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Abstract

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Keywords

dicarboxylate, simple, photodetachment, dianions, electron, ionic, arising, products, characterisation, GeoQuest

Disciplines

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Characterisation of the ionic products arising from electron photodetachment of simple dicarboxylate dianions.

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Abstract

Much of what we currently understand about the structure and energetics of multiply-charged anions in the gas phase is derived from the measurement of photoelectron spectra of simple dicarboxylate dianions. Here we have employed a modified linear ion-trap mass spectrometer to undertake complementary investigations of the ionic products resulting from laser-initiated electron photodetachment of two model dianions. Electron photodetachment (ePD) of the $[M - 2H]^{2-}$ dianions formed from glutaric and adipic acid were found to result in a significant loss of ion signal overall which is consistent with photoelectron studies that report the emission of slow secondary electrons [Xing *et al. J. Phys. Chem. A* **2010**, *114*, 4524]. The ePD mass spectra reveal no signals corresponding to the intact $[M - 2H]^{\bullet-}$ radical anions but rather $[M - 2H - CO_2]^{\bullet-}$ ions are identified as the only abundant ionic products indicating that spontaneous decarboxylation follows ejection of the first electron. Interestingly however, investigations of the structure and energetics of the $[M - 2H - CO_2]^{\bullet-}$ photoproducts by ion-molecule reaction and electronic structure calculation indicate that (i) these ions are stable with respect to secondary electron detachment and (ii) most of the ion population retains a distonic radical anion structure where the radical remains localised at the position of the departed carboxylate moiety. These observations lead to the conclusion that the mechanism for loss of ion signal involves unimolecular rearrangement reactions of the nascent $[M - 2H]^{\bullet-}$ carbonyloxy radical anion that compete favourably with direct decarboxylation. Several possible rearrangement pathways that facilitate electron detachment from the radical anion are identified and are computed to be energetically accessible. Such

pathways provide an explanation for prior observations of slow secondary electron features in the photoelectron spectra of the same dicarboxylate dianions.

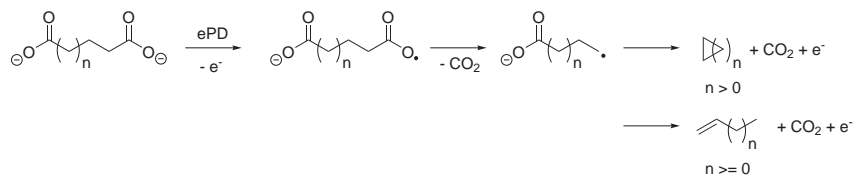
Keywords: Multiply charged anions, electron photodetachment, electrospray ionisation, ion-trap mass spectrometry

1. Introduction

Multiply-charged anions (MCA) are ubiquitous in the condensed phase where solvent and counter-ions serve to stabilise individual charges and minimise repulsive interactions. In the gas phase however, shielding of the repulsive interactions between like-charges is minimised and MCAs are destabilised towards electron detachment or dissociation [1, 2]. As such, many chemists were initially sceptical that gas-phase MCAs could be generated at all and the first reports of the detection of atomic oxygen and halogen dianions by Stuckey and Kiser [3] was warily questioned [4]. While subsequent investigations appeared to confirm this result [5, 6], later studies were unable to find evidence for atomic dianions [7–9]. Experiments soon demonstrated however, that molecular dianions could be generated in the gas phase, paving the way for a series of pioneering studies of this phenomenon. Bowie and Stapleton were the first to generate molecular dianions by secondary electron capture under chemical ionization conditions in a sector mass spectrometer [10]; while Compton and co-workers employed ion-sputtering and anion electron capture to produce fullerene and other carbon-cluster dianions [11–13]. With the advent of electrospray ionisation (ESI) [14] however, the preparation of gas-phase MCAs became almost immediately routine. The contemporary mass spectrometrists will now commonly observe dianions (and even much higher charge states) upon negative ion ESI analysis of biomolecules such as proteins, peptides, oligonucleotides and even some lipids [15–17]; although little thought is usually given to the structure and energetics that underpin the stability of these remarkable ions in the gas phase.

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Scheme 1: Putative fragmentation pathways proposed by Xing *et al.* to account for both high and near-zero kinetic energy electrons observed during photoelectron spectroscopy experiments of aliphatic dicarboxylate dianions [20].

22 Much of what we now understand about the structure and stability of gas-phase MCAs
 23 has arisen from experiments undertaken by Wang and co-workers who successfully coupled
 24 ESI with photoelectron spectroscopy (PES). In a series of elegant studies, a collection of
 25 simple dicarboxylate dianions of the form $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^{2-}$ (where $n = 2 - 8$) were
 26 formed by ESI of aliphatic diacids and subjected to laser photodetachment [18, 19]. The
 27 detection of energetic photoelectrons in these experiments was consistent with the formation
 28 of $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^{\bullet-}$ radical anions - that incorporate a reactive carbonyloxy radical
 29 motif - but the ionic products arising from the irradiation event could not be directly de-
 30 tected or mass-analysed on this apparatus. In their recent photoelectron imaging study
 31 of the same suite of dianions, Wang and co-workers also investigated a second population
 32 of electrons appearing at near-zero kinetic energy [1, 20, 21]. This spectral signature was
 33 assigned to electron autodetachment subsequent to decarboxylation of the nascent carbony-
 34 loxy radical as illustrated in Scheme 1. In essence, two photoelectrons are generated from
 35 one photoexcited dianion, the first with 1 - 3 eV kinetic energy (depending on the length of
 36 the chain) and the second electron with near-zero kinetic energy.

37 The first step in the process, described in Scheme 1, is facile decarboxylation of the
 38 carbonyloxy radical intermediate and is consistent with the behaviour of simple neutral
 39 carbonyloxy radicals that are known to undergo spontaneous decarboxylation [22–25]. Al-
 40 though there is general agreement that carbonyloxy radicals decompose *via* loss of carbon
 41 dioxide, estimates of their lifetimes of these intermediates vary. Results from neutralisation-
 42 reionisation mass spectrometry studies carried out by Schröder *et al.* suggested that the
 43 lifetime of the acetyloxy radical ($\text{CH}_3\text{CO}_2^{\bullet}$) in the gas phase could be as little as 100 ps,

44 while a photoelectron photofragment coincidence investigation by Lu and Continetti in-
45 dicated this species could be stable for microseconds [22]. In solution too, estimates for
46 the lifetimes of RCO_2^\bullet radicals range from 10^{-6} - 10^{-12} seconds depending on the mea-
47 surement techniques and the structure of the R-group [23–25]. Given the potentially wide
48 window of lifetimes for the carbonyloxy radical anions $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^\bullet-$ formed in the
49 PES experiments described above, it is interesting to consider whether unimolecular rear-
50 rangement may compete with the prompt decarboxylation indicated in Scheme 1. Indeed,
51 competition between rearrangement and decarboxylation channels for carbonyloxy radicals
52 was suggested by Schröder following his neutralisation studies of alkyl carboxylate anions
53 [26]. In the context of photodetached dicarboxylate dianions, rearrangement of the nascent
54 carbonyloxy radical anions could lead to a stable (and thus persistent) isomeric form or
55 alternatively present a pathway for direct detachment of the secondary electron. The latter
56 would represent an alternative pathway to that outlined as the second step in Scheme 1,
57 which points to unimolecular rearrangement of the carboxylate alkyl radical being the driver
58 of electron detachment. To the authors’ knowledge however, the structure and stability of
59 such carboxylatoalkyl radical anions has not been investigated and thus the likelihood of
60 such electron detachment reactions is unknown.

61 While PES has provided critical insights into the electronic structure of MCAs, determing
62 the ionic products from photodetachment of simple dianions has received less attention.
63 Ion-trap mass spectrometry coupled with laser photolysis has previously been employed
64 to generate and interrogate the ionic products arising from the photo-excitation of ions
65 [27–31]. In the present study, we have selected two dicarboxylate dianions from the ho-
66 mologues series previously studied by PES [1, 20, 21]. These two dianions, of the form
67 $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^{2-}$ where $n = 3$ and 4, have been generated by ESI of precursor diacids
68 and then isolated in a specially modified linear ion-trap mass spectrometer, where they
69 have been subjected to 266 nm laser irradiation. The results presented herein demonstrate
70 that neither $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^\bullet-$, nor rearranged isomers, are detected following pho-
71 todetachment but rather the major photoproduct pathway results in a loss of ion signal.
72 Product ions arising from spontaneous decarboxylation are detected, but both experiment

73 and electronic structure calculations suggest that they do not undergo electron detachment
74 processes. Electronic structure calculations further elucidate accessible electron detachment
75 pathways directly from the initially formed $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^\bullet-$ radical anion intermedi-
76 ates. These processes can account for the loss of ion signal observed in these experiments as
77 well as provide an explanation for the near-zero kinetic energy electrons previously detected
78 by PES.

79 **2. Experimental**

80 *2.1. Materials*

81 2-Bromovaleric acid, sodium iodide, glutaric and adipic acid were purchased from Sigma-
82 Aldrich (St. Louis, MO). Ajax branded HPLC-grade methanol, acetone and ammonia so-
83 lution (28%) were purchased from Thermo Fisher Scientific (Scoresby, VIC, Australia). 2-
84 Iodovaleric acid was generated from 2-bromovaleric acid by Finkelstein reaction with sodium
85 iodide in acetone [32] and used without further purification.

86 *2.2. Mass Spectrometry*

87 Experiments were performed on a modified Thermo Fisher Scientific LTQ (San Jose, CA)
88 linear quadrupole ion-trap mass spectrometer [33] fitted with a conventional IonMax elec-
89 trospray ionisation source and operating Xcalibur 2.0 SUR1 software. Typical instrumental
90 settings in negative ion mode were: spray voltage: -3.5 kV; capillary temperature: 200 - 250
91 °C); sheath gas flow: 10 - 30 (arbitrary units); sweep and auxillary gas flow: 0 - 10 (arbitrary
92 units). A methanolic solution of the precursor was basified with aqueous ammonia and was
93 infused at 3-5 $\mu\text{L min}^{-1}$ *via* electrospray ionisation to yield $[\text{M} - \text{H}]^-$ and $[\text{M} - 2\text{H}]^{2-}$ ions
94 in the case of diacids. In photodetachment experiments, the $[\text{M} - 2\text{H}]^{2-}$ dianion generated
95 from the diacids was isolated and subjected to a single 266 nm laser pulse timed to coincide
96 with the activation step of the MS cycle. For collision-induced dissociation experiments,
97 ions were mass-selected with a window of 2 - 5 Th, using a q -parameter of 0.250, and the
98 fragmentation energy applied was typically 10 - 45 (arbitrary units) with an excitation time
99 of 30 ms (unless otherwise noted).

100 *2.3. Ion-molecule reactions*

101 The process of measuring ion-molecule reactions in this mass spectrometer has been
102 described in detail previously [34]. Briefly, the atmospheric pressure ionisation source allows
103 adventitious oxygen to diffuse into the ion trap region of the mass spectrometer. Previous
104 studies of the 3-carboxylatoadamantyl + O₂ reaction have established a second-order rate
105 constant for this reaction, which is now used as a calibrant reaction to determine the O₂
106 concentration [34]. The temperature of the vacuum manifold has previously been measured
107 at 307 ± 1 K [34], which is taken as the effective temperature for the ion-molecule reactions
108 measured herein. Reaction times of 0.03 - 10 000 ms are set using the excitation time
109 parameter with the collision energy set at 0 (arbitrary units) within the mass spectrometer
110 control software. Each time point on the kinetic measurement is the average of at least 30
111 scans. Plotting the natural logarithm of the parent ion abundance at each time-point (R_t)
112 relative to its initial concentration (R_0) results in a straight line with slope $-k_1$ (Equation 1).
113 The second-order rate constant is calculated from the pseudo-first order rate constant and
114 the measured concentration of O₂ according to Equation 2. Finally, the reaction efficiency
115 is calculated as described in Equation 3, where k_2 is the second-order rate constant and
116 k_{col} is calculated using Trajectory collision rate theory (this value is the same as both the
117 Langevin and Average Dipole Orientation (ADO) collision rates when the neutral has no
118 dipole moment, such as O₂).

$$\ln \frac{[R]_t}{[R]_0} = -k_1 t + c \quad (1)$$

$$k_2 = \frac{k_1}{[O_2]} \quad (2)$$

$$\phi = \frac{k_2}{k_{col}} \quad (3)$$

119

120 Due to charge-loss channels observed during these experiments, R_0 is taken as the total
121 ion count measured at 30 ms, therefore, the rate constant calculated is not normalised at each

122 time-point and large fluctuations in the parent ion signal may increase the random error.
123 Random errors in these measurements were typically $2\sigma < 10\%$ where σ is the standard
124 deviation obtained from the least-squares fit to the pseudo-first order decay. Systematic
125 errors arise due to ions that form with a m/z less than the low-mass cutoff (15 - 25 Th during
126 isolation of dianions presented herein in low-mass mode and 50 Th in normal-mass range
127 mode). Overall, an upper limit for the absolute uncertainties of 50% has been estimated for
128 the measured rate constants, while random uncertainties in the measurements are typically
129 less than 10%.

130 *2.3.1. Electron Photodetachment*

131 The modification of the linear ion-trap to accommodate introduction of a laser pulse
132 into the ion-trapping region is similar to previous implementations [35, 36], and our specific
133 instrumentation has been described in detail elsewhere [37]. Briefly, a 2.75 in. quartz view-
134 port is attached to the backplate of the spectrometer vacuum housing with a CF flange to
135 allow transmission of 266 nm (fluence = 34 mJ cm^{-2}) laser pulses generated by a flashlamp-
136 pumped Nd:YAG laser (Minilite II, Continuum, Santa Clara, CA). The laser pulse is directed
137 through an aperture in the back lens of the ion-trap assembly and adjusted to optimise the
138 overlap with the ion cloud. The laser flashlamp is triggered by a TTL pulse generated by
139 the mass spectrometer at the beginning of a typical MS^n ion activation step. In these ePD
140 experiments, the activation energy is set to 0 and thus all product ions arise due to excitation
141 by the single laser pulse. Additionally, ePD was confirmed to proceed by a single photon
142 excitation by plotting photoproduct abundance against laser power to yield a straight line
143 (see Supporting Information, Figures S1 and S2). Photodetachment yield was determined
144 by measuring interleaved laser on/off spectra over 500 scans to minimise the effect of ion
145 signal and laser power fluctuations [38]. It should be noted that a marked difference in detec-
146 tion efficiency has been observed between monoanions and dianions, with a significant bias
147 towards the latter, during reaction of dianions with methyl iodide; therefore, comparisons
148 between dianion and monoanion abundances should be made with caution.

149 *2.4. Computational Chemistry*

150 All calculations were undertaken using the hybrid density functional theory M06-2X
151 method and the 6-311++G(d,p) basis set within the GAUSSIAN09 suite of programs [39].
152 All stationary points on the potential energy surface were characterised as either minima (no
153 imaginary frequencies) or transition states (one imaginary frequency) by calculation of the
154 frequencies using analytical gradient procedures. All reported energies include unscaled zero-
155 point energy corrections. Transition states between minima were confirmed by calculation
156 of the intrinsic reaction coordinate (IRC).

157 Vibrational partition functions (Q_{vib}) were calculated using a simple harmonic approxi-
158 mation employing Equations 4 and 5, where q^{ν} is the vibration partition function for each
159 normal mode, $\tilde{\nu}$ is the calculated vibrational frequency of the normal mode, h is the Planck
160 constant, k_B is the Boltzmann constant and T is temperature (298.15 K) [40–43].

$$Q_{vib} = q^{\nu}(0)q^{\nu}(1)\dots q^{\nu}(n) \quad (4)$$

$$q^{\nu} = \frac{1}{1 - e^{\frac{-hc\tilde{\nu}}{k_B T}}} \quad (5)$$

161 **3. Results**

162 *3.1. Photodetachment of the $[M-2H]^{2-}$ dianion of glutaric acid (\mathbf{G}^{2-})*

163 The $[M - 2H]^{2-}$ dianion (\mathbf{G}^{2-}) at m/z 65 formed by ESI of a methanolic solution of
164 glutaric acid was mass-selected in the ion trap. The mass spectrum measured after isolation
165 of this ion for 30 ms is presented in Figure 1(a). Product ions arise at m/z 74, 86 and 131
166 that are assigned as $[\mathbf{G} + \text{H}_2\text{O}]^{2-}$, $[\mathbf{G} - \text{CO}_2]^{\bullet-}$ and $[\mathbf{G} + \text{H}]^{-}$, respectively. The presence
167 of an ion-water cluster at m/z 74 suggests that the $[\mathbf{G} + \text{H}]^{-}$ at m/z 131 arises due to
168 proton transfer from background water, methanol or other proton donors present within the
169 ion-trapping region of the mass spectrometer. Indeed, increasing the isolation time to 5000
170 ms results in a significant increase in the abundance of these ions providing strong evidence
171 that both result from ion-molecule reactions with background neutrals present in the trap
172 (see Supporting Information, Figure S3). The relative abundance of the $[\mathbf{G} - \text{CO}_2]^{\bullet-}$ ion at

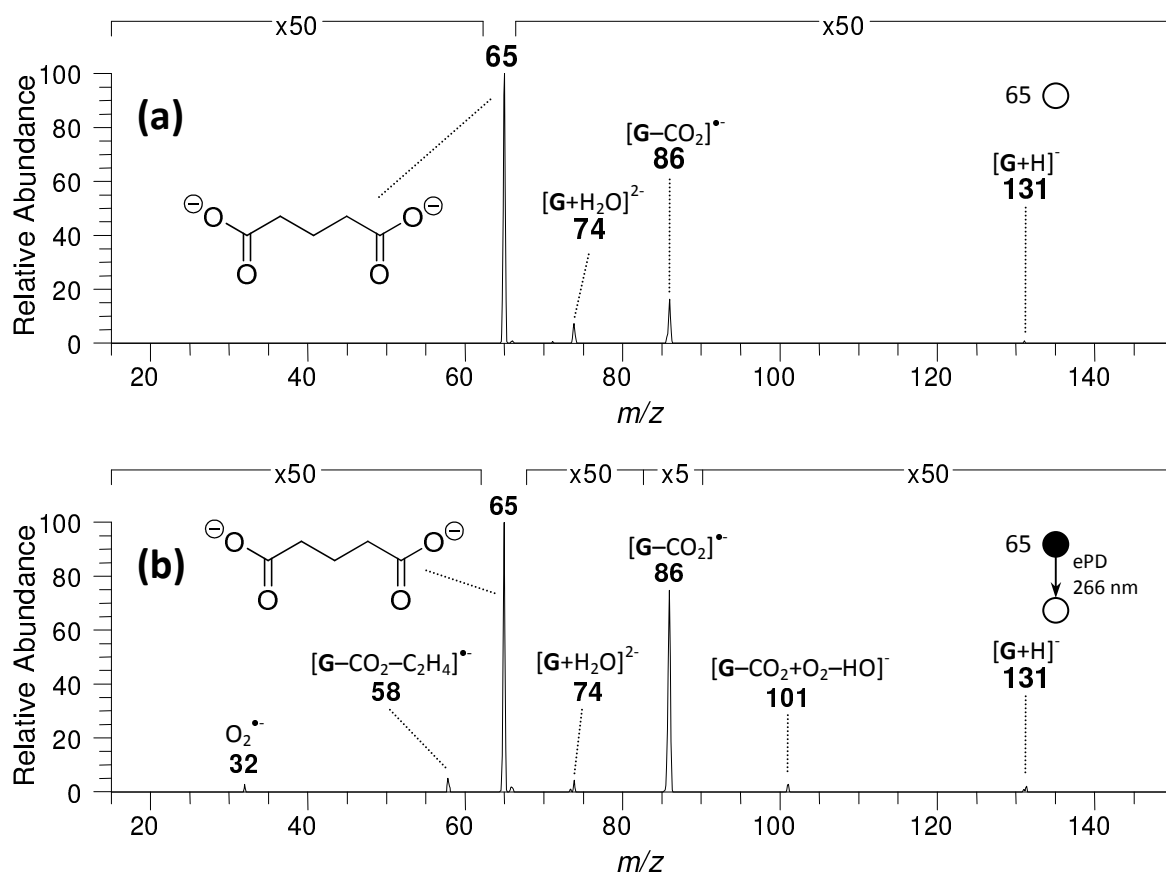


Figure 1: Mass spectrum measured after (a) isolation of the $[M - 2H]^{2-}$ dianion (G^{2-}) at m/z 65 formed by ESI of a methanolic solution of glutaric acid, and (b) 266 nm electron photodetachment (ePD) of the isolated m/z 65 dianion.

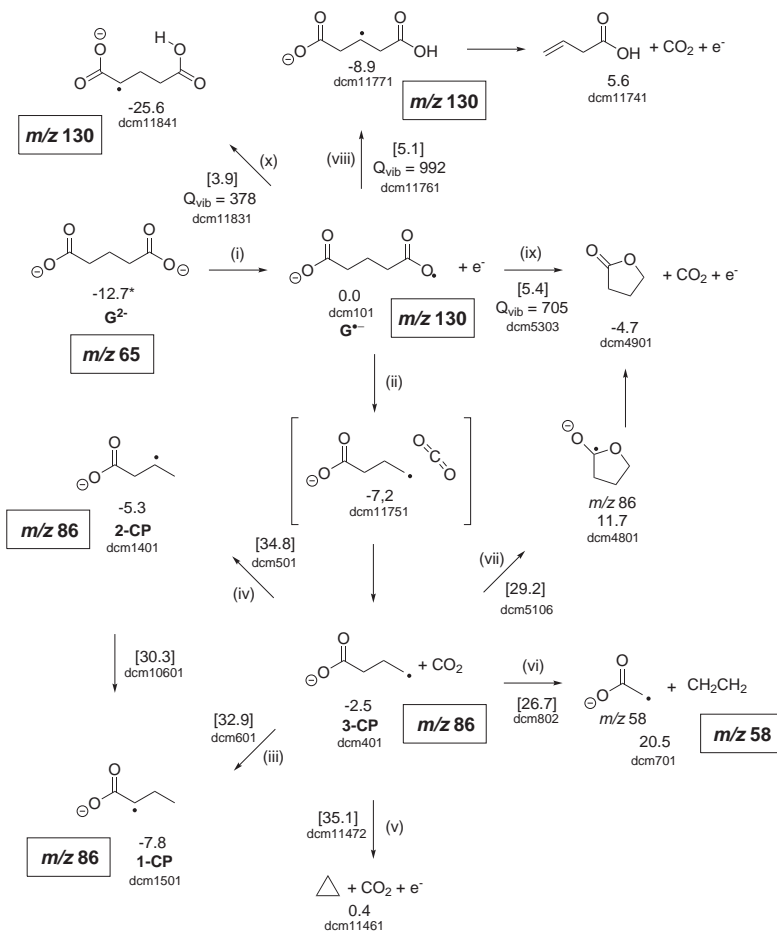
173 m/z 86 may be decreased by increasing the isolation width suggesting this ion arises due
174 to excitation of the precursor ion during the isolation process, resulting in decarboxylation
175 with concomitant electron detachment; a process well-known following CID of dicarboxylate
176 dianions [44, 45].

177 When \mathbf{G}^{2-} is subjected to a single 266 nm laser pulse the total ion count decreases by
178 *ca.* 50%, indicating either a large quantity of photoproducts reside below 15 Th (*i.e.* the
179 low-mass limit of the instrument while isolating m/z 65), or alternatively, detachment of a
180 second electron yields neutral products that cannot be detected by mass spectrometry. The
181 former is unlikely, while the latter is consistent with observation of near-zero kinetic electrons
182 in the PES experiments of Xing *et al.* [20]. We point out here, that the magnitude of the
183 electron loss pathway(s) cannot be quantified due to a significant detection bias towards
184 dianions over monoanions. Despite this limitation, the low recovery of ionic photoproducts
185 overall suggests that secondary electron emission is a major product channel, arising from
186 the initial ePD.

187 The glutarate radical anion ($\mathbf{G}^{\bullet-}$) is not detected at m/z 130 following ePD, consistent
188 with the expected short lifetime of carbonyloxyl radicals (*i.e.* 10^{-6} - 10^{-12} s) [22–24, 26] rel-
189 ative to the timescale for ion detection in our experiments (*ca.* 100 ms). Furthermore, it ex-
190 cludes rearrangement of the carbonyloxyl radical to a stable isomer. This leaves two possible
191 fates for the nascent radical anion: (a) prompt decarboxylation with subsequent secondary
192 electron detachment from an intermediate $[\mathbf{G} - \text{CO}_2]^{\bullet-}$ radical anion, or (b) rearrangement
193 of $\mathbf{G}^{\bullet-}$ itself, resulting in direct electron detachment, perhaps coupled with concerted de-
194 carboxylation. The former rationale can be explored by further examination of Figure 1(b)
195 which reveals a major $[\mathbf{G} - \text{CO}_2]^{\bullet-}$ ion at m/z 86, assigned as 3-carboxylatopropyl radical
196 anion (**3-CP**). While m/z 86 was identified during isolation of the precursor dianion (Figure
197 1a), subjecting \mathbf{G}^{2-} to ePD results in an marked enhancement in the abundance of this ion
198 (Figure 1b). As depicted in Scheme 1, Xing *et al.* previously postulated that near-zero
199 kinetic energy electrons arise after decarboxylation of the nascent carbonyloxyl radical *via*
200 β -scission, hydrogen atom transfer, or cyclisation, all resulting in ejection of $\text{CO}_2 + e^-$ [20].
201 Our ability to isolate this ion population over long timescales (> 1000 ms) suggests the

202 [**G** - CO₂]^{•-} ion is stable with respect to electron detachment and thus, these pathways
203 may not be significantly contributing to ion loss (or secondary electron emission). Never-
204 theless, electronic structure calculations at the M06-2X/6-311++G(d,p) level of theory for
205 the possible rearrangement and decomposition pathways of **3-CP** were undertaken and the
206 results are depicted in Scheme 2. While hydrogen atom transfer channels (iii) and (iv) to
207 form the isomeric radicals **1-CP** and **2-CP**, respectively, are exothermic overall, they have
208 significant barriers that reside at 32.9 and 34.8 kcal mol⁻¹ above **G**^{•-}. 1,3-Cyclisation of
209 **3-CP** to give cyclopropane (v) requires surmounting a higher barrier of 35.1 kcal mol⁻¹.
210 The lowest barriers to rearrangement from **3-CP** are β -scission (vi) at 26.7 kcal mol⁻¹ and
211 γ -lactonisation (vii), with a barrier at 29.2 kcal mol⁻¹ above **G**^{•-}. As postulated, these
212 computational and experimental observations confirm that secondary electron detachment
213 from **3-CP** is unlikely to significantly contribute to the observed loss of ion signal following
214 ePD.

215 These results suggest secondary electron emission may instead be arising directly from the
216 nascent **G**^{•-} radical anion. Two low-energy reaction channels were identified: 1,5-hydrogen
217 atom transfer and γ -lactonisation. The barrier for 1,5-hydrogen atom transfer (viii) resides
218 at only 5.1 kcal mol⁻¹ above **G**^{•-} to form the 1-carboxy-3-carboxylato-2-propyl radical an-
219 ion with a reaction exothermicity of -8.9 kcal mol⁻¹. Significantly, the barrier for direct
220 γ -lactonisation of **G**^{•-} (ix) is competitive with hydrogen atom transfer, residing at only 5.4
221 kcal mol⁻¹, to form γ -butyrolactone + CO₂ + e⁻ with an overall reaction exothermicity of
222 -4.7 kcal mol⁻¹. In both cases, rotation of the carboxylate group must occur prior to reac-
223 tion; however, this rotation is directly coupled with decarboxylation. The intrinsic reaction
224 coordinate calculated for the transition state of 1,5-hydrogen atom transfer (presented in
225 Supporting Information, Figure S7), for example, contains an inflection point where this
226 rotation joins the reaction path. The reactant optimisation minimises to the **3-CP** + CO₂
227 ion-dipole complex at -7.2 kcal mol⁻¹ below **G**^{•-}. These calculations therefore suggest that
228 decarboxylation will directly compete with hydrogen atom transfer. Taken together, exper-
229 imental and theoretical evidence suggests the observed ion signal loss arises due to direct
230 rearrangement of the nascent **G**^{•-} and further, accounts for the near-zero kinetic energy



Scheme 2: Putative fragmentation pathways of the glutarate dianion following electron photodetachment (ePD). Calculated at the M06-2X/6-311++G(d,p) level of theory with unscaled zero-point energy correction. All energies are given in kcal mol⁻¹ and are reported relative to $G^{\bullet-}$. Energies include all neutral fragments along the reaction channel (*i.e.*, the energy of the initial carbon dioxide is included). The codes provided beneath each structure are references to the raw geometry and energy data reported in Supporting Information. *Energy was calculated from the electron binding energy measured by Wang *et al.* [46]

231 electrons reported by Xing *et al.* [20].

232 *3.2. Identification of the $[\mathbf{G} - \text{CO}_2]^\bullet-$ ion formed after ePD of glutarate dianion (\mathbf{G}^{2-}).*

233 The $[\mathbf{G} - \text{CO}_2]^\bullet-$ ion that arises at m/z 86 ion is most certainly a carboxylatopropyl
234 radical anion; however, the location of the unpaired electron may vary depending on whether
235 the **3-CP** initially generated isomerises to either the 1-carboxylatoprop-2-yl (**2-CP**) or 1-
236 carboxylatoprop-1-yl (**1-CP**) radical anion *via* hydrogen atom transfer. As shown in Scheme
237 2, the barrier to hydrogen atom transfer from **3-CP** to the lowest energy **1-CP** isomer (iii)
238 was calculated at 35.4 kcal mol⁻¹ above **3-CP**. The barrier to β -scission (vi) is lower by 6.2
239 kcal mol⁻¹ at 29.2 kcal mol⁻¹ and there is evidence of a small contribution from this channel
240 at m/z 58 in the mass spectrum presented in Figure 1(b). It was therefore prudent to test
241 for isomerisation of the nascent alkyl carboxylate radical anion.

242 Reactions of alkyl radicals with molecular oxygen (O_2) have previously been used as a
243 diagnostic for distonic radical ions [47, 48]. In earlier studies, we have shown that molec-
244 ular oxygen adds to distonic radical anions to generate an $[\text{M} + 32]^-$ ion, assigned as an
245 alkylperoxyl radical, which may degrade to form either an $[\text{M} + 15]^-$ ion assigned as hy-
246 droxyl radical loss to form a ketone or epoxide, or an $[\text{M} - 1]^-$ ion arising due to loss of
247 hydroperoxyl radical from the nascent alkylperoxyl radical [37, 49, 50]. In contrast, for a
248 cross-conjugated α -carboxylate radical anion, reaction with O_2 leads primarily to formation
249 of carbonate radical anion ($\text{CO}_3^\bullet-$) with m/z 60 [37, 49]. In the present experiments, should
250 **3-CP** be formed after decarboxylation of $\mathbf{G}^\bullet-$ and rearrange to the lower energy **1-CP** iso-
251 mer, we would expect its reaction in the presence of O_2 to result in formation of $\text{CO}_3^\bullet-$.
252 Conversely, should **3-CP** thermalise without isomerisation, reaction in the presence of O_2
253 should lead to formation of a mixture of ions that may include $[\text{M} + 32]$, $[\text{M} + 15]$ and $[\text{M}$
254 $- 1]$ at m/z 118, 101 and 85, respectively.

255 We have therefore investigated the reaction of the nascent carboxylatopropyl radical
256 anion with O_2 . Allowing the $[\mathbf{G} - \text{CO}_2]^\bullet-$ ion at m/z 86 to react with O_2 (present in
257 background concentrations) for 4000 ms resulted in the mass spectrum shown in Figure 2.
258 Plotting the natural logarithm of the m/z 86 ion decay against time demonstrated that this

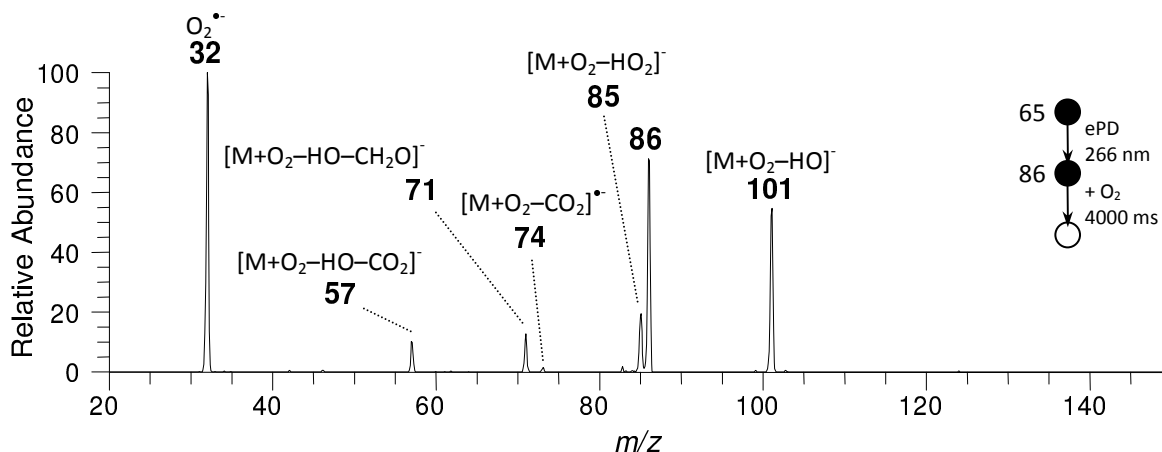
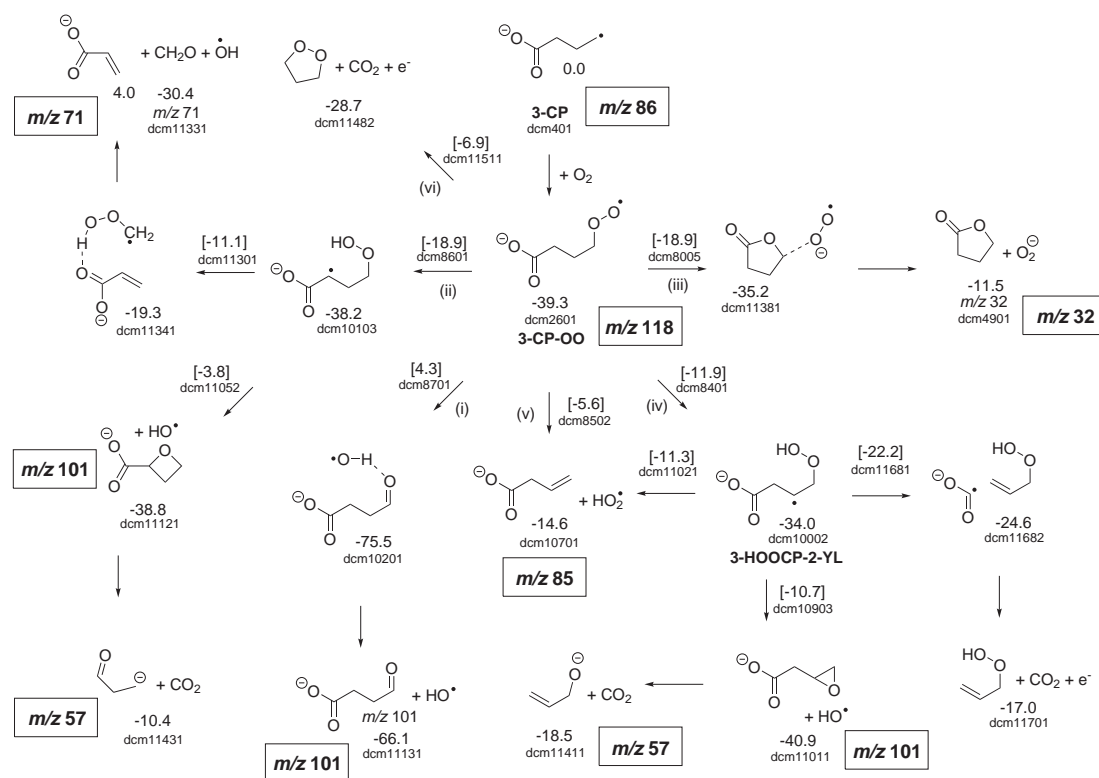


Figure 2: Mass spectrum measured after reaction of the $[\mathbf{G} - \text{CO}_2]^\bullet-$ ion at m/z 86 generated by electron photodetachment (ePD) of the glutarate dianion (\mathbf{G}^{2-} , m/z 65) in the presence of O_2 for 4000 ms.

259 reaction follows pseudo-first order kinetics and suggests there is a single isomer present in
 260 this ion population. Using a calibration reaction to determine the concentration of O_2 (*vide*
 261 *supra*), a second-order rate constant was measured for this reaction at $k_2(\mathbf{R} + \text{O}_2) = 7.1$
 262 $\pm 0.3 \times 10^{-11}$ molecules $^{-1}$ cm 3 s $^{-1}$, which represents a reaction efficiency of 12% ($k_{\text{coll}} =$
 263 6.1×10^{-10} molecules $^{-1}$ cm 3 s $^{-1}$). Interestingly, the total ion count decreases significantly
 264 after reaction of the m/z 86 ion with O_2 . Calculation of the product branching ratios
 265 indicate low-mass ions or product channels that result in electron detachment account for
 266 39% of reaction products. Note that measurement of the ion count is now quantitative as
 267 we are comparing ion abundances of monoanions only. Importantly, an ion of m/z 60, a key
 268 indicator for the presence of the α -carboxylate isomer **1-CP**, is entirely absent suggesting
 269 that this isomerisation has not occurred [37, 49]. Instead the mass spectrum reveals a
 270 dominant ion at m/z 32, assigned as superoxide ($\text{O}_2^\bullet-$). In addition, a range of ions including
 271 $[\mathbf{M} + 15]^-$, $[\mathbf{M} - 1]^-$, $[\mathbf{M} - 12]^-$, $[\mathbf{M} - 15]^-$ and $[\mathbf{M} - 29]^-$ ions arise at m/z 101, 85, 74, 71 and
 272 57, assigned as addition of O_2 to form the nascent peroxy radical with subsequent loss of
 273 HO, HO_2 , CO_2 , HO + CH_2O and HO + CO_2 , respectively. The presence of these ions is
 274 consistent with the ions at m/z 86 being a distonic carboxylatopropyl radical anion. The
 275 absence of **1-CP** suggests that **2-CP** is similarly not formed, as the barrier for this 1,3-
 276 hydrogen atom transfer is higher still than the 1,4-hydrogen atom transfer to form **1-CB**



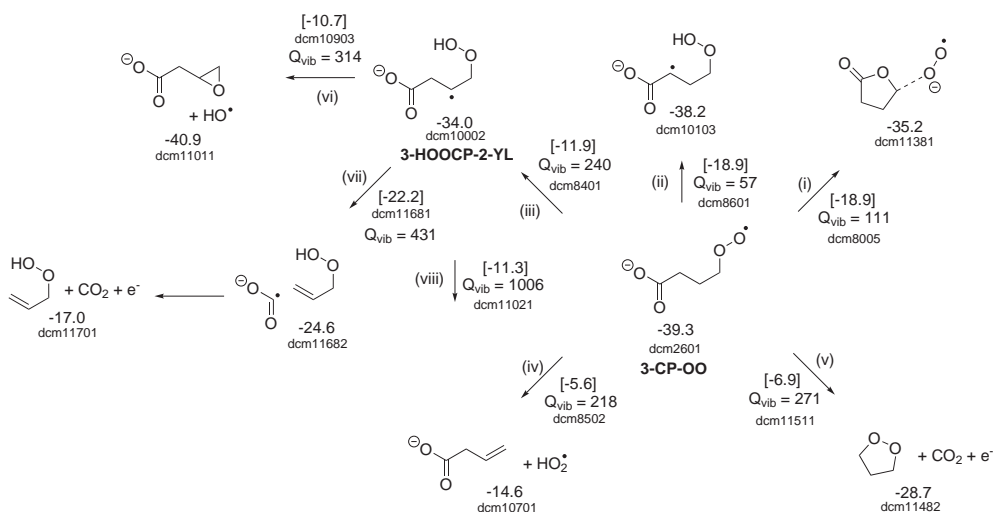
Scheme 3: Potential reaction pathways of the 3-carboxylpropyl radical anion + O₂ reaction. Calculated at the M06-2X/6-311++G(d,p) level. Energies are reported in kcal mol⁻¹ and include unscaled zero-point energy corrections. The codes provided beneath each structure are references to the raw geometry and energy data reported in Supporting Information.

277 (Scheme 2). Taken together, these data suggest the only isomer present in the *m/z* 86 [**G** -
 278 CO₂]^{•-} ion population is **3-CP**.

279 Electronic structure calculations of putative reaction channels at the M06-2X/6-311++G(d,p)
 280 level of theory reveal all reaction products arising from the **3-CP** + O₂ reaction are ener-
 281 getically accessible (Scheme 3). Addition of O₂ results in the 3-carboxylatopropylperoxyl
 282 radical anion (**3-CP-OO**) with a reaction exothermicity of -39.3 kcal mol⁻¹. The abundance
 283 of potential reaction channels accessible to the nascent peroxy radical provides a clear ex-
 284 planation for the absence of an [M + O₂]^{•-} ion at *m/z* 118 in Figure 2. 1,4-Hydrogen atom
 285 transfer to generate 3-carboxypropanone + HO• (i) is unlikely to occur due to a barrier that
 286 resides 4 kcal mol⁻¹ above the energy of the reactants. The lowest energy pathways are 1,6-
 287 hydrogen atom transfer (ii) and γ -lactonisation (iii) with isoenergetic transition states -18.9

288 kcal mol⁻¹ below the entrance channel. 1,6-hydrogen atom transfer (ii) results in forma-
289 tion of the 1-carboxylato-1-hydroperoxyl-3-propyl radical anion, exothermic overall by 38.2
290 kcal mol⁻¹. This intermediate may either eject HO through a barrier of 34.4 kcal mol⁻¹ to
291 form 1-carboxylato-1,3-epoxypropane residing -38.8 kcal mol⁻¹ below the entrance channel,
292 or proceed *via* β -scission with a barrier of 27.1 kcal mol⁻¹ to form an ion-dipole complex
293 between propenoate anion and the hydroperoxylmethyl radical 19.3 kcal mol⁻¹ below the
294 reactants. While no transition state was calculated, it is assumed this ion-dipole complex
295 may eject CH₂O, then HO to generate propenoate anion with an overall reaction exother-
296 micity of -30.4 kcal mol⁻¹, accounting for the ion that arises at m/z 71 in Figure 2. The
297 loose barrier to β -scission is both lower in energy and entropically favoured with respect to
298 the tight barrier to epoxidation, therefore, one would not expect the epoxidation channel to
299 contribute significantly to the population of m/z 101 ions, or after decarboxylation, the ions
300 of m/z 57. In comparison, γ -lactonisation (iii) results in formation of an ion-dipole complex
301 35.2 kcal mol⁻¹ below the entrance channel; γ -butyrolactone and O₂^{•-} are held together by
302 23.7 kcal mol⁻¹ and when separated form the individual products with an overall reaction
303 exothermicity of -11.5 kcal mol⁻¹, accounting for facile formation of O₂^{•-} at m/z 32.

304 Two pathways may proceed *via* 1,5-hydrogen atom transfer; concerted 1,5-hydrogen atom
305 transfer and HO₂ ejection requires 33.7 kcal mol⁻¹ to form propenoate anion + HO₂ at -14.6
306 kcal mol⁻¹ below the energy of the reactants, while 1,5-hydrogen atom transfer to form the 1-
307 carboxylato-3-hydroperoxyl-2-propyl radical anion (**3-HOOC-2-YL**) has a barrier of 27.4
308 kcal mol⁻¹ and overall reaction exothermicity of -28.6 kcal mol⁻¹. The latter may either eject
309 HO₂ through a barrier of 17.3 kcal mol⁻¹, or release HO, which requires 17.9 kcal mol⁻¹ to
310 form 1-carboxylato-2-epoxypropane + HO with a reaction exothermicity of -40.9 kcal mol⁻¹.
311 The former accounts for the ion signal at m/z 85, while the latter the ions at m/z 101.
312 Decarboxylation of the 1,2-epoxide results in formation of prop-2-en-1-olate anion residing
313 -18.5 kcal mol⁻¹ below the entrance channel to account for the ion of m/z 57. Alternatively,
314 the intermediate may undergo β -scission with a barrier residing at -22 kcal mol⁻¹ to form an
315 ion-dipole complex at -24.8 kcal mol⁻¹ that may release 3-hydroperoxypropene + CO₂ + e⁻
316 with a reaction exothermicity of -17.0 kcal mol⁻¹. Significantly, this reaction channel results



Scheme 4: Potential reaction pathways of the 3-carboxylatopropylperoxyl radical anion with estimated vibrational partition functions (Q_{vib}). Calculated at the M06-2X/6-311++G(d,p) level. Energies include unscaled zero-point energy corrections. The codes provided beneath each structure are references to the raw geometry and energy data reported in Supporting Information.

317 in neutral products not detected by mass spectrometry. Similarly, the nascent **3-CP-OO**
 318 radical anion may cyclise to form a cyclic peroxide (v). The barrier to 1,5-cyclisation of
 319 **3-CP-OO** (v) was calculated to reside at $-6.9 \text{ kcal mol}^{-1}$ with respect to the reactants to
 320 form 1,2-dioxolane + $\text{CO}_2 + \text{e}^-$ with an overall exothermicity of $-28.7 \text{ kcal mol}^{-1}$ below the
 321 reactants again leading to neutral products that could not be detected.

322 When multiple reaction channels are accessible during radical reactions, estimating the
 323 vibrational partition functions (Q_{vib}) of key transition states can be informative, where a
 324 larger value indicates a greater density of states with which to accommodate transmission
 325 through the barrier [40–42]. While the barriers to γ -lactonisation (i) and 1,6-hydrogen atom
 326 transfer (ii) are isoenergetic, the 5-membered ring transition state for γ -lactonisation is
 327 the entropically favoured pathway, as indicated by the larger Q_{vib} for this transition state
 328 (depicted in Scheme 4) and demonstrated by the dominant $\text{O}_2^{\bullet-}$ ion at m/z 32 in Figure 2.
 329 Both 1,5-hydrogen atom transfer (iii) and concerted 1,5-hydrogen atom transfer and HO_2
 330 ejection (iv) have even higher Q_{vib} values. As these transition states are also energetically
 331 accessible, they compete with (i) and (ii); 1,5-hydrogen atom transfer reaction pathways

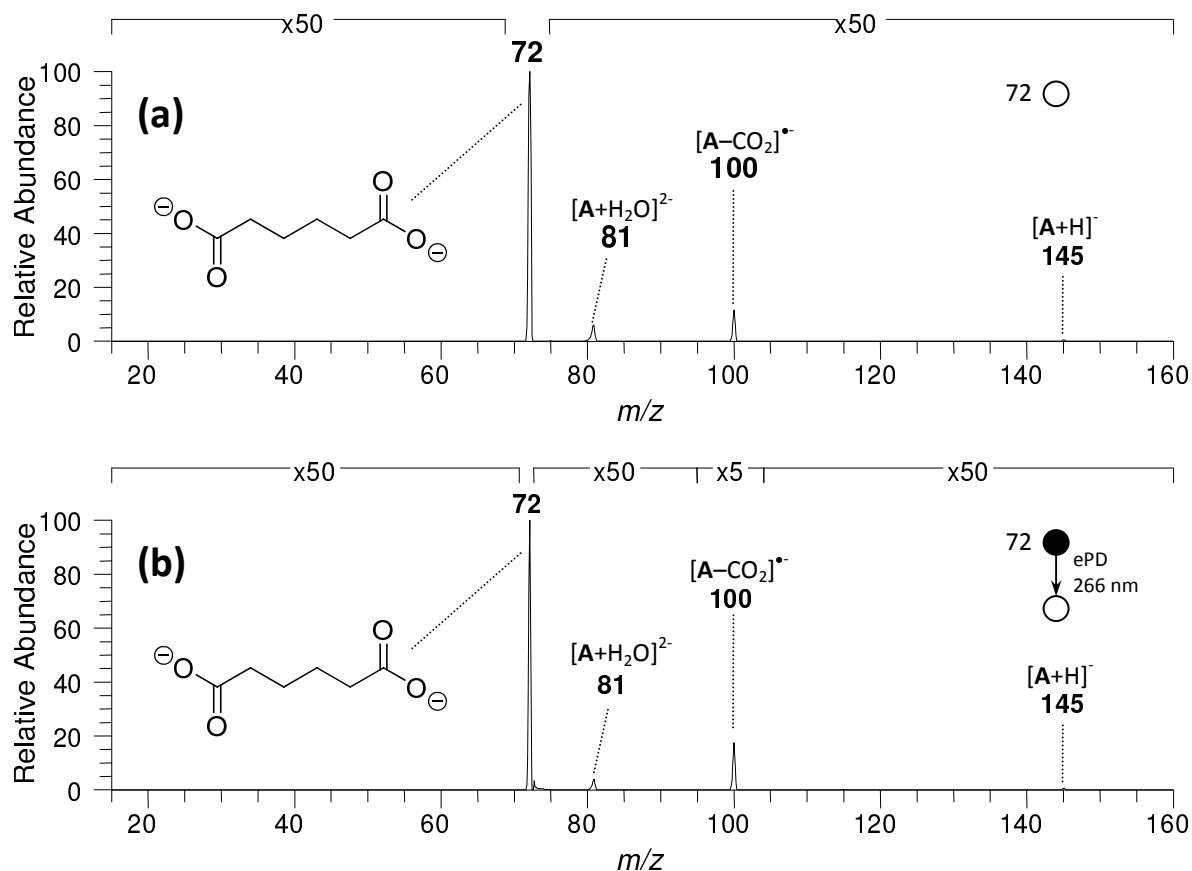


Figure 3: Mass spectrum measured after (a) isolation of the $[M - 2H]^{2-}$ dianion (A^{2-}) at m/z 72 formed by ESI of a methanolic solution of adipic acid, and (b) 266 nm electron photodetachment (ePD) of the isolated dianion (m/z 72).

332 (iii) and (iv) are favoured entropically leading to the high abundance of $[M + O_2 - HO]^-$
 333 and $[M + O_2 - HO_2]^-$ at m/z 101 and 85, respectively, in the mass spectrum depicted
 334 in Figure 2. The combination of two energetically and entropically favourable reaction
 335 channels: 1,5-cyclisation to form 1,2-dioxolane + $CO_2 + e^-$; and 1,5-hydrogen atom transfer
 336 and β -scission to form 1-hydroperoxyl-2-propene + $CO_2 + e^-$, provides a clear rationale for
 337 the 39% depletion in the m/z 86 ion population not accounted for in the mass spectrum.

338 3.3. Photodetachment of the $[M - 2H]^{2-}$ dianion of adipic acid (A^{2-})

339 The $[M - 2H]^{2-}$ adipate dianion (A^{2-}) at m/z 72 was generated by ESI of a methanolic
 340 solution of adipic acid. Isolation of the m/z 72 dianion resulted in low abundance $[A +$
 341 $H_2O]^{2-}$ and $[A + H]^-$ ions at m/z 81 and 145, respectively (shown in Figure 3a). As

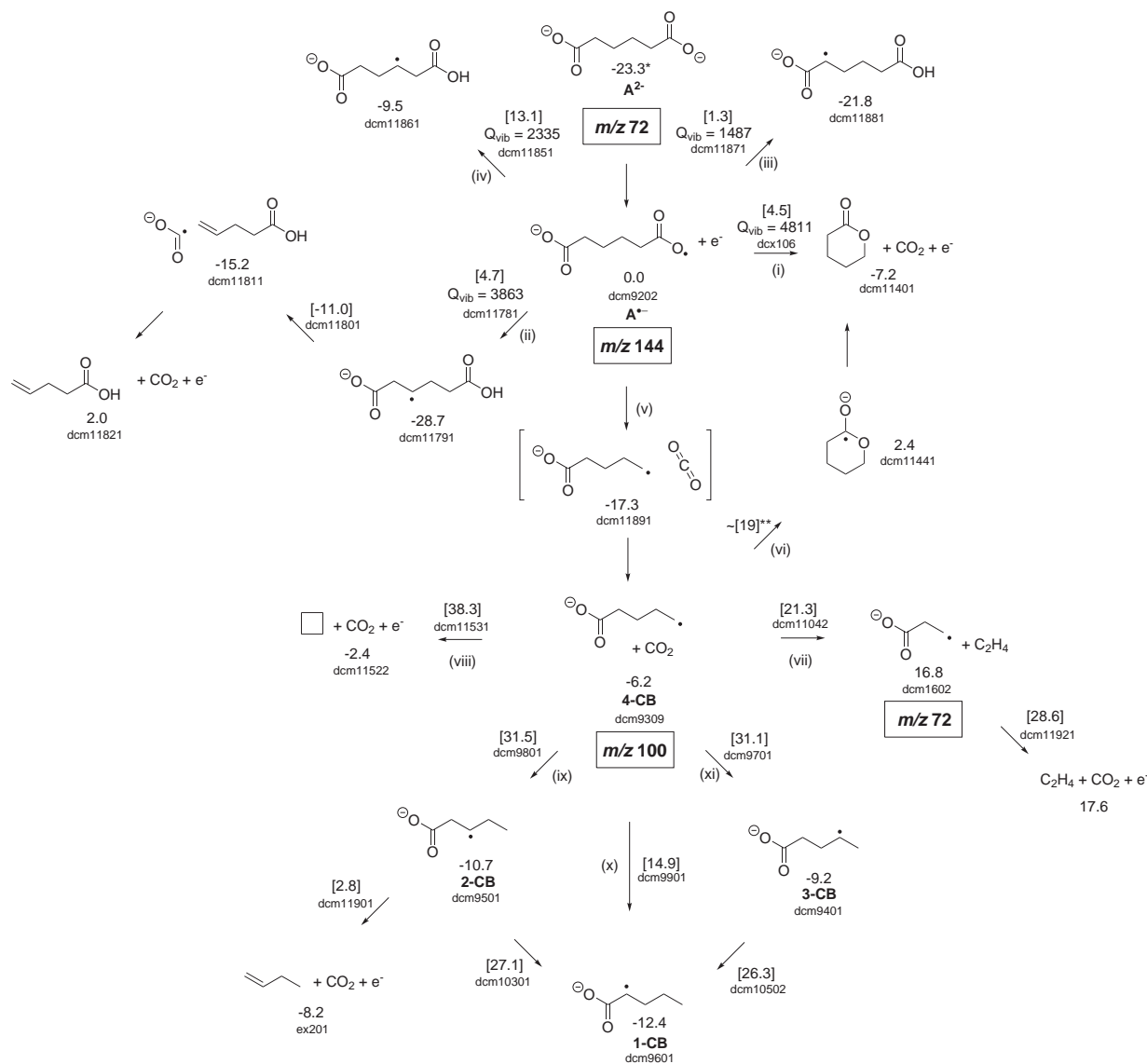
342 observed during isolation of the glutarate dianion, the $[\mathbf{A} + \text{H}]^-$ ion increases in abundance
343 with longer isolation times, suggesting this ion arises due to proton transfer from either
344 water, methanol or other proton donor present in the ion-trap (see Supporting Information,
345 Figure S4). Subjecting isolated \mathbf{A}^{2-} at m/z 72 to 266 nm ePD resulted in a significant
346 enhancement in the yield of the $[\mathbf{A} - \text{CO}_2]^{\bullet-}$ ion at m/z 100. There were no other ions
347 of notable abundance identified in the ePD mass spectrum. Importantly, an m/z 144 ion
348 corresponding to the adipate radical anion $\mathbf{A}^{\bullet-}$ was not observed, demonstrating the nascent
349 carbonyloxyl radical generated after ePD is not stable on a millisecond timescale, nor are
350 any stable isomers formed. The total ion count measured after ePD of the \mathbf{A}^{2-} at m/z 72
351 decreases by *ca.* 50%, as observed for \mathbf{G}^{2-} , suggesting secondary electron detachment, or
352 generation of ions that reside below 25 Th (*i.e.* the low-mass cutoff at m/z 72). This is
353 again consistent with the PES experiments of Xing *et al.* where near-zero kinetic electrons
354 were observed after ePD of \mathbf{A}^{2-} .

355 Electronic structure calculations of the putative reaction pathways leading to secondary
356 electron loss channels after initial ePD of the \mathbf{A}^{2-} were performed and the results are de-
357 scribed in Scheme 5. δ -Lactonisation of the nascent $\mathbf{A}^{\bullet-}$ carbonyloxyl radical (i) is the
358 lowest energy electron loss channel, with a barrier of only 4.5 kcal mol⁻¹ and an overall
359 exothermicity of -7.2 kcal mol⁻¹. 1,6-Hydrogen atom transfer (ii) proceeds over a barrier
360 at 4.7 kcal mol⁻¹ to form 1-carboxylato-4-carboxybut-2-yl radical anion with a reaction
361 exothermicity of -28.7 kcal mol⁻¹. The barrier to subsequent β -scission resides at -11.0
362 kcal mol⁻¹ yielding an ion-dipole complex at -15.2 kcal mol⁻¹ below $\mathbf{A}^{\bullet-}$ and held together
363 by 17.2 kcal mol⁻¹ that releases 1-carboxybutene + CO₂ + e⁻ with an overall reaction en-
364 dothermicity of 2.0 kcal mol⁻¹. Decarboxylation of the nascent carbonyloxyl radical (v) to
365 form 4-carboxylatobutyl radical anion (**4-CB**) is exothermic overall, with the products re-
366 siding -6.2 kcal mol⁻¹ below the precursor. In this case, electron detachment may arise after
367 δ -lactonisation (vi), β -scission reactions (vii), 1,4-cyclisation (viii), or 1,4-hydrogen atom
368 transfer (ix). No transition state was calculated for the lactonisation channel (vi); however,
369 a relaxed scan places the barrier *ca.* 19 kcal mol⁻¹ above $\mathbf{A}^{\bullet-}$ to form an intermediate
370 δ -valerolactone radical anion at 2.4 kcal mol⁻¹ that promptly emits an electron to form the

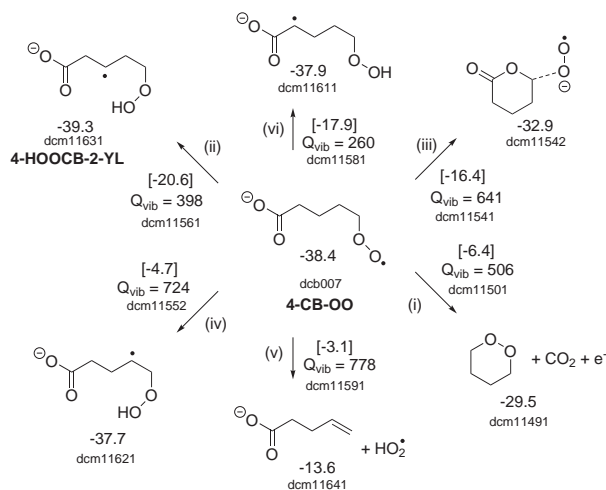
371 neutral lactone with an overall reaction exothermicity of $-7.2 \text{ kcal mol}^{-1}$. 1,4-Cyclisation
372 (viii) and 1,4-hydrogen atom transfer (ix) have high barriers residing at $38.3 \text{ kcal mol}^{-1}$ and
373 $31.5 \text{ kcal mol}^{-1}$, respectively. 1,4-Cyclisation results in formation of cyclobutane + $\text{CO}_2 + \text{e}^-$
374 with an overall reaction exothermicity of $-2.4 \text{ kcal mol}^{-1}$, while 1,4-hydrogen atom transfer
375 results in generation of 2-carboxylatobutyl radical anion (**2-CB**) at $-10.7 \text{ kcal mol}^{-1}$. The
376 barrier to subsequent β -scission of **2-CB** resides at $2.8 \text{ kcal mol}^{-1}$ to generate 1-butene +
377 $\text{CO}_2 + \text{e}^-$ with a reaction exothermicity of $-8.2 \text{ kcal mol}^{-1}$. Alternatively, **4-CB** may undergo
378 β -scission directly with a barrier at $21.3 \text{ kcal mol}^{-1}$ to form 2-carboxylatoethyl radical an-
379 ion + C_2H_4 with a reaction endothermicity of $16.8 \text{ kcal mol}^{-1}$. The barrier to β -scission of
380 2-carboxylatoethyl radical anion resides at $28.6 \text{ kcal mol}^{-1}$ to form $\text{C}_2\text{H}_4 + \text{CO}_2 + \text{e}^-$ with an
381 overall reaction endothermicity of 17.6 kcal mol . Each of these reaction pathways, however,
382 contain barriers significantly higher than either direct δ -lactonisation (i) or 1,6-hydrogen
383 atom transfer (ii) of **A \bullet^-** providing strong evidence to suggest electron detachment arises
384 from direct rearrangement of the nascent **A \bullet^-** radical anion and not *after* decarboxylation.

385 Notably, 1,5-hydrogen atom transfer of **4-CB** to form the α -carboxylate isomer, 1-
386 carboxylatobutyl radical anion (**1-CB**), was calculated to require only $14.9 \text{ kcal mol}^{-1}$ ad-
387 ditional energy corresponding to a barrier of $21.1 \text{ kcal mol}^{-1}$ with respect to **4-CB**. This is
388 substantially less energy than the $35.4 \text{ kcal mol}^{-1}$ predicted for the analogous 1,4-hydrogen
389 atom transfer of **3-CP** to form **1-CP**. Furthermore, this barrier is 9.8 and $10.8 \text{ kcal mol}^{-1}$
390 lower than both 1,3- and 1,4-hydrogen atom transfer resulting in the 2-carboxylatobutyl
391 (**2-CB**) and 3-carboxylatobutyl (**3-CB**) radical anions, respectively. It was not possible to
392 distinguish between the dianion and the β -scission product 2-carboxylatoethyl radical anion,
393 as the parent and product are isobaric; however, the barrier for this process is $6.4 \text{ kcal mol}^{-1}$
394 higher than 1,5-hydrogen atom transfer.

395 In order to test for isomerisation of the nascent **4-CB** to **1-CB**, the m/z 100 ion was
396 isolated in the presence of background O_2 and the resulting mass spectrum is shown in Figure
397 5(a). The natural logarithm of the m/z 100 ion decay plotted against isolation time was
398 non-linear, suggesting that there are multiple isomers with different rate constants present
399 in the ion population. Furthermore, the total ion count decreased by 82% after isolating



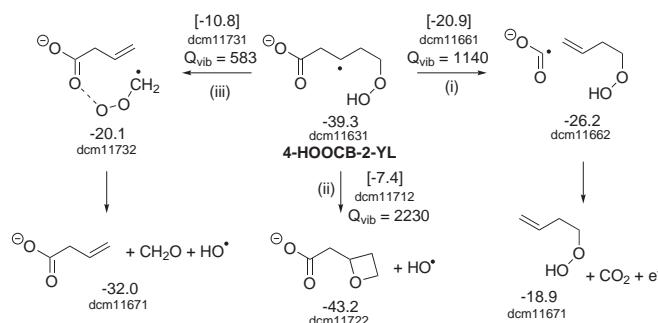
Scheme 5: Potential fragmentation pathways of the adipate dianion. Energies were calculated at the M06-2X/6-311++G(d,p) level and include unscaled zero-point energy corrections. Energies are reported relative to $\text{A}^{\bullet-}$ and include all neutral fragments along the reaction channel (*i.e.*, the energy of the initial carbon dioxide is included). The codes provided beneath each structure are references to the raw geometry and energy data reported in Supporting Information. * Energy was calculated from the electron binding energy measured by Wang *et al.* [46]. ** Energy estimated from a relaxed potential energy scan (see Supporting Information, Figure S8) and does not include zero-point energy correction.



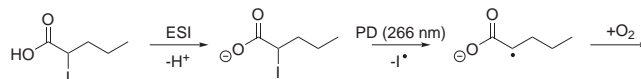
Scheme 6: Potential reaction pathways of the 4-carboxylatobutylperoxy radical anion with estimated vibrational partition functions (Q_{vib}). Calculated at the M06-2X/6-311++G(d,p) level. Energies are provided relative to the 4-carboxylatobutyl radical anion (**4-CB**) + O₂ entrance channel and include unscaled zero-point energy corrections. The codes provided beneath each structure are references to the raw geometry and energy data reported in Supporting Information.

400 the m/z 100 ion in the presence of O₂ for 5000 ms, suggesting a significant proportion of
 401 product ions reside below the low-mass cutoff (50 Th in these experiments) or are accessing
 402 product channels that involve electron detachment. Dominant ions arose at m/z 60, 99 and
 403 115, assigned as CO₃^{•-}, [M + O₂ - HO₂]⁻ and [M + O₂ - HO]⁻ ions, respectively. The
 404 presence of CO₃^{•-} at m/z 60 demonstrates that some proportion of the ion population at
 405 m/z 100 has rearranged to the more energetically stable α -carboxylate isomer **1-CB**. [M -
 406 13]⁻, [M-15]⁻, [M-27]⁻, [M - 29]⁻ ions arise at m/z 87, 85, 73 and 71 and were assigned as
 407 addition of O₂ followed by subsequent ejection of HO + CO, HO + CH₂O, HO + C₂H₂O and
 408 HO + CO₂, respectively. The observation of [M + O₂ - HO₂]⁻, [M + O₂ - HO]⁻, in addition
 409 to the ions just identified, suggests a significant quantity of distonic carboxylatobutyl radical
 410 anion(s) (**2-CB**, **3-CB** or **4-CB**) remain in the m/z 100 precursor ion population.

411 To investigate whether the additional products may be formed from **1-CB**, an indepen-
 412 dent synthesis of this isomer was developed. As described in Scheme 8, 2-iodovalerate anion
 413 was subjected to photodissociation (266 nm) to yield **1-CB** at m/z 100 (Figure 4). Isolation
 414 of **1-CB** in the presence of O₂ resulted in the spectrum depicted in Figure 5(b). The major



Scheme 7: Potential fragmentation pathways of the 1-carboxylato-4-hydroperoxylbut-2-yl radical anion with estimated vibrational partition functions (Q_{vib}). Energies were calculated at the M06-2X/6-311++G(d,p) level and include unscaled zero-point energy corrections. The codes provided beneath each structure are references to the raw geometry and energy data reported in Supporting Information.



Scheme 8: Reaction scheme for generation of authentic 1-carboxylatobutyl radical anion by photodissociation of 2-iodovalerate anion generated by ESI of 2-iodovaleric acid.

415 ion in this spectrum arises at m/z 60, assigned as $\text{CO}_3^{\bullet-}$, consistent with previous reports of
 416 α -carboxylate reactivity towards O_2 [37]. Interestingly, the total ion count did not decrease
 417 over increasing isolation time indicating that no electron loss channels arise during reaction
 418 of **1-CB** with O_2 . An $[\text{M} - 1]^-$ ion is featured at m/z 99; however, this ion is present during
 419 the initial isolation of the m/z 100 ion (*i.e.* isolation time of 0.03 ms), which requires a large
 420 isolation width and furthermore, does not increase in abundance over increased trapping
 421 time. Therefore, the m/z 99 ion is assigned as arising due to loss of HI from the parent
 422 2-iodovalerate ion and not due to reaction of **1-CB** with O_2 . As such, the only ion arising
 423 from reaction with O_2 is $\text{CO}_3^{\bullet-}$ at m/z 60.

424 To account for the significant decrease in total ion count after reaction of **4-CB** with
 425 O_2 , we allowed the product ions generated after ePD of A^{2-} (m/z 72) to react with O_2 ,
 426 without secondary isolation of the carboxylatobutyl radical anion (m/z 100) photoproduct.
 427 This allows us to decrease the low-mass cutoff to 25 Th. After subtracting the spectrum
 428 measured when the dianion is isolated without ePD (presented in Supporting Information,
 429 Figure S4 and S5), $\text{O}_2^{\bullet-}$ at m/z 32 ion was observed with an abundance only 10% lower

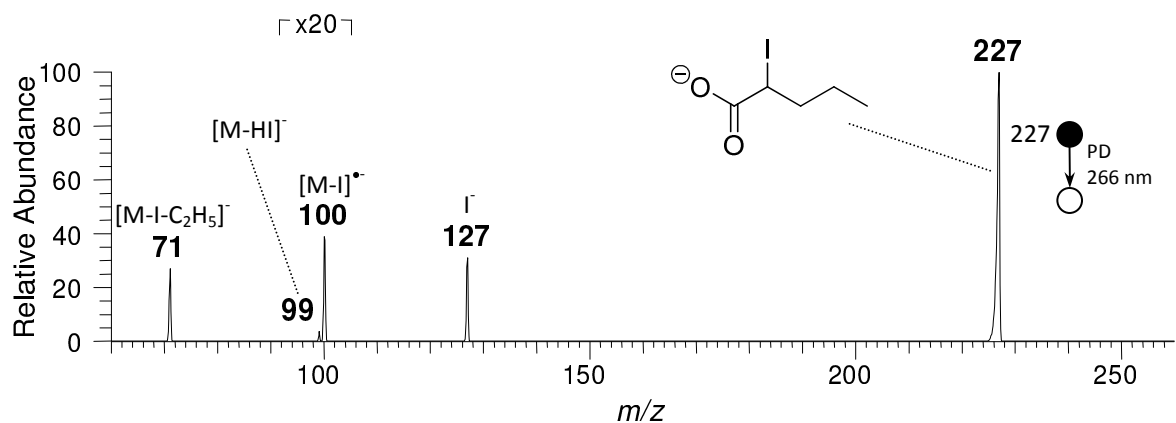


Figure 4: Mass spectrum measured after 266 nm photodissociation of 2-iodovalerate (m/z 227)

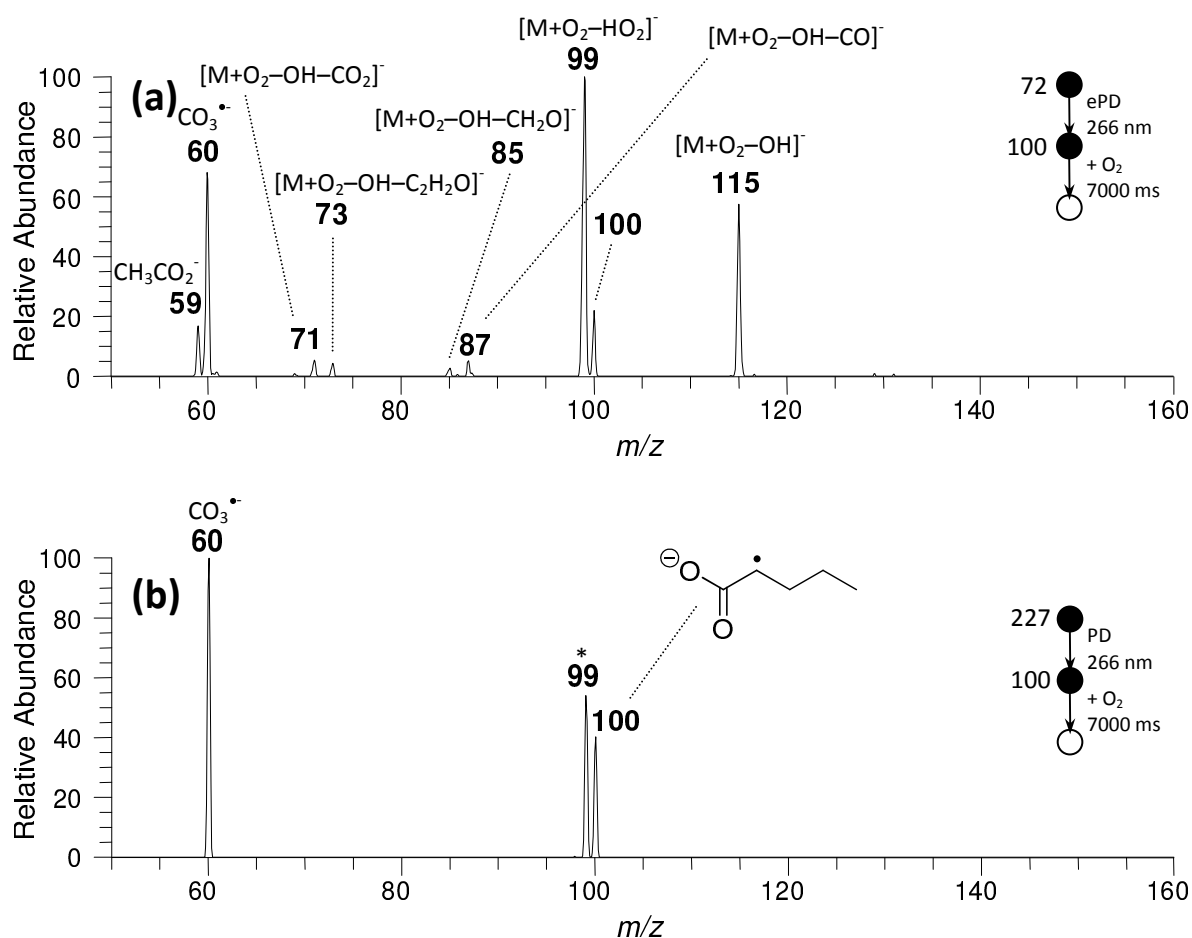


Figure 5: Mass spectrum measured after reaction of the (a) $[A - CO_2]^{•-}$ ion at m/z 100 generated after ePD of the adipate dianion (A^{2-} , m/z 72), and (b) genuine 1-carboxylatobutyl radical anion (m/z 100) generated by PD of 2-iodovaleric acid with O_2 for 7000 ms. * This ion arises due to loss of HI from the precursor 2-iodovalerate and not due to reaction of the 1-carboxylatobutyl radical anion (m/z 100) with O_2 .

430 than $\text{CO}_3^{\bullet-}$ at m/z 60. However, this ion accounts for only 2% of the lost total ion count
431 and there is therefore still an 80% loss of the precursor ion signal that cannot be accounted
432 for by detectable product ions.

433 Analogous to the pathways described for **3-CP-OO**, we have calculated two alterna-
434 tive channels that result in electron loss during rearrangement of **4-CB-OO** (Scheme 6):
435 cyclisation to form a cyclic peroxide (i) and 1,6-hydrogen atom transfer with concomitant
436 β -scission (ii). The 1,6-cyclisation pathway (i) requires $32.0 \text{ kcal mol}^{-1}$ to form 1,2-dioxane
437 + $\text{CO}_2 + e^-$ with the products residing $-29.5 \text{ kcal mol}^{-1}$ below the entrance channel. Analysis
438 of the vibrational partition functions (Q_{vib}) however, suggests that this channel is entropi-
439 cally disfavoured over δ -lactonisation (iii) or 1,5-hydrogen atom transfer (iv and v) and its
440 barrier is significantly higher than both 1,6- and 1,7-hydrogen atom transfers (pathways ii
441 and vi, respectively). 1,6-Hydrogen atom transfer (ii) is the lowest energy reaction channel
442 with a barrier at $-20.6 \text{ kcal mol}^{-1}$ resulting in formation of 4-hydroperoxyl-1-carboxylato-
443 2-butyl radical anion (**4-HOOCB-2-YL**) with an exothermicity of $-39.3 \text{ kcal mol}^{-1}$. As
444 described in Scheme 7, the lowest energy reaction pathway subsequent to formation of **4-**
445 **HOOCB-2-YL** is β -scission to generate 3-hydroperoxylbutene + $\text{CO}_2 + e^-$, which proceeds
446 over a barrier residing at $-20.9 \text{ kcal mol}^{-1}$ to form an ion-dipole complex at $-26.2 \text{ kcal mol}^{-1}$
447 releasing the products with a reaction exothermicity of $-18.9 \text{ kcal mol}^{-1}$. Overall, these
448 calculations suggest 1,6-hydrogen atom transfer with concomitant β -scission to generate 3-
449 hydroperoxylbutene is the most favourable electron detachment pathway accessible from
450 reaction of **4-CB** with O_2 .

451 4. Discussion

452 We have generated two short-chain aliphatic dicarboxylate dianions, glutarate (\mathbf{G}^{2-}) and
453 adipate (\mathbf{A}^{2-}) dianion, and subjected both to 266 nm laser ePD in an ion-trap mass spec-
454 trometer. A significant abundance of the total ion count was lost in each case, indicating
455 product branching includes electron loss channels to form neutral molecules or generation
456 of product ions residing below the low-mass cutoff that are not detected by mass spectrom-
457 etry. It is unlikely that we have generated ions lower than the low-mass cutoff; therefore, we

458 expect that the total ion count loss is predominantly due to secondary electron detachment
459 consistent with the PES measurements of Xing *et al.* [20]. An energetically competitive
460 lactonisation pathway was calculated for both the glutarate ($\mathbf{G}^{\bullet-}$) and adipate ($\mathbf{A}^{\bullet-}$) rad-
461 ical anions with barriers of only 5.4 kcal mol⁻¹ and 4.5 kcal mol⁻¹ (Schemes 2ix and 5i),
462 respectively. The nascent $\mathbf{G}^{\bullet-}$ and $\mathbf{A}^{\bullet-}$ radical anions may also undergo hydrogen atom
463 transfers with similar barriers of only 5.1 kcal mol⁻¹ and 4.7 kcal mol⁻¹, respectively, to form
464 intermediates that release CO₂ + e⁻ after β -scission (Schemes 2viii and 5ii). Interestingly,
465 the intrinsic reaction coordinates calculated for both lactonisation and hydrogen transfer
466 transition states suggest decarboxylation directly intersects these reaction pathways (see
467 Supporting Information, Figure S7). Furthermore, the two respective 1,6- and 1,7-hydrogen
468 atom transfers for $\mathbf{G}^{\bullet-}$ and $\mathbf{A}^{\bullet-}$ that result in stable cross-conjugated α -carboxylate rad-
469 ical anions (Schemes 2x and 5iii for $\mathbf{G}^{\bullet-}$ and $\mathbf{A}^{\bullet-}$, respectively) are the least entropically
470 favoured pathways predicted by their relative Q_{vib} values. This explains why we may not see
471 stable [M - 2H]^{•-} ions at m/z 130 or m/z 144 arising from rearrangement to stable isomers.
472 In contrast, should $\mathbf{G}^{\bullet-}$ and $\mathbf{A}^{\bullet-}$ promptly decarboxylate after ePD, β -scission, cyclisation
473 and hydrogen atom transfer driven electron detachment pathways require significantly more
474 energy (Schemes 2 and 5). Our ability to isolate the [M - 2H - CO₂]^{•-} radical anion gener-
475 ated in each case for a number of seconds provides strong evidence that these radical anions
476 are stable with respect to electron detachment. Taken together, these experimental and
477 theoretical results suggest secondary electron detachment occurs by direct rearrangement of
478 the nascent $\mathbf{G}^{\bullet-}$ and $\mathbf{A}^{\bullet-}$ radical anions and not after prompt decarboxylation as previously
479 proposed (Scheme 1) [20].

480 Photoelectron spectra of \mathbf{G}^{2-} and \mathbf{A}^{2-} previously reported by Xing *et al.* suggest that
481 after 266 nm ePD the nascent carbonyloxyl radicals generated may have up to *ca.* 1.4 eV
482 (32.3 kcal mol⁻¹) and 1.2 eV (27.7 kcal mol⁻¹) vibronic excitation energy, respectively. In
483 the case of $\mathbf{G}^{\bullet-}$ radical anion, decarboxylation resulting in the formation of **3-CP** with a
484 reaction energy of -2.5 kcal mol⁻¹ provides a maximum of 34.8 kcal mol⁻¹ of vibrational
485 energy. There is, therefore, insufficient energy for 1,3-cyclisation and only very small popu-
486 lations of ions will contain sufficient energy for either 1,3- or 1,4-hydrogen atom transfer. In

487 comparison, γ -lactonisation resulting in electron autodetachment requires 31.7 kcal mol⁻¹,
488 while the β -scission reaction channel generating acetate radical anion contains a barrier of
489 29.2 kcal mol⁻¹. Acetate radical anion was detected only in small quantities (see Figure
490 1b), suggesting γ -lactonisation of **3-CP** likely occurs to an even lesser extent. Taken to-
491 gether, these data suggest the major decarboxylated product generated was **3-CP** and it
492 is unlikely that this product releases secondary electrons. Similarly, after decarboxylation
493 of the **A**^{•-} radical anion, *ca.* 33.9 kcal mol⁻¹ of vibronic excitation energy is available for
494 isomerisation of **4-CB**. There is insufficient energy for 1,3-cyclisation and only small pop-
495 ulations of ions will have the required energy for 1,3- and 1,4-hydrogen atom transfer. A
496 barrier for δ -lactonisation that results in electron autodetachment was estimated at *ca.* 19
497 kcal mol⁻¹ with respect to **A**^{•-} residing well within the energy available; however, the low-
498 est energy pathway is 1,5-hydrogen atom transfer with a barrier residing at only 14.9 kcal
499 mol⁻¹, suggesting this pathway will be favourable to form **1-CB**.

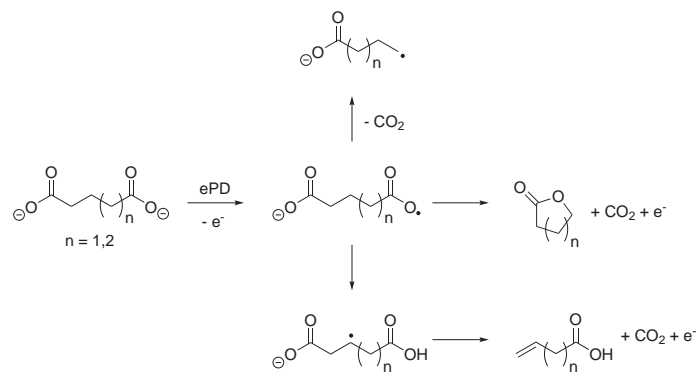
500 The diagnostic reaction of alkyl carboxylates with O₂ was used to confirm the identity
501 of both the propyl and butyl carboxylate radical anions generated by decarboxylation of
502 the nascent [M - 2H]^{•-} carbonyloxy radicals formed after ePD of **G**²⁻ and **A**²⁻ dianions.
503 Reaction of the [**G** - CO₂]^{•-} propyl carboxylate radical anion population resulted in no car-
504 bonate radical anion (CO₃^{•-}) at *m/z* 60, confirming **3-CP** does not isomerise to the lowest
505 energy **1-CP** radical anion. 1,4-Hydrogen atom transfer of **3-CP** resulting in formation of
506 **1-CP** requires 1.9 kcal mol⁻¹ less energy than 1,3-hydrogen atom transfer to form **2-CP**,
507 suggesting that **2-CP** is not generated during decarboxylation of the glutarate radical anion
508 and the only isomer present in the decarboxylated ion population is **3-CP** (Scheme 2). In
509 contrast, reaction of the [**A** - CO₂]^{•-} butyl carboxylate radical anion population results in
510 formation of abundant CO₃^{•-} at *m/z* 60 (see Figure 5a). In this case, *m/z* 60 accounted
511 for *ca.* 20% of the isolated ionic products. An approximation of the contribution of **1-CB**
512 isomers to the *m/z* 100 ion population may be made by considering the reaction of authentic
513 **1-CB**, generated by PD of 2-iodovalerate anion, with O₂. This reaction resulted exclusively
514 in formation of CO₃^{•-} and importantly, the total ion count did not decrease at longer reac-
515 tion times, indicating there are no reaction channels resulting in low-mass ions or electron

516 autodetachment. As such, the 80% decrease in total ion count must arise due to reaction
517 of one of the distonic isomers and not **1-CB**. Therefore, **1-CB** can account for only 3% of
518 the total butyl carboxylate radical anion population. The barriers to 1,5- and 1,6-hydrogen
519 atom transfer of **4-CB** are higher than the highest vibronic excitation energy measured by
520 Xing *et al.* [20], which suggests the remaining 97% of the carboxylatobutyl radical anion
521 population generated after decarboxylation of the nascent adipate radical anion is **4-CB**.

522 The most likely explanation for the ion loss observed during reaction of **3-CP** and **4-**
523 **CB** with O₂ is competitive β -scission reactions after hydrogen atom transfer generates a
524 β -carboxylate radical. For example, **3-CP-OO** may undergo β -scission after 1,5-hydrogen
525 atom transfer of **3-HOOC-2-YL** to release CO₂ + e⁻ (Scheme 3). This process is en-
526 ergetically favourable over both ejection of HO and HO₂ with a barrier of 11.8 kcal mol⁻¹
527 compared with barriers of 23.3 kcal mol⁻¹ and 22.7 kcal mol⁻¹, respectively. However, this β -
528 scission channel will likely compete entropically with HO₂ loss, as indicated by their relative
529 Q_{vib} parameters (depicted in Scheme 4). Furthermore, while 1,5-hydrogen atom transfer
530 is entropically favourable, the barrier to 1,5-hydrogen atom transfer is higher than both
531 1,6-hydrogen atom transfer and γ -lactonisation. In contrast, 1,6-hydrogen atom transfer of
532 **4-CB-OO** resulting in **4-HOOC-2-YL** is the lowest energy reaction pathway. This inter-
533 mediate may eject CO₂ + e⁻ after β -scission, requiring 18.4 kcal mol⁻¹ to overcome the barrier
534 to form an ion-dipole complex -26.2 kcal mol⁻¹ below the entrance channel. This ion-dipole
535 complex is held together by 7.3 kcal mol⁻¹ and releases the products 1-hydroperoxylbut-3-
536 ene + CO₂ + e⁻ with a reaction exothermicity of -18.9 kcal mol⁻¹. Importantly, β -scission to
537 release CO₂ + e⁻ from the **4-HOOC-2-YL** is both energetically and entropically favoured
538 over the alternative β -scission to eject CH₂O + HO, or epoxidation generating HO. Taken
539 together, the difference in total ion count loss can be explained by considering formation of
540 **3-HOOC-2-YL** is not the lowest energy pathway and after its generation and must com-
541 pete with HO and HO₂ ejection, whereas formation of **4-HOOC-2-YL** and subsequent
542 β -scission and ejection of CO₂ + e⁻ is overall the lowest energy reaction channel and is both
543 energetically and entropically favourable.

544 **5. Conclusion**

545 We have identified low-energy hydrogen atom transfer and lactonisation pathways can
 546 facilitate secondary electron detachment directly from $[\text{O}_2\text{C}-(\text{CH}_2)_n-\text{CO}_2]^{\bullet-}$ carbonyloxy
 547 radical anions. These reaction pathways are illustrated in a general form in Scheme 9 and can
 548 account for the loss of ion signal observed following ePD of glutarate and adipate dianions in
 549 the ion-trap mass spectrometer. Similarly, these pathways most likely account for the detec-
 550 tion of near-zero kinetic energy electrons observed in the PES studies of the same dianions
 551 by Wang and co-workers [20]. Importantly our results indicate that these rearrangement
 552 pathways of the radical anion intermediate (resulting in electron autodetachment) compete
 553 kinetically with decarboxylation. Competition between decarboxylation and intramolecular
 554 rearrangement has previously been observed; Schröder *et al.* found long-chained alkylcar-
 555 bonyloxy radicals ($n \geq 5$) had a lifetime sufficient during neutralisation-reionisation exper-
 556 iments to undergo hydrogen atom transfers prior to reionisation [26]. Similarly, while this
 557 phenomenon is not discussed in their investigation, Joly *et al.* measured stable $[\text{M} - 2\text{H}]^{\bullet-}$
 558 radical anions following ePD of $[\text{M} - 2\text{H}]^{2-}$ dianions formed from peptides [51, 52]. In all
 559 likelihood, such ions are stable isomers resulting from rearrangement of the nascent radical
 560 anion: a process that again competes favourably with prompt decarboxylation. These ob-
 561 servations from our own work and that of others suggest that ePD of dicarboxylate dianions
 562 may in the future provide an interesting laboratory within which to explore the chemistry



Scheme 9: Putative fragmentation pathways of dicarboxylate dianions after electron photodetachment resulting in secondary electron detachment.

563 of carbonyloxy radicals that have proved somewhat elusive to the experimentalist.

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