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Radicals

Direct Detection of a Persistent Carbonyloxyl Radical in the Gas Phase**

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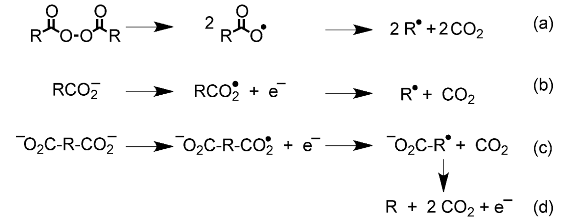
Carbonyloxyl radicals ($RCO_2^{\bullet}$; where R represents aromatic or aliphatic substituents) are reactive intermediates that play key roles in initiating polymerization reactions[1] and their unique reactivity is exploited synthetically for hydrogen abstraction,[2] addition to carbon–carbon double[3,4] and triple bonds.[5] They are often synthesized by thermal decomposition of diacyl peroxides, as indicated in Scheme 1 a.



Scheme 1. Pathways for formation for carbonyloxyl radicals and their associated decomposition products: a) peroxide decomposition, b) electron stripping, c) electron stripping from a multiply charged anion, and d) subsequent decarboxylation leading to secondary electron ejection. The group R represents aliphatic or aromatic substituents.

The same reactivity that makes carbonyloxyl radicals useful chemical tools also makes their direct observation difficult, with the first reported observation in 1985 of benzoyloxyl ($C_6H_5CO_2^{\bullet}$) prepared and detected in solution using a modified electron spin resonance spectrometer.[6] Subsequently, other studies have detected carbonyloxyl radicals in solution and have reported lifetimes on the order of μs,[7–9] however in the gas phase, direct detection of carbonyloxyl radicals themselves has thus far proved challenging. While gas-phase spectroscopy of fluorocarbonyloxyl radicals has been reported[29,30] the lifetimes for just a few organic carbonyloxyl radicals have been inferred by applying electron-stripping techniques to appropriate carboxylate anion precursors (Scheme 1 b). One such system is the acetyloxyl radical ($CH_3CO_2^{\bullet}$), for which a lower limit for the lifetime of the radical of 10 μs was estimated using photoelectron–photofragment coincidence spectroscopy,[10] while a lifetime of 100 ps was derived from collision-based electron stripping in neutralization–reionization experiments.[11] These solution and gas-phase data suggest two things: that different carbonyloxyl radicals have different lifetimes when measured with the same method and, more problematically, lifetime measurements of the same carbonyloxyl radical by different experimental approaches yield conflicting results.

Multiply charged anions, particularly dicarboxylates, present a convenient route to synthesize and interrogate carbonyloxyl radicals in the gas phase using mass spectrometry, owing to the residual charge remaining following detachment of a single electron (Scheme 1 c). Since the initial observation of gas-phase multiply charged anions generated by electrospray ionization,[12,13] the intrinsic properties of these systems have presented an intriguing problem for experimental and theoretical chemists alike. Some of the first photoelectron spectroscopy (PES) experiments on small multiply charged anions elegantly demonstrated that the photodetachment dynamics of even very similar dianions can be dramatically different. Anion photoelectron spectra of succinate ($[O_2CCH_2\text{-}CH_2CO_2]^{2-}$) and fumarate ($[O_2CCH{=}CHCO_2]^{2-}$) reported by Wang and co-workers both display low kinetic energy photoelectron signatures that appear to be independent of the photon energy used and these electrons

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are conspicuously absent in the PES of acetylene dicarboxylate ($[O_2CC{\equiv}CCO_2]^{2-}$).[14,15] It was proposed that in the succinate and fumarate cases, the low kinetic energy electrons arise from the nascent carbonyloxyl radical anion through a secondary detachment process, such as decarboxylation coupled with prompt autodetachment (Scheme 1 d).[15] Whereas the acetylene dicarboxylate case could possibly be explained by either a persistent carbonyloxyl radical and/or the absence of electron detachment pathways coupled with decarboxylation. Herein, we present the first mass-spectrometric evidence that persistent carbonyloxyl radical anions can be generated by electron detachment from acetylene dicarboxylate dianions, and report the longest-lived organic carbonyloxyl radicals identified to date.

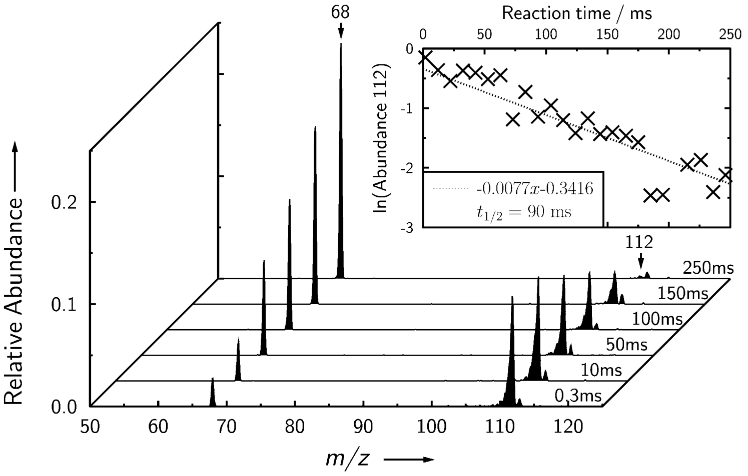

Figure 2. Mass spectra acquired by isolating the detached carbonyloxyl radical ($[O_2CC{\equiv}CCO_2]^{\bullet-}$; *m*/*z* 112) and monitoring the production of the decarboxylated radical species ($[O_2CC{\equiv}C]^{\bullet-}$; *m*/*z* 68). The corresponding first-order kinetic decay of the monoanion radical is shown as an inset, yielding a half-life of 90 ms.

Electrospray ionization of an alkaline methanolic solution of acetylene dicarboxylic acid produces an abundant dianion at *m*/*z* 56 that can be mass-selected using an isolation width of 2 Th on a quadrupole linear ion trap. A representative mass spectrum of the purified dianion is shown in the top panel of Figure 1 and is dominated by the target acetylene dicarboxylate dianion $[O_2CC{\equiv}CCO_2]^{2-}$. Small contributions from a $[O_2CC{\equiv}CCO_2{\cdots}H_2O]^{2-}$ adduct with background water observed at *m*/*z* 65 and a $[O_2CC{\equiv}C]^{\bullet-}$ decarboxylation product at *m*/*z* 68 arise from unavoidable activation of the ion during the isolation process. Exposing the mass-selected acetylene dicarboxylate dianion to a single pulse from a Nd:YAG laser ($\lambda = 266$ nm, $h\nu = 4.66$ eV) results in electron photodetachment and production of a carbonyloxyl radical anion at *m*/*z* 112, shown in the lower panel of Figure 1. The asymmetric peak shape tailing towards lower *m*/*z* is indicative of fragile ions,[16] wherein some of the ion population undergoes decomposition during resonant ion ejection. Comparing mass spectra acquired in an interleaved laser-on/laser-off measurement (as described in the Supporting Information) demonstrates that the ions at *m*/*z* 68 and 112 are photoproducts. Oxidative decarboxylation of dicarboxylate dianions has been reported[13,17] and even used as a route to synthesize distonic radical anions,[18–20] however the observation of *m*/*z* 112 in this experiment represents the first time that the oxidized radical species itself has been directly detected and isolated. Isolating the *m*/*z* 112 ion and interrogating the *m*/*z* 68 product formed over increasing time periods (Figure 2) establishes a first-order decay with a half-life of 90 ± 8 ms. Essentially the same lifetime (86 ± 8 ms) and dissociation products are measured when collision-induced dissociation (CID) is used to generate the *m*/*z* 112 radical anion. Furthermore, altering the isolation conditions by varying the ion-trap *q*-parameter (thereby changing the effective trapping temperature[21]) does not significantly affect the lifetime, implying that our measurement reflects the intrinsic lifetime of the thermalized radical population and not an artifact of the generation, activation or mass-selection process.

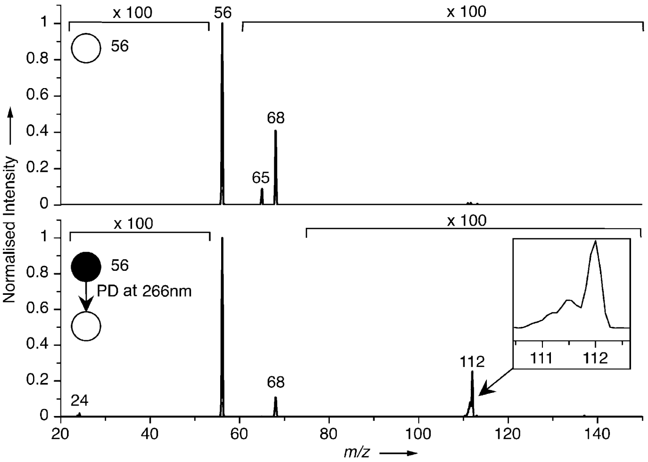

Figure 1. Mass spectra of the mass-isolated acetylene dicarboxylate dianion $[O_2CC{\equiv}CCO_2]^{2-}$; *m*/*z* 56 (top) and the products resulting from exposure to 266 nm laser radiation (bottom, PD = photodetachment). Note that the *m*/*z* 68 peak has not been magnified in the bottom trace. The asymmetric peak shape of the detached carbonyloxyl radical at *m*/*z* 112 is shown as an inset.

Notwithstanding that this decarboxylation process is relatively well known and often exploited, the lifetime determined in this case is three orders of magnitude longer than those measured for other carbonyloxyl radicals.[22] For example, the lifetime of the neutral acetyloxyl radical lies between 10 μs and 100 ps.[10,11] For charged dicarboxylate species, including aliphatic,[23] substituted aliphatic,[20] and aromatic dicarboxylates (Supporting Information), lifetimes for the analogous carbonyloxyl radicals are too short for the detached monoanion radical to be detected using our ion trap, with only decarboxylation and fragmentation products observed. Even in solution, the lifetimes reported for carbonyloxyl radicals range between μs and ps,[8,24,25,31] again much shorter than observed here for the acetylene dicarboxylate radical anion.

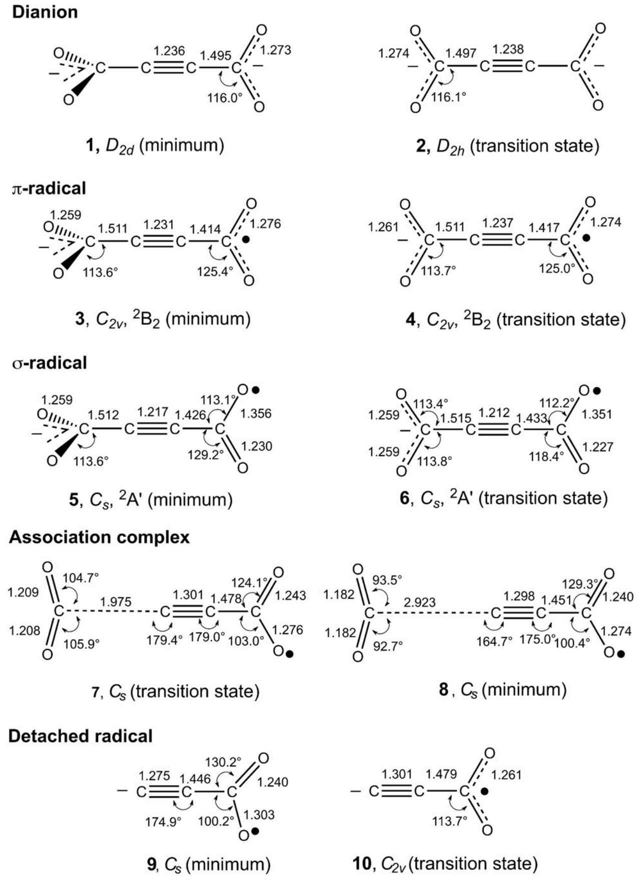

Figure 3. Calculated structures (MP2/6-31 + G(d)) for the acetylene dicarboxylate dianion, the σ and π forms for the detached monoanion radical, the association complex between the decarboxylated radical and CO_2, and the decarboxylated acetylene carboxylate radical.

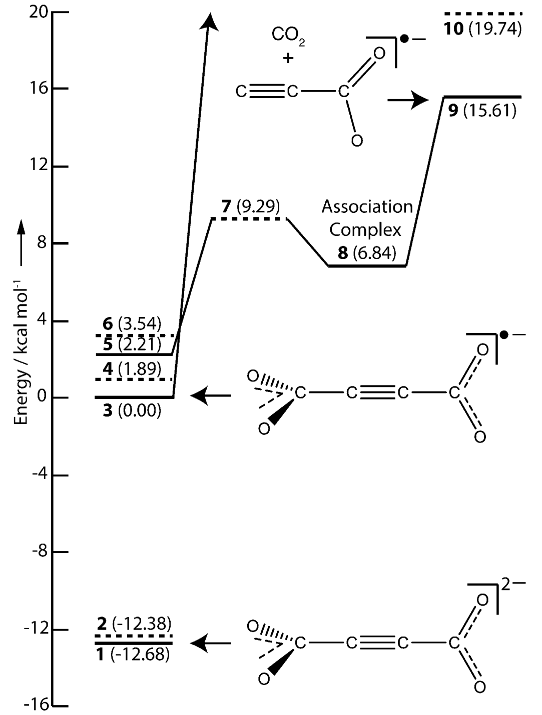

Figure 4. Relative energetics (CCSD(T)/aug-cc-pVTZ//MP2/6-31 + G(d)) of the species shown in Figure 3 relative to the detached monoanion π-radical, **3**. Stable structures are denoted as solid lines and transition states by dashed lines.

Clearly, the energetics of the decarboxylation process plays a crucial role in the persistence of the acetylene dicarboxylate radical anion. The MP2/6-31 + G(d) optimized structures shown in Figure 3 display a D_{2d} minimum (Structure **1**) for the dianion with the two CO_2 groups orthogonal to one another, in agreement with previous calculations.[14,26] At the approximately 310 K temperatures within the ion trap[18] rotation of the CO_2 groups is likely to be unrestricted owing to the small rotation barrier (0.7 and 0.3 kcal mol^{-1} for MP2/6-31 + G(d) and CCSD(T)/aug-cc-pVTZ, respectively). The calculated electron binding energy of **1** at 0 K is 0.61 eV at MP2/6-31 + G(d) and 0.55 eV from the CCSD(T) single-point calculations, reasonably close to the 0.3 ± 0.1 eV adiabatic binding energy determined from photoelectron studies.[14] Upon photodetachment, both a π-state (**3**) and a σ-state (**5**) are calculated for the carbonyloxyl radical anion and the two states are found to be very close in energy; both MP2 and CCSD(T) predict a π-ground state, although the energy differences are too small (< 0.1 eV) for a ground state to be assigned definitively. The perpendicular conformation is the minimum for both states, with rotation barriers comparable to those calculated for the dianion. Formation of the charged product fragments involves surmounting a 15.6 kcal mol^{-1} barrier that involves decarboxylation to the association complex (**8**) and subsequent dissociation of the complex to yield a $C_3O_2^{\bullet-}$ radical anion (**9**) and CO_2 (Figure 4). Given the barrier to dissociation, perhaps it is surprising that these thermalized radical anions decarboxylate within the ion trap, however, the barrier height calculated for this process is higher than the 5–10 kcal mol^{-1} barriers estimated for other carbonyloxyl radicals that exhibit facile decarboxylation.[22] Treating this barrier as the Arrhenius activation energy E_a and using the experimentally determined dissociation rate constant of 7.7 s^{-1}, we derive a frequency factor of $A = 7.9 \times 10^{11}$ s^{-1} for the decarboxylation process. We find a larger barrier height is the only significant point of difference between $[O_2CC{\equiv}CCO_2]^{\bullet-}$ and other carbonyloxyl radicals (Table S2, Supporting Information), and it is thus simply the greater activation energy that gives rise to the prolonged lifetime of the acetylene dicarboxylate radical anion. Interestingly, when compared at the MP2/6-31 + G(d) level, the barrier to decarboxylation of $[O_2CC{\equiv}CCO_2]^{\bullet-}$ lies between the barriers calculated for the analogous neutral radical $[HO_2CC{\equiv}CCO_2]^{\bullet}$ and the closed-shell carboxylate anion $[HO_2CC{\equiv}CCO_2]^{-}$ (see Supporting information Table S5). These comparisons suggest that the presence of the negative charge in the $[O_2CC{\equiv}CCO_2]^{\bullet-}$ system has a significant role in stabilizing this carbonyloxyl radical with respect to dissociation. The persistence of this carbonyloxyl radical suggests that if secondary electron detachment occurs following dissociation, the timescale for this process would be on the order of ms. For conventional PES, this implies that a secondary detachment event would likely occur outside the acceptance window of the analyzer, which could account for the lack of low-energy photoelectrons in the spectra obtained by Wang and co-workers.[14,15]

Decarboxylation of the acetylene dicarboxylate radical anion results in formation of the acetylene carboxylate radical anion (**9**). Experimental observations suggest that this anion is stable towards further electron detachment and further reaction. First, isolation of **9** for trapping times of up to 5 s does not yield further fragmentation products or loss of ion signal, which is also corroborated by the consistency of the integrated ion signal intensity over the course of the measurements presented in Figure 2 (see Figure S5 and S6, Supporting Information). Second **9** does not react with molecular oxygen in the same manner as many distonic radical anions.[18,19] Both observations suggest that the radical is delocalized across the acetylene carbon atoms and the carboxylate group. Indeed, our calculations indicate that upon decarboxylation, **9** exhibits strong and unexpected geometrical distortions; the carboxyl group is asymmetric, with the ∡CCO angle to the "singly" bonded oxygen reduced to 100° and the charge delocalized between the -CO_2 and the acetylide position. It is the combination of all of these factors—the persistent carbonyloxyl radical, the absence of electron loss channels from the radical anion (i.e. all products are ions, see Figure S5), and the inability of the decarboxylated product to lose a second electron through a concerted loss of CO_2—that accounts for the absence of low-energy photoelectrons following photodetachment from the acetylene dicarboxylate dianion reported in previous experiments.[14,15]

The data reported herein represent the first time that a persistent organic $RCO_2^{\bullet}$ radical has been detected in the gas phase, and provide a unique opportunity to investigate a carbonyloxyl radical directly. The extraordinary longevity of the acetylene dicarboxylate radical anion is attributable to the high barrier towards fragmentation owing to the endothermicity of the decarboxylation products, that is, the acetylene carboxylate radical anion, and it is likely that other such persistent carbonyloxyl radicals may be directly observable provided they exhibit a similarly high barrier to CO_2 loss. Interestingly, radical anions formed from photodetachment of polyanions (including peptides and proteins) have been reported.[27,28] Our results suggest that such radical anions are unlikely to be $RCO_2^{\bullet}$ radicals, but rather rearrangement products, the formation of which competes with decarboxylation.

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