 kcal/mol for the $C_5H_6O^{\bullet-}$ anion, it appears to consist entirely of isomer $\mathbf{4}^{\bullet-}$, because the computed PAs of $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$, 386.6 and 372.2 kcal/mol, respectively, are much higher than the value of PA = 363.2 kcal/mol, calculated for $\mathbf{4}^{\bullet-}$.

If $\mathbf{5}^{\bullet-}$ and/or $\mathbf{6}^{\bullet-}$ is formed in the reaction of **3** with $O^{\bullet-}$, why does the observed PA for the $C_5H_6O^{\bullet-}$ radical anion appear to be that of pure $\mathbf{4}^{\bullet-}$? Why is it that the more strongly basic radical anions do not accept a proton from acids that are too weak to protonate $\mathbf{4}^{\bullet-}$? For example, if $C_5H_6O^{\bullet-}$ contains isomer $\mathbf{6}^{\bullet-}$ (predicted PA = 372.2 kcal/mol), proton transfer is expected to occur upon reaction with the more acidic CHF_2CH_2OH ($\Delta H_{\mathrm{acid}} = 366.4 \pm 2.2$ kcal/mol). However, no proton transfer was observed.

A possible explanation is that isomerization of $\mathbf{6}^{\bullet-}$ to $\mathbf{4}^{\bullet-}$ occurs through a pair of proton exchanges in the ion–dipole complex of $\mathbf{6}^{\bullet-}$ with CHF_2CH_2OH. As shown in Scheme 4, $CHF_2CH_2O^-$, formed by proton transfer to C-4 of $\mathbf{6}^{\bullet-}$, is initially generated in an ion–dipole complex with **8**, the other product formed by this acid–base reaction. Within this complex, the $CHF_2CH_2O^-$ can abstract a proton from C-5 of **8**. Being α to the carbonyl group, the proton at C-5 is more acidic than the proton at C-4. This second proton transfer completes the isomerization of $\mathbf{6}^{\bullet-}$ to $\mathbf{4}^{\bullet-}$, the lower energy radical anion. The ion–dipole complex between $\mathbf{4}^{\bullet-}$ and CHF_2CH_2OH can then dissociate to the $C_5H_6O^{\bullet-}$ radical anion, plus the alcohol, without any observable sign of the isomerization reaction that has occurred by double proton transfer.



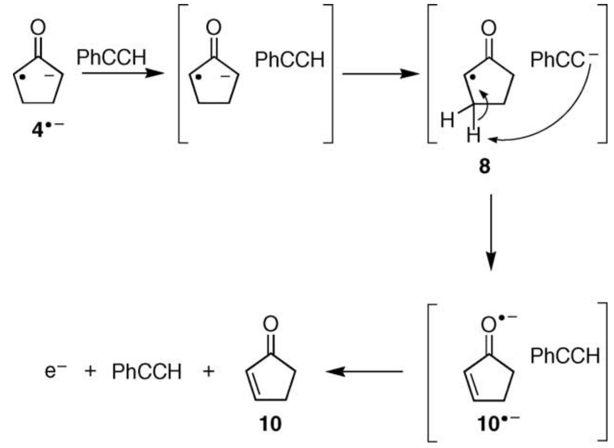
Scheme 4.

Similarly, the low PA observed for $C_5H_6O^{\bullet-}$ does not rule out the presence of $\mathbf{5}^{\bullet-}$, since any $\mathbf{5}^{\bullet-}$ that does not fragment could, like $\mathbf{6}^{\bullet-}$, isomerize to $\mathbf{4}^{\bullet-}$ when treated with CHF_2CH_2OH. Wenthold and Squires have, in fact, observed isomerizations, similar to those proposed for $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$, in attempting to bracket the PAs of the *meta*- and *para*-chlorophenyl anions with methanol and water [34].

The kinetics plots for the proton transfer rate measurements were found to be fairly linear. For nonlinear plots to be clearly observed, the ion mixture must consist of comparable amounts of both the reactive and distinctly less reactive component(s). The above isomerization mechanism could easily hamper observation of such subtle deviation from linearity.

The mechanism shown in Scheme 4 can be tested, in principle, by allowing the $C_5H_6O^{\bullet-}$ radical anion(s) to react with deuterated reagents (e.g., CHF_2CH_2OD) and observing deuterium incorporation. Through repeated collisions with the reagent, $\mathbf{6}^{\bullet-}$ may incorporate up to three deuterium atoms via the proposed isomerization (Scheme 4) followed by two H/D exchanges with the more stable radical anion, $\mathbf{4}^{\bullet-}$. On the other hand, radical anions $\mathbf{4}^{\bullet-}$ and $\mathbf{5}^{\bullet-}$ would incorporate only two deuterium atoms via H/D exchange and isomerization-H/D exchange, respectively. However, detecting 3D incorporation in $\mathbf{6}^{\bullet-}$ has been found to be experimentally challenging. Deuterated reagents CD_3OD and C_2H_5OD form adducts with $C_5H_6O^{\bullet-}$ efficiently and exclusively. Encounters with more acidic (and hence more reactive) reagents lead primarily to $C_5H_6O^{\bullet-}$ signal loss (presumably via isomerization to $\mathbf{10}^{\bullet-}$ followed by detachment, vide infra). Thus, exploring higher reagent concentrations for detection of 3D incorporation becomes progressively difficult in terms of the signal to noise ratio.

It is noteworthy that signal loss is observed upon reaction of $C_5H_6O^{\bullet-}$ with proton transfer reagents that are slightly less acidic than **8** (e.g. PhCCH and *i*-PrOH). This loss of the $C_5H_6O^{\bullet-}$ signal can be explained by invoking a mechanism similar to that shown in Scheme 4. The reaction of $\mathbf{4}^{\bullet-}$ with reagents that are not acidic enough to undergo proton transfer might catalyze the isomerization of $\mathbf{4}^{\bullet-}$ to $\mathbf{10}^{\bullet-}$. In addition, instead of isomerizing to $\mathbf{4}^{\bullet-}$, isomers $\mathbf{5}^{\bullet-}$ and $\mathbf{6}^{\bullet-}$ could isomerize directly to $\mathbf{10}^{\bullet-}$. Any $\mathbf{10}^{\bullet-}$ that is formed would then autodetach and result in loss of the $C_5H_6O^{\bullet-}$ signal (Scheme 5).



4$^{\bullet-}$ **8** **10** **10**$^{\bullet-}$

Scheme 5.

3.2. Cyclopentanone-2,2,5,5-d_4 + $O^{\bullet-}$

In order to determine whether radical anion **6**$^{\bullet-}$ is formed in the reaction of **3** with $O^{\bullet-}$, cyclopentanone-2,2,5,5-d_4 (**3**-d_4) was allowed to react with $O^{\bullet-}$. Formation of both **4**$^{\bullet-}$ and **5**$^{\bullet-}$ requires net loss of $D_2^{\bullet+}$; whereas, formation of **6**$^{\bullet-}$ would be signaled by formation of an M–3 radical anion, resulting from net loss of $HD^{\bullet+}$.

The product distributions in the reaction of **3**-d_4 with $O^{\bullet-}$ are shown in Eq. (2). They have not been adjusted for the 5% **3**-d_3 impurity in the **3**-d_4 sample, but the contribution of this small amount of **3**-d_3 to the distribution of products should be minor. Specifically, the amount of the M–HD ion that could be formed from the **3**-d_3 impurity via 2,5- and 2,2-abstraction should not be greater than 0.2%. This is negligibly small compared to the experimentally observed yield of 2% (Eq. (2)).

$$
\begin{array}{l}
\mathbf{3\text{-}d_4} + O^{\bullet-} \\
\longrightarrow \left.\begin{array}{l} C_5H_3D_3O + HDO + e^- \\ \quad\quad\text{and} \\ C_5H_2D_4O + H_2O + e^- \end{array}\right\} \ (83\%) \\
\longrightarrow C_5H_4D_2O^{\bullet-} + D_2O \quad (4\%) \\
\longrightarrow C_5H_3D_3O^{\bullet-} + HOD \quad (2\%) \\
\longrightarrow C_3H_2O^{\bullet-} + C_2H_2D_2 + D_2O \quad (1\%) \\
\longrightarrow C_5H_4D_3O^- + DO^\bullet \quad (1\%) \\
\longrightarrow HO^- + C_5H_3D_4O^\bullet \quad (5\%) \\
\longrightarrow DO^- + C_5H_4D_3O^\bullet \quad (4\%)
\end{array}
\qquad (2)
$$

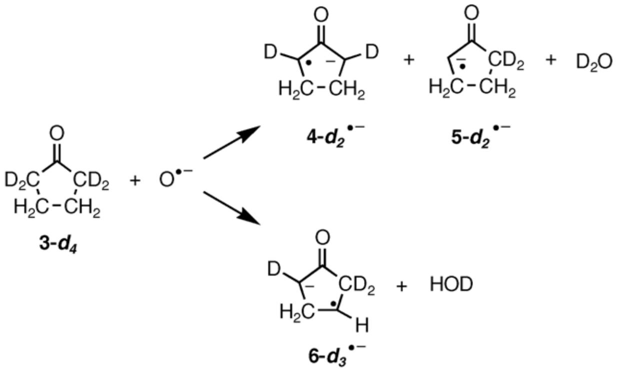
The 83% loss of product ion signal, observed in the reaction of **3**-d_4 with $O^{\bullet-}$, is even larger than the 75% loss found in the same reaction of perprotio-**3** (Eq. (1)). The larger loss of signal for product in the reaction of **3**-d_4 may, in part, be due to mass discrimination effects in ion detection. However, it seems likely that deuterium kinetic isotope effects also play a role. The observed isotope effect on ion loss is consistent with the postulate that reactive electron detachment proceeds through the transient formation of radical anion **10**$^{\bullet-}$. Since, in the reaction of **3**-d_4 with $O^{\bullet-}$, formation of **4**-$d_2^{\bullet-}$ and **5**-$d_2^{\bullet-}$ requires breaking two C–D bonds; whereas, formation of **10**-$d_3^{\bullet-}$ requires breaking only one C–D bond, a smaller primary kinetic isotope effect on formation of **10**-$d_3^{\bullet-}$ than on formation of **4**-$d_2^{\bullet-}$ and **5**-$d_2^{\bullet-}$ would be expected. The smaller kinetic isotope effect, expected for formation of **10**-$d_3^{\bullet-}$, should lead to an increase in the amount of reactive electron detachment, as was observed.

The reaction of **3**-d_4 with $O^{\bullet-}$ resulted in the formation of six primary products – $C_5H_4D_2O^{\bullet-}$, $C_5H_3D_3O^{\bullet-}$, $C_5H_4D_3O^-$, $C_3H_2O^{\bullet-}$, HO^-, and DO^- (Eq. (2)). This same reaction in Lin and Grabowski's FA experiments was reported to generate only $C_5H_4D_2O^{\bullet-}$, $C_5H_4D_3O^-$, DO^-, and *m*/*z* 99 [18]. The observed M–D_2 radical anion ($C_5H_4D_2O^{\bullet-}$) could be due to either 2,5-$D_2^{\bullet+}$ abstraction to form distonic ion **4**-$d_2^{\bullet-}$, to 2,2-$D_2^{\bullet+}$ abstraction to generate carbene radical ion **5**-$d_2^{\bullet-}$, or to formation of a mixture of **4**-$d_2^{\bullet-}$ and **5**-$d_2^{\bullet-}$. Since **7**$^{\bullet-}$ does not have any hydrogens α to the carbonyl group, it should not contain any deuterium if it is produced by fragmentation of **5**-$d_2^{\bullet-}$. In fact, in the reaction of **3**-d_4 with $O^{\bullet-}$ an *m*/*z* 54 ion ($C_3H_2O^{\bullet-}$) was detected, but no ions were observed at either *m*/*z* 55 or *m*/*z* 56. This finding confirms the results of Harrison and Jennings [17] and supports their hypothesis that the $C_3H_2O^{\bullet-}$ ion is **7**$^{\bullet-}$, formed by loss of ethylene from the carbene radical anion **5**$^{\bullet-}$.

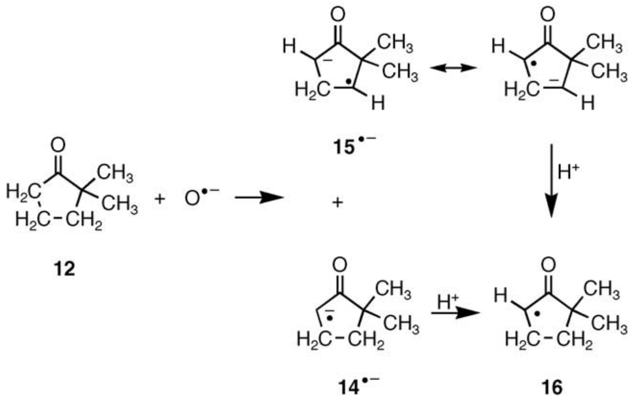
The formation of HO^-, as well OD^-, means that, in addition to abstracting an α-deuterium atom from **3**-d_4, $O^{\bullet-}$ also abstracts a β-hydrogen atom to generate cyclopentanone-3-yl and HO^-. Although the C–H bond dissociation enthalpy (BDE) of **3** is computed to be 7.8 kcal/mol higher at the carbon β to the carbonyl group than at the α carbon, hydrogen abstraction by $O^{\bullet-}$ from the β carbon is still calculated to be exothermic by 6.6 kcal/mol at (U)B3LYP/6-31+G*. Therefore, β-hydrogen atom abstraction is thermodynamically possible and is presumably the route by which HO^- is formed.

The formation of $C_5H_3D_3O^{\bullet-}$ is attributed to D^+ abstraction from C-2 and $H^\bullet$ abstraction from C-4 to generate anion **6**-$d_3^{\bullet-}$ (Scheme 6). Abstraction of D^+ from C-2 and $H^\bullet$ from C-3 would also form a $C_5H_3D_3O^{\bullet-}$ radical anion (**10**-$d_3^{\bullet-}$); but, as already discussed, **10**-$d_3^{\bullet-}$ should not bind an electron. Therefore, while formation of **10**-$d_3^{\bullet-}$ is most likely the cause of the large amount of ion loss which is observed in the reaction of **3**-d_4 with $O^{\bullet-}$, formation of **10**-$d_3^{\bullet-}$ is unlikely to provide any $C_5H_3D_3O^{\bullet-}$ ions that live long enough to be detected.

It is, in principle, possible that the $C_5H_3D_3O^{\bullet-}$ radical anion is actually **4**-$d_3^{\bullet-}$, resulting from initial formation of **6**-$d_3^{\bullet-}$, followed by HOD-catalyzed isomerization of **6**-$d_3^{\bullet-}$ to **4**-$d_3^{\bullet-}$ in the ion–dipole complex. Squires has noted that the reaction of deuterated hydrocarbons with $O^{\bullet-}$ does not necessarily give reliable ratios of the relative yields of M–H_2, M–HD, and M–D_2, because the nascent radical anion



Scheme 6.



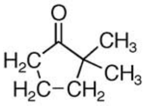
Scheme 7.

can undergo H/D exchange with the water molecule in the ion–dipole complex before dissociation [31b,35]. However, the $C_5H_3D_3O^{\bullet-}$ radical anion was found to have different reactivity than the **4**-$d_2^{\bullet-}$ ion, $C_5H_4D_2O^{\bullet-}$. For example, upon reaction with NO, $C_5H_3D_3O^{\bullet-}$ forms an adduct more efficiently than $C_5H_4D_2O^{\bullet-}$; and $C_5H_3D_3O^{\bullet-}$ is more reactive than $C_5H_4D_2O^{\bullet-}$ toward CS_2. These observations strongly suggest that $C_5H_3D_3O^{\bullet-}$ is not **4**-$d_3^{\bullet-}$, but is, instead, the distonic radical anion, **6**-$d_3^{\bullet-}$.

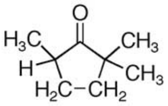
3.3. 2,2-Dimethyl- and 2,2,5-trimethylcyclopentanone + O$^{\bullet-}$

The results of the FA-SIFT experiments on the reaction of $O^{\bullet-}$ with both **3** and **3**-d_4 indicate formation of **4**$^{\bullet-}$, **5**$^{\bullet-}$, and **4**-$d_2^{\bullet-}$, **5**-$d_2^{\bullet-}$ respectively. In addition, the reaction of **3**-d_4 with $O^{\bullet-}$ suggests that **6**-$d_3^{\bullet-}$ is also generated in this reaction; so, presumably, **6**$^{\bullet-}$ is formed in the reaction of perprotio-**3** with $O^{\bullet-}$.

In order to confirm these conclusions, we studied the reactions of $O^{\bullet-}$ with 2,2-dimethylcyclopentanone (**12**) and 2,2,5-trimethylcyclopentanone (**13**). Ketone **12** can form the 2,2-dimethyl derivatives of **5**$^{\bullet-}$ and **6**$^{\bullet-}$, but the geminal methyls at C-2 preclude the formation of a radical anion analogous to **4**$^{\bullet-}$. Similarly, the three methyl groups at the α carbons of **13** allow the formation of the 2,2,5-trimethyl derivative of **6**$^{\bullet-}$, but preclude formation of radical anions analogous to **4**$^{\bullet-}$ and **5**$^{\bullet-}$



12



13

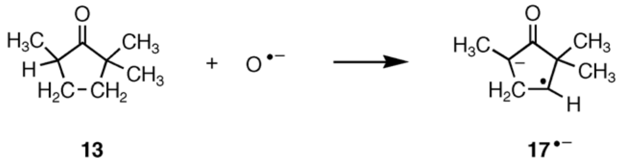
The reaction of **12** with $O^{\bullet-}$ produced a $C_7H_{11}O^-$ anion by proton abstraction, a $C_7H_{10}O^{\bullet-}$ radical anion by loss of $H_2^{\bullet+}$, and a $C_3H_2O^{\bullet-}$ radical anion in a ratio of roughly 3:2:3. The formation of $C_3H_2O^{\bullet-}$ suggests that carbene radical anion **14**$^{\bullet-}$ is formed; but, like **5**$^{\bullet-}$, **14**$^{\bullet-}$ fragments to **7**$^{\bullet-}$, in this case by loss of isobutylene.

The structure of the $C_7H_{10}O^{\bullet-}$ radical anion was investigated by combining DFT calculations with PA bracketing experiments. UB3LYP/6-31+G* calculations predict distonic radical anion **15**$^{\bullet-}$ to be 15.1 kcal/mol lower in energy than carbene radical anion **14**$^{\bullet-}$. Since both **14**$^{\bullet-}$ and **15**$^{\bullet-}$ would form radical **16** upon protonation (Scheme 7), **15**$^{\bullet-}$ is computed to be less basic than **14**$^{\bullet-}$ by this amount of energy. The calculated PAs are 385.5 kcal/mol for **14**$^{\bullet-}$ and 370.4 kcal/mol for **15**$^{\bullet-}$.

No proton transfer was observed upon reaction of $C_7H_{10}O^{\bullet-}$ with EtOH ($\Delta H_{\mathrm{acid}} = 378.3 \pm 1.0$ kcal/mol) or PhCCH ($\Delta H_{\mathrm{acid}} = 370.6 \pm 2.3$ kcal/mol). These experiments give an upper limit of 370.6 kcal/mol for the PA of $C_7H_{10}O^{\bullet-}$, which is too low for $C_7H_{10}O^{\bullet-}$ to be carbene radical anion **14**$^{\bullet-}$. This finding could indicate that all of the carbene radical anion **14**$^{\bullet-}$ that is formed fragments to **7**$^{\bullet-}$ and isobutylene. Alternatively, as discussed in Section 3.1 for **5**$^{\bullet-}$ and **6**$^{\bullet-}$, **14**$^{\bullet-}$ could isomerize to the more stable distonic radical anion **15**$^{\bullet-}$ in the ion–dipole complexes formed with EtOH and PhCCH.

In order to test whether the $C_7H_{10}O^{\bullet-}$ radical anion, formed by reaction of **12** with $O^{\bullet-}$, contains any **14**$^{\bullet-}$, we generated the $C_7H_{10}O^{\bullet-}$ radical anion in the source flow tube, then mass selected and injected it into the second flow tube. The methylene ketene radical anion (**7**$^{\bullet-}$) was produced by CID. This finding indicates that, as with carbene radical anion **5**$^{\bullet-}$ formed from **3**, the reaction of **12** with $O^{\bullet-}$ does generate **14**$^{\bullet-}$, which is sufficiently long-lived to be injected into the second flow tube.

The reaction of **12** with $O^{\bullet-}$ could produce distonic radical anion **15**$^{\bullet-}$, and experiments with 2,2,5-trimethylcyclopentanone (**13**) indicate that **15**$^{\bullet-}$ is, in fact, formed from **12**. Upon reaction of **13** with $O^{\bullet-}$ an *m*/*z* 125 anion was formed by proton loss, and a radical anion (*m*/*z* 124) was produced by loss of $H_2^{\bullet+}$. Since, in the latter reaction channel, only formation of the distonic radical anion **17**$^{\bullet-}$ is structurally feasible (Scheme 8), we assign this structure to the $C_8H_{12}O^{\bullet-}$ radical anion that is formed by the reaction of **13** with $O^{\bullet-}$.



Scheme 8.

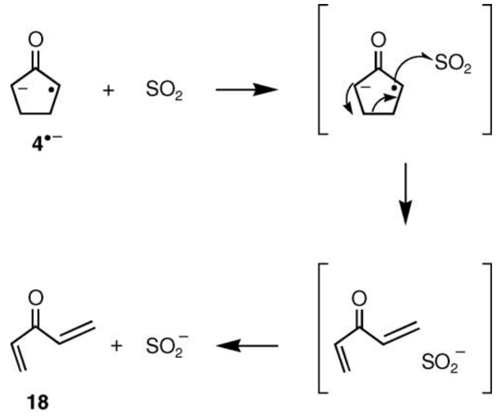
3.4. Electron binding energy (EBE) of $C_5H_6O^{\bullet-}$

In order to investigate further the nature of the $C_5H_6O^{\bullet-}$ radical anions formed in the reaction of $O^{\bullet-}$ with **3**, electron affinity bracketing experiments were performed. Rapid electron transfer was observed when the mixture of $C_5H_6O^{\bullet-}$ ions was allowed to react with SO_2 (EA = 1.107 ± 0.008 eV). The observed rate constant was $k = 1.41 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} (efficiency = 91%), and SO_2^- was essentially the sole product from this reaction.

Electron transfer was also observed with CS_2 (EA = 0.51 ± 0.10 eV). CS_2^- amounted to about 48% of the products, but an adduct [$C_5H_6O^{\bullet-} + CS_2$] was also formed (∼11%). In addition, the reaction of mass-selected $C_5H_6O^{\bullet-}$ with CS_2 generated an *m*/*z* 130 ion, while reaction of $C_5H_4D_2O^{\bullet-}$ with CS_2 produced an *m*/*z* 132 ion. The identity of this ion will be discussed in Section 3.6.2. The overall rate constant for disappearance of $C_5H_6O^{\bullet-}$, $k = 2.93 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (efficiency = 26%), was about a factor of five smaller than that for reaction of $C_5H_6O^{\bullet-}$ with SO_2.

When $C_5H_6O^{\bullet-}$ was allowed to react with O_2 (EA = 0.451 ± 0.007 eV), the major product was O_2^- (∼68%), while a small amount of adduct was formed (∼1%). The overall rate for disappearance of $C_5H_6O^{\bullet-}$ was $k = 1.69 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (efficiency = 28%), an order of magnitude smaller than that for reaction of $C_5H_6O^{\bullet-}$ with SO_2. A minor product at *m*/*z* 97 was observed in the reaction of $C_5H_6O^{\bullet-}$ with O_2. A discussion of this minor product can be found in Section 3.6.1.

Since the overall reaction rates with CS_2 and O_2 are far below the collision limits, competition between electron transfer and other chemical processes would be insignificant. Exothermic electron transfer would thus be expected to produce CS_2^- or O_2^- very efficiently. Compared to the reaction with SO_2, however, the observed electron transfer rates are small; 1.4×10^{-10} cm^3 molecule^{-1} s^{-1} for CS_2 (efficiency = 13%) and 1.1×10^{-10} cm^3 molecule^{-1} s^{-1} for O_2 (efficiency = 19%). Significant amounts of an adduct were also formed with CS_2, however adduct formation may not be facile with the non-polar diatomic O_2. These results suggest that the electron transfer reactions are slightly endothermic with CS_2 and O_2. This indicates that the experimental EBE for $C_5H_6O^{\bullet-}$ is probably close to 0.5 eV. However, as shown in Table 1, the predicted EBEs for all three of the $C_5H_6O^{\bullet-}$ isomers (**4**$^{\bullet-}$, **5**$^{\bullet-}$, and **6**$^{\bullet-}$) are about 1.6 eV. Thus, the (U)B3LYP/6-31+G* calculations appear to overestimate the EBE of one or more of the $C_5H_6O^{\bullet-}$ isomers, not by a few tenths of an eV, but by ca. 1.1 eV.



Scheme 9.

Although in many cases (U)B3LYP calculates EAs accurately [31], B3LYP is a single determinantal method. Therefore, B3LYP is likely to overestimate the energies of singlet diradicals, such as **4** and **6** [36]. For example, using multireference CASPT2/6-311G(2d,p) calculations, Powell and Borden predicted $\Delta E_{ST} = -7.0$ kcal/mol for **4** [9b]. However, using B3LYP/6-31+G*, $\Delta E_{ST} = -2.8$ kcal/mol is computed, because the energy of the singlet is overestimated.

We circumvented the problem that B3LYP has in describing singlet diradicals by computing the energy difference between radical anion **4**$^{\bullet-}$ and triplet **4**, using UB3LYP, and then adding ΔE_{ST}, computed by CASPT2. Combining the UB3LYP value of EA = 1.78 eV for forming triplet **4** with the CASPT2 value of $\Delta E_{ST} = -7.0$ kcal/mol, a value of EA = 1.48 eV is obtained for forming **4**$^{\bullet-}$ from singlet **4**.[3] This value is 7.0–2.8 = 4.2 kcal/mol = 0.18 eV lower than the value of 1.66 eV, computed from the difference between the (U)B3LYP energies of **4**$^{\bullet-}$ and singlet **4** (Table 1).

Nevertheless, the corrected EBE of **4**$^{\bullet-}$, and the calculated EBEs of isomers **5**$^{\bullet-}$ and **6**$^{\bullet-}$, are still significantly (ca. 1.0 eV) greater than the experimentally determined EBE of 0.5 eV. A possible explanation for this very large difference between the calculated and measured EBEs is that adiabatic electron transfer from **4**$^{\bullet-}$ does not lead to **4**, as the calculations assume. Instead, concomitant with electron transfer to an acceptor (e.g., SO_2), **4**$^{\bullet-}$ undergoes cleavage of the C_3–C_4 σ-bond to form 1,4-pentadien-3-one (**18**) in the collision complex, as shown in Scheme 9.

The retro-Nazarov reaction [37], shown in Scheme 9, forms a product (**18**) that is predicted to be lower in energy than **4** by 27.1 kcal/mol at the B3LYP/6-31+G* level of theory.[4] Thus, the adiabatic reaction energy, computed for **4**$^{\bullet-}$ → **18**, is 0.48 eV, a value that is in excellent agreement with the experimentally observed EBE for $C_5H_6O^{\bullet-}$.

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[3] At CASPT2/6-31+G*, EA = 1.32 eV was obtained for forming triplet **4**. However, we believe that CASPT2 is more likely than B3LYP to underestimate the EBE of **4**$^{\bullet-}$.

[4] Closure of **4** to form bicyclo[2,1,0]pentan-5-one is highly unlikely since the bicyclic ketone is computed to be 28.9 kcal/mol higher in enthalpy than **18**.

It is highly unlikely that the radical anion of 1,4-pentadien-3-one (**18**$^{\bullet-}$) is generated directly from the reaction of **3** with $O^{\bullet-}$, since **18**$^{\bullet-}$ is predicted to have a PA of 347.5 kcal/mol to form the most stable neutral. This value is much lower than the observed value of PA = 362 ± 5 kcal/mol. As discussed in Section 3.1, the experimental PA of $C_5H_6O^{\bullet-}$ is close to the value of PA = 363.2 kcal/mol, computed for **4**$^{\bullet-}$.

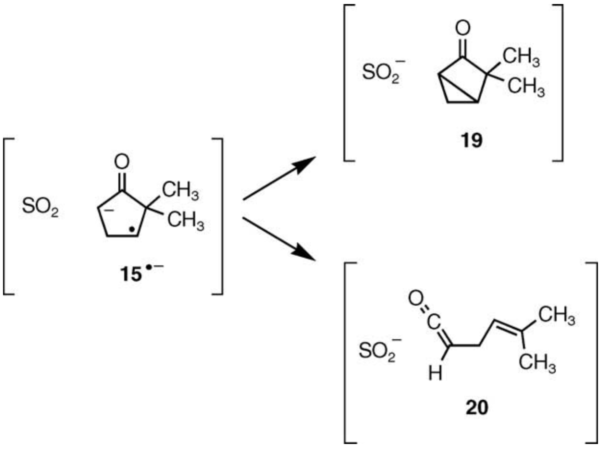
An experimental test of this hypothesis – that the EBE measured for **4**$^{\bullet-}$ actually is the EBE for formation of **18** and not **4** – would be to measure the EBE of $C_5H_6O^{\bullet-}$ by NIPES. NIPES can provide both the vertical and adiabatic EAs when the $0–0^1$ band origins are identified. If the $C_5H_6O^{\bullet-}$ radical anion consists of a mixture of **4**$^{\bullet-}$, **5**$^{\bullet-}$, and **6**$^{\bullet-}$, the adiabatic EA of the radical determined by NIPES should be ca. 1.5 eV (Table 1), and not the 0.5 eV that was obtained by the EA bracketing experiments. Preliminary NIPES experiments on **4**$^{\bullet-}$ are consistent with our hypothesis.

3.5. EBE of $C_7H_{10}O^{\bullet-}$

Upon electron loss, distonic radical anion **15**$^{\bullet-}$ is predicted to form a neutral diradical (**15**), which is calculated to have a triplet ground state. UB3LYP/6-31+G* calculations predict EA = 1.65 eV for formation of **15**$^{\bullet-}$ from triplet **15**.

Experimentally, electron transfer was observed when $C_7H_{10}O^{\bullet-}$ was allowed to react with SO_2 and O_2, thus indicating an experimental EBE of roughly 0.5 eV for **15**$^{\bullet-}$. Rate measurements were not possible given the small signal of $C_7H_{10}O^{\bullet-}$, so we have not determined whether the electron transfer reaction with O_2 is exothermic or endothermic. As in the case of electron transfer from the mixture of $C_5H_6O^{\bullet-}$ radical anions, there is a very large discrepancy between the predicted EBE (1.65 eV) and the experimental EBE (∼0.5 eV).

Once again, this discrepancy can be explained by formation of a closed-shell species, rather than a diradical of higher energy, upon loss of an electron from the radical anion. As illustrated in Scheme 10, distonic radical anion **15**$^{\bullet-}$ can, in concert with electron transfer, either close to bicyclic ketone **19** or cleave to ketene **20**.



Scheme 10.

The triplet ground state of diradical **15** is computed to be 23.4 kcal/mol higher in enthalpy than **19** and 30.3 kcal/mol higher in enthalpy than **20**. The experimental EBE, involving isomerization of **15**$^{\bullet-}$ to **19**, is thus predicted to be 0.63 eV, and the EBE for **15**$^{\bullet-}$ → **20** is predicted to be 0.33 eV. Both of these EBEs, computed for **15**$^{\bullet-}$, are consistent with the experimental finding that the EBE of **15**$^{\bullet-}$ is approximately 0.5 eV, but formation of the lower energy product (**20**) is expected to be the more favored pathway.

3.6. Reactivity of $C_5H_6O^{\bullet-}$

3.6.1. $C_5H_6O^{\bullet-}$ with O_2

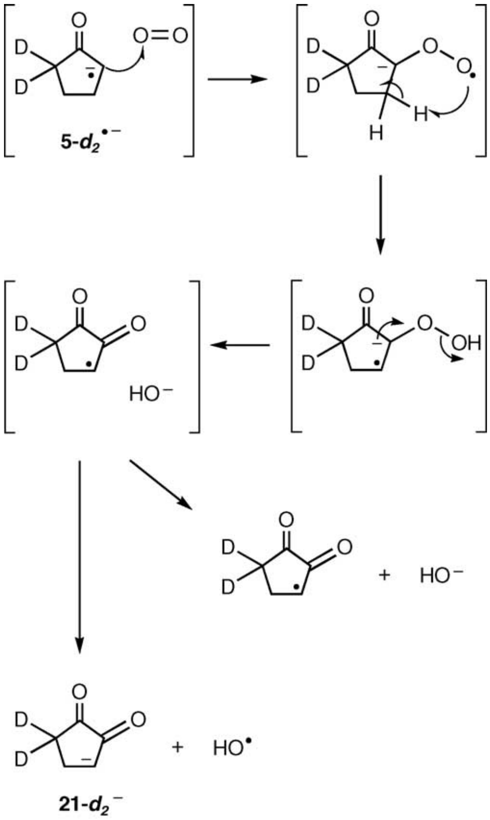
Lin and Grabowski observed an *m/z* 97 ion as a secondary product in the reaction of **3** with $O^{\bullet-}$ [18]. Their observations led them to assign this ion as the enolate of 1,2-cyclopentadione (**21**$^-$), resulting from the oxidation of **5**$^{\bullet-}$ by **3**. Although we did not observe this secondary reaction in our FA-SIFT, the reaction of mass-selected $C_5H_6O^{\bullet-}$ (*m/z* 82) with O_2 not only resulted in electron transfer (as discussed in Section 3.4), but also produced HO^- and an *m/z* 97 ion (82 + O_2–HO). Likewise, mass-selected $C_5H_4D_2O^{\bullet-}$ reacted with O_2 to produce an *m/z* 99 ion and HO^-, with no observed DO^- formation.

Carbene radical anions have been shown to react with O_2 by addition of dioxygen and loss of hydroxyl radical [38]. Although carbene radical anion **5**$^{\bullet-}$ has been found to fragment to methylene ketene radical anion (**7**$^{\bullet-}$) and ethylene, this unimolecular decomposition reaction does not appear to be complete (Section 3.1). If any carbene radical anion persists, upon reaction with O_2, **5**$^{\bullet-}$ might be expected to add O_2 and lose HO to generate enolate **21**$^-$, as shown in Scheme 11 for **5**-$d_2^{\bullet-}$. Therefore, the major product in the reaction of **5**$^{\bullet-}$ with O_2 is expected to be **21**$^-$, since this ion is calculated by (U)B3LYP/6-31+G* to have an EBE of 2.31 eV (compared with EBE = 1.828 eV for HO^-) [20].

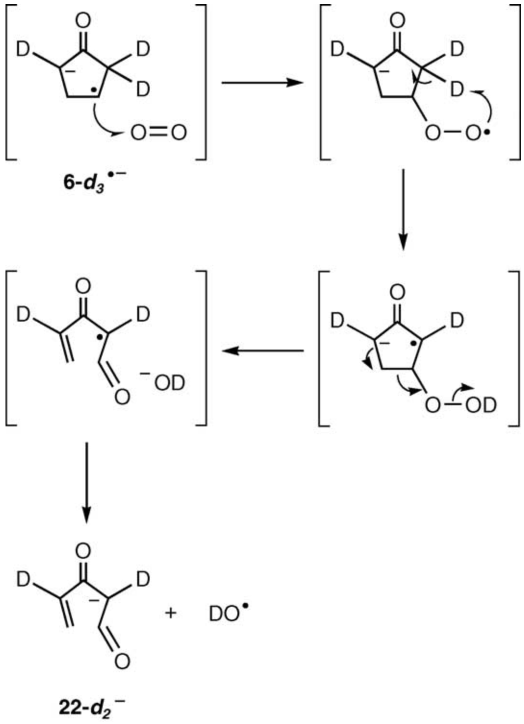
Alternatively, distonic radical anions **4**$^{\bullet-}$ and **6**$^{\bullet-}$ could be the precursors of *m/z* 97 in the reaction of $C_5H_6O^{\bullet-}$ with O_2. Carbanions, such as benzyl and pentenyl anions have been found to react with O_2 via addition and HO loss [39]. As shown in Scheme 12, distonic ion **6**-$d_3^{\bullet-}$ might be expected to add O_2 and lose DO to generate enolate ion **22**-d_2^- (*m/z* 99). In this reaction, no DO^- would be observed, because **22**$^-$ is predicted by (U)B3LYP/6-31+G* to have EBE = 3.00 eV.

Similarly, two O_2 addition/HO loss mechanisms can be written for **4**-$d_2^{\bullet-}$. In both mechanisms, O_2 adds to **4**-$d_2^{\bullet-}$ and the resulting peroxy radical undergoes ring-opening to generate ketene aldehyde **23**-d_2 and $O^{\bullet-}$ (Scheme 13). The $O^{\bullet-}$ thus generated could either abstract an α or β hydrogen atom (relative to the ketene functionality).

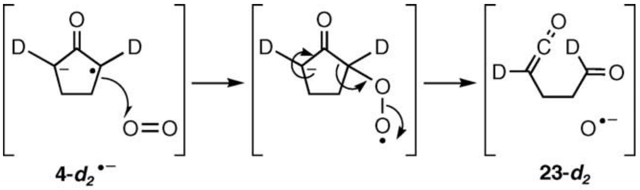
If an α hydrogen atom were abstracted, HO^- would be expected to be the observed product (Scheme 14), since radical **24** is calculated to have EA = 1.13 eV at the UB3LYP/6-



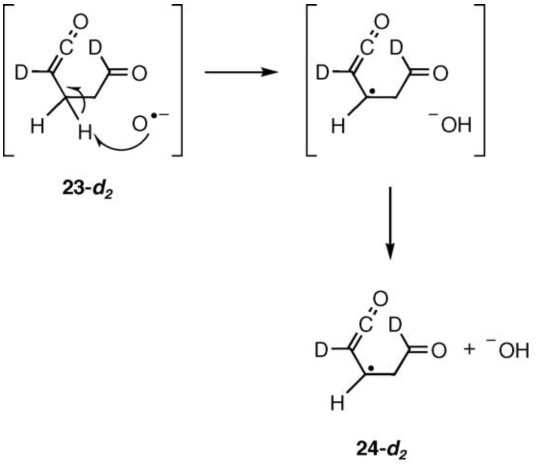
Scheme 11.



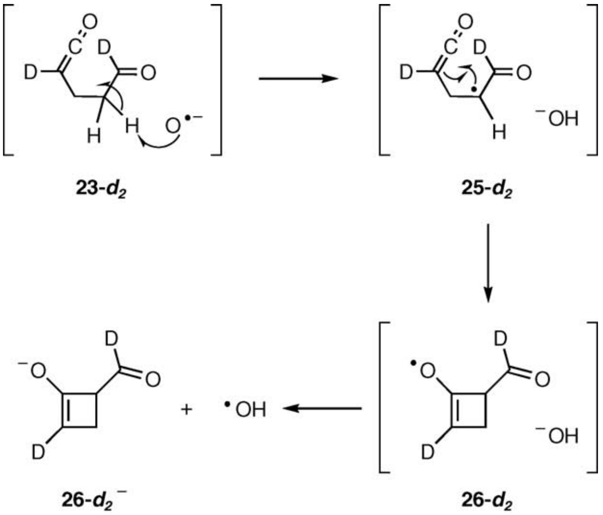
Scheme 12.



Scheme 13.



Scheme 14.



Scheme 15.

31+G* level of theory, much lower than EBE = 1.828 eV for HO− [20]. However, if a β hydrogen atom is abstracted from **23**-d_2, the resulting radical (**25**-d_2) could ring-close to form radical **26**-d_2 (Scheme 15).[5] Since (U)B3LYP/6-31+G* calculations predict radical **26** to have EA = 2.35 eV, *m*/*z* 99 would then be the observed product.

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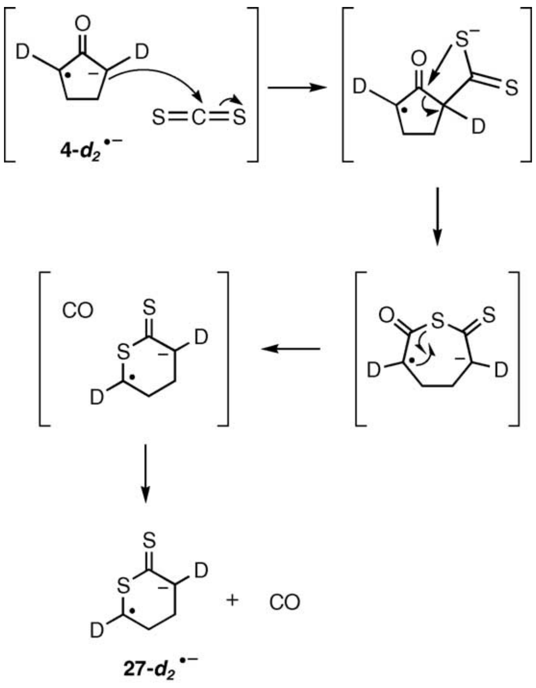
[5] In fact, all attempts to locate a stationary point for radical **25** at the UB3LYP/6-31+G* level of theory were unsuccessful.



Scheme 16.

3.6.2. $C_5H_6O^{\bullet -}$ with CS_2

The major product of the reaction of mass-selected $C_5H_6O^{\bullet -}$ with CS_2 was CS_2^{-}, as discussed in Section 3.4. However, a minor product of this reaction was observed at *m*/*z* 130. Likewise, the reaction of $C_5H_4D_2O^{\bullet -}$ with CS_2 produced an *m*/*z* 132 ion. The shift in mass in the deuterium labeled experiments suggests that the molecular formula of the *m*/*z* 130 ion is $C_5H_6S_2^{\bullet -}$.

Distonic ion **4**-$d_2^{\bullet -}$ could react with CS_2 via an addition/CO loss mechanism, such as that indicated in Scheme 16, to produce radical anion **27**-$d_2^{\bullet -}$. Although the formation of $C_5H_6S_2^{\bullet -}$ is consistent with CS_2 addition to **4**$^{\bullet -}$, we cannot rule out the possibility that $C_5H_6S_2^{\bullet -}$ results from reaction of either distonic radical anion **6**$^{\bullet -}$ or carbene radical anion **5**$^{\bullet -}$ with CS_2.

4. Conclusions

Our experiments and calculations indicate that the reaction of cyclopentanone (**3**) with $O^{\bullet -}$ initially generates four isomeric radical anions, namely, **4**$^{\bullet -}$, **5**$^{\bullet -}$, **6**$^{\bullet -}$, and **10**$^{\bullet -}$. The last of these ions is not observed directly, presumably because it is unbound and rapidly loses an electron to form 2-cyclopentenone. Therefore, formation of **10**$^{\bullet -}$ is the reason for the large amount of electron loss in the reaction of **3** with $O^{\bullet -}$.

The most abundant of the stable radical anions, formed in the reaction of **3** with $O^{\bullet -}$, is **4**$^{\bullet -}$. This ion was found to have a PA of 362 ± 5 kcal/mol and an apparent EBE of ca. 0.5 eV. The PA is in good agreement with the value of 363.3 kcal/mol predicted for **4**$^{\bullet -}$ by UB3LYP/6-31+G*, but loss of an electron from **4**$^{\bullet -}$, to form cyclopentanone-2,5-diyl (**4**), is predicted to require 1.48 eV, However, the 1 eV discrepancy between the measured and computed EBEs can be rationalized by proposing that the experimentally observed electron transfer process leads, not to **4**, but to 1,4-pentadien-3-one (**18**). Divinyl ketone **18** is, in fact, computed to be 1.0 eV lower in enthalpy than **4**.

The bracketed PA for the radical anion formed by reaction of 2,2-dimethylcyclopentanone (**12**) with $O^{\bullet -}$ is consistent with the PA predicted for distonic radical anion **15**$^{\bullet -}$. Evidence for generation of this type of ion comes from the observation of a radical anion, formed by loss of $H_2^{\bullet +}$, in the reaction of 2,2,5-trimethylcyclopentanone (**13**) with $O^{\bullet -}$.

However, as in the case of **4**$^{\bullet -}$, there is a large discrepancy between the EBE measured for radical anion **15**$^{\bullet -}$ and the EBE computed for the formation of the corresponding diradical. This difference between the measured and calculated EBEs can again be explained by proposing that, when **15**$^{\bullet -}$ loses an electron in the ion–dipole complex with electron acceptors, electron transfer leads to either bicyclic ketone **19** or, more likely, to ketene **20**, rather than to diradical **15**.

Thus, the results of our calculations and experiments on the EBEs of **4**$^{\bullet -}$ and **15**$^{\bullet -}$ lead us to conclude that rearrangements, which occur concomitant with electron transfer, can result in large differences (ca. 1 eV) between experimentally measured and computationally predicted EBEs. This general conclusion may provide the explanation for the very large difference between the calculated value for the EBE in the acenaphthyne radical anion and the EBE found experimentally [40]. Indeed, previous gas-phase experiments have shown that carbocation rearrangements can make the adiabatic PAs of alkenes very different from the values computed for protonation without rearrangement [41].

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.ijms.2004.12.009.

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