# Direct Observation of the Gas Phase Reaction of the Cyclohexyl Radical with Dioxygen Using a Distonic Radical Ion Approach

Benjamin B. Kirk, David. G. Harman, and Stephen J. Blanksby\*

School of Chemistry, University of Wollongong, NSW, Australia 2522 Received: July 31, 2009; Revised Manuscript Received: November 30, 2009

Alkylperoxyl radicals are intermediates in the oxidation of hydrocarbons. The reactive nature of these intermediates, however, has made them elusive to direct observation and isolation. We have employed ion trap mass spectrometry to synthesize and characterize 4-carboxylatocyclohexyl radical anions ( $C_6H_{10}-CO_2^{-}$ ) and observe their reactivity in the presence of dioxygen. The resulting reaction is facile ( $k = 1.8 \times 10^{-10} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> or 30% of calculated collision rate) and results in (i) the addition of  $O_2$  to form stabilized 4-carboxylatocyclohexylperoxyl radical anions ( $OO-C_6H_{10}-CO_2^{-}$ ), providing the first direct observation of a cyclohexylperoxyl radical, and (ii) elimination of HO2 and HO radicals consistent with recent laser-induced fluorescence studies of the reaction of neutral cyclohexyl radicals with  $O_2$ . Electronic structure calculations at the B3LYP/6-31+G(d) level of theory reveal viable pathways for the observed reactions showing that formation of the peroxyl radical is exothermic by 37 kcal mol<sup>-1</sup> with subsequent transition states as low as -6.6 kcal mol<sup>-1</sup> (formation of HO<sub>2</sub>) and -9.1 kcal mol<sup>-1</sup> (formation of HO) with respect to the entrance channel. The combined computational and experimental data suggest that the structures of the reaction products correspond to cyclohexenes and epoxides from HO<sub>2</sub><sup>•</sup> and HO<sup>•</sup> loss, respectively, while alternative pathways leading to cyclohexanone or ring-opened isomers are not observed. Activation of the charged peroxyl radical  $OO-C_6H_{10}-CO_2^-$  by collision induced dissociation also results in the loss of HO<sub>2</sub> and HO radicals confirming that these products are directly connected to the peroxyl radical intermediate.

## Introduction

In the gas phase, alkylperoxyl radicals are formed from the combination of alkyl radicals and dioxygen during the oxidation of hydrocarbons in the atmosphere and during combustion.<sup>1,2</sup> Tropospheric processing of alkanes is initiated predominantly by hydroxyl radicals via hydrogen abstraction reactions, resulting in the formation of alkyl radicals and water (reaction 1). In the presence of oxygen, the nascent alkyl radical undergoes rapid addition to form an alkylperoxyl radical (reaction 2).<sup>3,4</sup> This reaction is highly exothermic (e.g.,  $\Delta_{rxn}H_{298}$ [CH<sub>3</sub>CH<sub>2</sub>·+ O<sub>2</sub>  $\rightarrow$  $CH_3CH_2O_2$  = 36 kcal mol<sup>-1</sup>)<sup>5</sup> and thus, depending on the capacity of the peroxyl radical to accommodate the excess energy, a third body collision is usually required to stabilize the product. In the troposphere, alkylperoxyl radicals oxidize NO to NO<sub>2</sub>, which is photolabile in sunlight, leading to production of ozone (reactions 4 and 5). Given that NO and hydrocarbons are both byproducts of combustion, reactions 1-5form a crucial part of the chemistry responsible for the formation of photochemical smog in urban areas.<sup>3,4</sup>

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \tag{1}$$

$$R^{\bullet} + O_2 + M \rightarrow ROO^{\bullet} + M$$
 (2)

$$ROO^{\bullet} + {}^{\bullet}NO \rightarrow RO^{\bullet} + {}^{\bullet}NO_{2}$$
 (3)

$$^{\circ}NO_2 + \text{sunlight} \rightarrow ^{\circ}NO + O(^{3}P)$$
 (4)

$$O_2 + O(^{3}P) + M \rightarrow O_3 + M$$
 (5)

During combustion, the unimolecular chemistry of the intermediate alkylperoxyl radical is critical in controlling product distribution and ultimately the efficacy of the process. In particular, rearrangement of the peroxyl radical via hydrogen abstraction from the hydrocarbon backbone (e.g., reaction 8) followed by subsequent addition of oxygen are proposed as key chain-branching events in the radical chain reaction<sup>6,7</sup> leading to autoignition (the cause of engine knock) in internal combustion engines.<sup>8</sup> The importance of the unimolecular chemistry of alkylperoxyl radicals has prompted innumerable experimental and theoretical studies with a particular focus on reactions of the simple, archetypal ethylperoxyl radical. The available data have been critically reviewed by Rienstra-Kiracofe et al.,<sup>9</sup> and the most significant reaction pathways are summarized in reactions 6-10.

$$CH_3CH_2^{\bullet} + O_2 \rightarrow C_2H_4 + HO_2^{\bullet}$$
(6)

$$CH_{3}CH_{2}^{\bullet} + O_{2} \rightarrow CH_{3}CH_{2}O_{2}^{\bullet} \rightarrow C_{2}H_{4} + HO_{2}^{\bullet}$$
(7)

$$\mathrm{CH_3CH_2}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{CH_3CH_2O_2}^{\bullet} \rightarrow {}^{\bullet}\mathrm{CH_2CH_2O_2H} \rightarrow$$

$$C_2H_4 + HO_2$$
 (8)

$$CH_{3}CH_{2}^{\bullet} + O_{2} \rightarrow CH_{3}CH_{2}O_{2}^{\bullet} \rightarrow {}^{\bullet}CH_{2}CH_{2}O_{2}H \rightarrow c - C_{2}H_{4}O + HO^{\bullet}$$
(9)

$$CH_3CH_2^{\bullet} + O_2 \rightarrow CH_3CH_2O_2^{\bullet} \rightarrow CH_3^{\bullet}CHO_2H \rightarrow CH_3CHO + HO^{\bullet}$$
 (10)

The weight of evidence suggests that direct abstraction of a hydrogen atom from the ethyl radical (reaction 6) does not play a significant role in hydrocarbon oxidation at low temperatures (below ca. 800 K). Two mechanisms are proposed for the experimentally observed formation of ethylene and the hydroperoxyl radical; the first involves direct elimination from the ethylperoxyl radical (reaction 7), while the second involves rearrangement facilitated by a 1,4-hydrogen shift to form the 2-hydroperoxylethyl radical followed by elimination (reaction 8). The rearranged 2-hydroperoxylethyl radical can give rise to

<sup>&</sup>lt;sup>†</sup> Part of the "W. Carl Lineberger Festschrift".

<sup>\*</sup> Corresponding author. E-mail: blanksby@uow.edu.au.

oxirane and hydroxyl radical (reaction 9) while an analogous 1,3-hydrogen atom transfer can result in acetaldehyde with concomitant loss of hydroxyl radical (reaction 10). Reactions 7-10 are competitive processes and all occur through the intermediacy of the ethylperoxyl radical. In recent investigations of longer chain alkylperoxyl radicals (e.g., propyl-, butyl-, and pentylperoxyl radicals) hydrogen atom transfer from more remote sites on the carbon chain have been shown to play an important role.<sup>6,10</sup>

Despite the apparent importance of alkylperoxyl radicals in directing reaction outcomes in alkane oxidation, relatively few experimental studies of these intermediates have been reported. Most mechanistic insight into these gas phase reactions is the result of kinetic analysis of the formation of detectable reaction products. Direct observation of the peroxyl radical intermediates in situ has been undertaken by UV absorption but this is often complicated by overlapping absorptions from the wide range of peroxyl and peroxide species present in the reaction mixture.<sup>11</sup> Alternatively, high resolution spectroscopy of a range of alkylperoxyl radicals has been undertaken in the gas phase using cavity ring down techniques,<sup>12-16</sup> while matrix isolation has provided detailed infrared signatures for these intermediates.<sup>17</sup> These studies provide essential insight into the molecular structure and energetics of alkylperoxyl radicals, but they are not well suited to careful mechanistic investigation of their reactions. Similarly, indirect methods to probe the thermochemistry of peroxyl radicals<sup>5,18</sup> are essential but do not provide for direct observation of peroxyl radical reactions. As such, the most detailed mechanistic insight into the reactions of alkylperoxyl radicals relies on theory with a raft of computational studies undertaken on the processes 6-10,<sup>9</sup> as well as higher alkylperoxyl radicals.<sup>10,19</sup> In this paper we outline a new approach to the formation, isolation and the direct observation of reactions of alkylperoxyl radicals in the gas phase using distonic radical anions.

Distonic radical ions were originally defined as ions arising from the one-electron oxidation or reduction of biradicals, ylides, or zwitterions<sup>20,21</sup> but are more commonly considered as radical ions in which the charge and radical are separated.<sup>22</sup> This separation between charge and radical provides these ions with unique reactivity and the pioneering work of Kenttämaa and others has demonstrated that for systems with a sufficiently inert charge, distonic radical ions can provide effective probes of neutral radical reactivity.<sup>23-25</sup> In such instances, the charge acts as a spectator to the radical reactivity but provides an effective handle to allow isolation and detection of reactants and products by mass spectrometry. Putative distonic peroxyl radicals have been previously reported, with the addition of 32 Da to N-ethylpyridinium radical cations observed by mass spectrometry.<sup>26,27</sup> More recently, McLuckey has reported on the addition of 32 Da to radical cations formed from the electron transfer dissociation of proteins.<sup>28</sup> While it is likely that these ions do possess a peroxyl radical moiety, their structures do not serve to provide clear spatial and electronic separation of charge and radical sites and as such they do not present good models for neutral reactivity. We have previously reported the formation and characterization of an adamantylperoxyl radical where the adamantyl cage provides for rigid separation between the charge and unpaired electron (Scheme 1).<sup>29,30</sup> In this instance, however, the inherent ring strain of the adamantyl system significantly perturbs the intrinsic reactivity of the nascent carbon-centered radical<sup>31</sup> and further, the restricted geometry prohibits the observation of important unimolecular reactions of the peroxyl radical following addition of oxygen.<sup>29</sup> As

**SCHEME 1** 



outlined in Scheme 1, addition of oxygen to the 3-carboxylatoadamantyl radical anion (**A**) yields the 3-carboxylatoadamantylperoxyl radical anion (**B**), which upon dissociation gives the oxirane **C** via loss of the hydroxyl radical (cf., reaction 9). In this system, however, no hydroperoxyl radical loss is observed (cf., reactions 7 and 8) presumably due to the excessive ring strain in formation of the resulting adamantene **D**.

In the present study we have selected the 4-carboxylatocyclohexyl distonic radical anion as a case study for the unimolecular reactivity neutral alkyl radicals with dioxygen. This molecule is significantly less strained than the adamantyl system but retains sufficient rigidity to spatially separate the radical and negative charge. Cycloalkanes are a major component of gasoline and diesel fuels<sup>32</sup> and as such the peroxyl radicals formed from these compounds are of significant interest in both combustion and atmospheric oxidation processes. Detailed kinetic modeling of the oxidation of cyclohexane has recently been reported and forms an excellent reference point for this study.<sup>32,33</sup>

### Methods

Mass Spectrometry. Experiments were performed on a modified ThermoFisher LTQ (San Jose, CA) linear quadrupole ion trap mass spectrometer<sup>34</sup> fitted with a conventional IonMax electrospray ionization source and operating Xcalibur 2.0 SUR1 software. Ions were generated by infusion at  $3-5 \ \mu L \ min^{-1}$  of a methanolic solution (10-50  $\mu$ M) into the electrospray ion source. In some instances, aqueous ammonia was added to raise the pH and facilitate the formation of dianions. Typical instrumental settings were spray voltage -2.5 to +3.5 kV, capillary temperature 200-250 °C, sheath gas flow between 10 and 30 (arbitrary units), and sweep and auxiliary gas flow set at between 0 and 10 (arbitrary units). For collision experiments, ions were mass-selected with a window of 1-4 Th, using a Q-parameter of 0.250 and the fragmentation energy applied was typically 10-45 (arbitrary units) with an excitation time of 30 ms (unless otherwise noted). Modifications to the mass spectrometer to allow the introduction of neutral gases into the ion trap region of the instrument have been previously described.<sup>30</sup> Briefly, liquid and gas reagents are introduced into a flow of Ultra High Purity (UHP) helium (3–5 psi) via a heated septum inlet (25–250 °C). The reagent flow (e.g.,  ${}^{18}O_2$ , NO) is controlled using a syringe pump, while the mixture is supplied via a variable leak valve to provide a total ion gauge reading of  $\sim 0.9 \times 10^{-5}$  Torr representing an estimated trap pressure of 2.5 mTorr. The temperature of the vacuum manifold surrounding the ion trap was measured at  $307 \pm 1$  K, which is taken as being the effective temperature for ion-molecule reactions observed herein.35 Reaction times of 30-10000 ms were set using the excitation time parameter within the control software using a fragmentation energy of 0 (arbitrary units). All spectra presented represent an average of at least 50 scans. Reaction

rate coefficients were determined as previously described and collision rates for the ion-molecule reactions were estimated by average dipole orientation (ADO) theory for 307 K<sup>36</sup> using an available Fortran routine.<sup>37</sup> Branching ratios were calculated using the method of Grabowski and Zhang.<sup>38</sup>

Computational Chemistry. Previous studies of the reaction coordinates for alkylperoxyl radicals have found good agreement between B3LYP methods and more sophisticated approaches such as CBS-QB310 and CCSD(T).9 Importantly, the computationally economical B3LYP method faithfully reproduced the transition state and reaction energies of the high level approaches and thus can be expected to provide reliable predictions as to the lowest energy reaction pathways. Indeed, the hybrid density functional B3LYP approach has been recommended for studying the unimolecular potential energy surfaces of large alkylperoxyl radicals.<sup>10</sup> On the basis of these recommendations, all calculations were undertaken using the hybrid density functional theory B3LYP method<sup>39,40</sup> and the 6-31+G(d) basis set within the GAUSSIAN03 suite of programs.<sup>41</sup> All stationary points on the potential energy surface were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. All reported energies include zero-point energy corrections. Minima were confirmed to join a transition state by intrinsic reaction coordinate calculation.<sup>42,43</sup> Cartesian coordinates, raw energies, and frequencies for all minima and transition states are provided as Supporting Information.

**Materials.** 1,1-Cyclohexanedicarboxylic acid (95%) was obtained from Matrix Scientific (Columbia, SC). *trans*-1,2-Cyclohexanedicarboxylic acid (95%), 1,3-cyclohexanedicarboxylic acid (98%), and 1,4-cyclohexanedicarboxylic acid (99%) were purchased from Aldrich (Milwaukee, WI) with the latter two diacids obtained as mixtures of both cis and trans stereoisomers. Isotopically labeled oxygen <sup>18</sup>O<sub>2</sub> (95%) was obtained from Cambridge Isotope Laboratories (Andover, MA). Methanol (HPLC grade) and ammonia solution (28%, AR grade) were obtained from Ajax (Sydney, Australia). All commercial compounds were used without further purification. 4-Oxocyclohexane carboxylic acid and 3,4-epoxycycolohexane carboxylic acid was freshly prepared in a disposable syringe as previously reported.<sup>30,46</sup>

Synthesis of Dimethyl Cyclohexane-1,4-dicarboxylate. To a stirred solution of 1,4-cyclohexanedicarboxylic acid (2.002 g, 11.6 mmol, mixture of cis and trans diastereomers) in methanol (50 mL) was added sulfuric acid (10 drops, concentrated). When addition was complete, the mixture was heated at reflux overnight. The solvent was removed in vacuo and the residue diluted with water (50 mL) and extracted with dichloromethane (3 × 30 mL). The combined extracts were dried over magnesium sulfate, and the solvent was removed in vacuo to yield a colorless oil (2.604 g, 85%), which was purified by distillation under reduced pressure before further use. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  1.43–2.48 (10H, m, ring protons), 3.68 (6H, s, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  25.84, 27.86 (CH<sub>2</sub>), 40.48, 42.23 (CH), 51.39, 51.42 (CH<sub>3</sub>), 127.26 (CO).

Synthesis of Dimethyl 1,4-Dideuteriocyclohexane-1,4-dicarboxylate. *n*-Butyllithium (1.700 mL, 2.2 mmol) was added to a stirred solution of diisopropylamine (308  $\mu$ L, 2.20 mmol) in tetrahydrofuran (2 mL) under dry nitrogen at 0 °C. The mixture was cooled to -70 °C, after which dimethyl cyclohexane-1,4-dicarboxylate (100 mg, 0.50 mmol) was slowly added. The mixture was allowed to warm to room temperature over 3 h after, after which it was cooled to -70 °C and D<sub>2</sub>O (1 mL, 45.1 mmol) added slowly. Further tetrahydrofuran (1 mL) was added to aid stirring of the mixture, after which it was allowed to warm to room temperature over 1 h. The mixture was then extracted with dichloromethane ( $3 \times 2$  mL), the combined extracts dried over magnesium sulfate, and the solvent removed in vacuo to yield a colorless oil that was used without further purification.

Synthesis of 1,4-Dideuteriocyclohexane-1,4-dicarboxylic Acid. A solution of lithium hydroxide (148.7 mg, 3.5 mmol) in water (2.5 mL) was added to a stirred solution of dimethyl 1,4-dideuteriocyclohexane-1,4-dicarboxylate (104.6 mg, 0.5 mmol) in tetrahydrofuran (2.5 mL). The mixture was allowed to stir overnight, after which it was washed with dichloromethane (3 × 2 mL) and acidified to pH 1 with dilute hydrochloric acid. The mixture was then extracted with ethyl acetate (3 × 5 mL), the combined extracts were dried over magnesium sulfate, and solvent was removed in vacuo to yield a white powder that was used without further purification. Electrospray ionization mass spectrometry gives  $[M - H]^-$  173 (100%), 172 (84), 171 (22); D<sub>2</sub>:D<sub>1</sub>:D<sub>0</sub> (<sup>13</sup>C-isotope corrected) 4.5:3.8:1.

Synthesis of Methyl Cyclohexanecarboxylate. To a stirred solution of cyclohexanecarboxylic acid (2.102 g, 16.3 mmol) in methanol (50 mL) was added sulfuric acid (10 drops, concentrated). When addition was complete, the solution was heated at reflux (2.5 h), after which it was allowed to cool to room temperature and left overnight. The reaction mixture was diluted with water (50 mL) and extracted with dichloromethane ( $3 \times 30$  mL). The combined extracts were dried over magnesium sulfate, and the solvent was removed in vacuo to yield a pale yellow oil (2.196 g, 99% yield), which was used without further purification. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CD):  $\delta$  1.11–3.59 (10H, m, ring protons), 3.59 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  25.40, 25.71, 28.98 (CH<sub>2</sub>), 43.07 (CH), 51.39 (CH<sub>3</sub>), 176.54 (CO).

Synthesis of Methyl 1-Deuteriocyclohexanecarboxylate. *n*-Butyllithium (2.4 mL, 3.10 mmol) was added to a stirred solution of diisopropylamine (434  $\mu$ L, 3.1 mmol) in tetrahydrofuran (2 mL) under dry nitrogen at 0 °C. The mixture was cooled to -70 °C, after which methyl cyclohexanecarboxyate (200 mg, 1.4 mmol) was slowly added. The mixture was allowed to warm to room temperature over 3 h, after which it was cooled to -70 °C and D<sub>2</sub>O (1 mL, 45.1 mmol) added slowly. The mixture was allowed to warm to room temperature, after which it was extracted with dichloromethane (4 × 3 mL), the combined extracts were dried over magnesium sulfate, and the solvent was removed in vacuo to yield a yellow oil, which was used without further purification. Electron ionization mass spectrometry gives [M<sup>++</sup>] 143 (100%) and 142 (65%); D<sub>1</sub>:D<sub>0</sub> (<sup>13</sup>C-isotope corrected) 1.45:1.

#### **Results and Discussion**

Gas-Phase Synthesis and Characterization of the 4-Carboxylatocyclohexyl Radical Anion (E). Electrospray ionization (ESI) of a methanolic solution of 1,4-cyclohexanedicarboxylic acid yields abundant ions at m/z 171 and 85 corresponding to the  $[M - H]^-$  and  $[M - 2H]^{2-}$  molecular ions, respectively. Isolation of the dianion within the ion trap mass spectrometer and application of collision induced dissociation (CID) results in formation of an  $[M - 2H - CO_2]^{--}$  ion at m/z 126 consistent with oxidative decarboxylation processes, as previously reported for dicarboxylate dianions (Scheme 2a).<sup>29,47</sup>

It has previously been demonstrated that oxidative decarboxylation of dicarboxylate dianions produces distonic radical Gas Phase Reaction of the Cyclohexyl Radical with O2





anions in a nondestructive and regiospecific manner,<sup>29,47</sup> and thus the 1,4-carboxylatocyclohexyl radical anion (E) is expected to be the major product of this reaction. It is important to recognize, however, that there are another three possible cyclic isomers (F, G, and H) that might arise from rearrangement of E through rapid hydrogen transfer reactions in addition to a ring-opened radical that could be formed via  $\beta$ -scission (Scheme 3). Of the cyclic isomers, two are distonic (F and G) and would thus be expected to exhibit similar behavior to E, while H is resonance stabilized and might thus be expected to behave as a conventional radical anion. In an effort to assess the energetic accessibility of these structures, electronic structure calculations were conducted at the B3LYP/6-31+G(d) level of theory to identify minima on the potential energy surface as well as any transition states for rearrangement. The results are summarized in Scheme 3 and suggest that the distonic radical anions E, F, and G are essentially isoenergetic, while the conventional radical anion **H** is the global minimum: ca. 8 kcal  $mol^{-1}$  lower in energy. Ring-opening of the radical E yields a primary radical some 17 kcal  $mol^{-1}$  higher in energy. Computed activation energies for isomerization of E range from 26.8 to 44.2 kcal mol<sup>-1</sup> and represent significant barriers to rearrangement. Indeed, activation energies of this magnitude are expected to be more than sufficient to prevent rearrangement of E under the experimental conditions given that (i) there is little reverse activation energy in the oxidative decarboxylation process to provide excess internal energy to the nascent radical anion, (ii) any excess energy is partitioned between the radical anion, carbon dioxide, and the departing electron, (iii) CID in an iontrap instrument does not produce energetic secondary collisions, and (iv) ions within the trap are rapidly thermalized by collisions with the helium buffer gas.

Although calculations suggest that rearrangement of the 4-carboxylatocyclohexyl radical anion (E) is unlikely, it is prudent to investigate this possibility to provide confidence in the structural assignment of the ion at m/z 126. The  $[M - 2H]^{2-1}$ molecular ion at m/z 85 was successfully generated from the 1,3-cyclohexanedicarboxylic acid, and CID of this ion yields a radical anion at m/z 126 with the putative structure of **F** (Scheme 2b). Attempts were made to generate the isomers G and H using the same oxidative decarboxylation pathway but, not surprisingly, efforts to generate the requisite dianions by electrospray ionization of the 1,1-cyclohexanedicarboxylic acid and 1,2cyclohexanedicarboxylic acid were unsuccessful: presumably due to excessive Coulombic repulsion between the closely spaced carboxylate moieties.<sup>48</sup> As an alternative synthesis for H, CD<sub>3</sub>O<sup>-</sup> anions, generated by negative ion electrospray ionization of CD<sub>3</sub>OD, were allowed to react with neutral methyl cyclohexanecarboxylate added to the ion trap at a low concentration in the helium buffer gas (Scheme 4). The resulting proton transfer is estimated to be exothermic<sup>49</sup> by ca. 10 kcal mol<sup>-1</sup> and produced abundant  $[M - H]^-$  molecular anions at m/z 141. The analogous experiment with methyl 1-deuteriocyclohexanecarboxylate was found to yield m/z 141 via exclusive abstraction of deuterium from the  $\alpha$ -carbon thus confirming the ester—enolate structure of this anion. CID of the precursor anion gave a small amount of m/z 126 arising from the neutral loss of a methyl radical (Scheme 4). Literature precedent for homolytic dissociation of ester—enolate anions<sup>50,51</sup> suggests that the structure of the product ion corresponds to **H**: the most stable of the four carboxylatocyclohexyl radical anions (Scheme 3).

Ion-molecule reactions were undertaken to probe the structural differences between the three isomeric cyclohexyl radicals **E**, **F**, and **H**. Mass-selected m/z 126 ions formed via the three independent syntheses (Schemes 2a,b and 4) were allowed to react with both dioxygen and nitric oxide under comparable conditions in the ion trap and examples of the resulting mass spectra after reaction times of 2000 ms are presented in Figure 1. Addition of 32 Da to a radical ion upon reaction with oxygen has previously been cited as evidence for distonic character<sup>26,27,29,30</sup> and indeed the putative distonic ions E and F both undergo addition of dioxygen to form adduct ions at m/z 158 under these conditions (Figure 1a,b, respectively). The ions observed at m/z141 and 125 are assigned as products arising from the addition of dioxygen with concomitant loss of HO<sup>•</sup> and HO<sub>2</sub><sup>•</sup> radicals, respectively. A detailed discussion of the mechanistic origin of these ions is presented later but importantly the relative abundance of these ions in the spectra of the two isomers are significantly different, indicating that the two isomers are structurally distinct. In addition, the CID spectra of the two m/z158 ions (Figure S1, Supporting Information) show very distinct fragment ion abundances further differentiating the precursor radicals E and F. In contrast to the distonic ions, the 1-carboxylatocyclohexyl radical anion (H) shows no appreciable addition of  $O_2$  at m/z 158 but instead exhibits a major product ion at m/z 60 (Figure 1c). As far as we are aware, this transformation has not previously been reported, and it seems likely to result from the formation of the carbonate radical anion  $CO_3^{\bullet-}$  via the mechanism outlined in Scheme 5a. Support for this proposal is provided by the observation of the product ion at m/z 62 when the reaction is carried out in the presence of  $^{18}O_2$  (Figure S2, Supporting Information). The absence or very low abundance of the m/z 60 ion in Figure 1a,b suggests that most of the m/z 126 ions in these experiments are indeed the putative distonic ions E and F and rearrangement to the global minimum during formation or subsequent reaction only occurs to a very minor degree if at all.

Nitric oxide is expected to undergo rapid radical-radical combination reactions with carbon-centered radicals, and indeed, we have previously shown that this reaction occurs rapidly for the distonic 3-carboxylatoadamantyl radical anion (**A**).<sup>30</sup> When trapped in the presence of nitric oxide, the putative distonic ions **E** and **F** undergo rapid addition of 30 Da to form [M + 'NO]<sup>-</sup> product ions at m/z 156 (Figure 1d,e, respectively). In contrast, reaction of the conventional radical anion **H** with NO yields no significant formation of the adduct ion at m/z 156 and instead abundant product ions at m/z 112 are observed corresponding to a net neutral loss of 14 Da (Figure 1f). This observation can be rationalized as the displacement of CO<sub>2</sub> by NO (Scheme 5b) and has previously been observed by Wenthold and Squires for the reaction of the analogous acetate radical anion with nitric oxide (i.e., 'CH<sub>2</sub>CO<sub>2</sub><sup>-</sup> + 'NO  $\rightarrow$  -CH<sub>2</sub>NO +

#### **SCHEME 3**



**SCHEME 4** 



 $CO_2$ ).<sup>52</sup> This observation lends further support to the putative structure of the radical anion **H**.

The combination of computational and experimental data provides compelling evidence for assigning distinct structures for all three independently synthesized, isomeric m/z 126 ions. Significantly, in the context of this study, the ions of m/z 126 formed by oxidative decarboxylation of 1,4-cyclohexanedicarboxylate dianion (Scheme 2a) can be confidently assigned to the distonic 4-carboxylatocyclohexyl radical (E) and any rearrangement of this ion during formation or isolation occurs only to a very minor extent.

**Reaction of a 4-Carboxylatocyclohexyl Radical Anion (E)** with Dioxygen. The reaction of cyclohexyl radical with dioxygen has previously been studied in the context of the combustion of cycloalkanes. Previous experimental work has identified several of the stable even electron reaction products,<sup>53,54</sup> while recent laser-induced fluoresence measurements have quantified HO<sup>•</sup> and HO<sub>2</sub><sup>•</sup> production.<sup>19,33</sup> On the basis of these data and ab initio calculations, a manifold for the c-C<sub>6</sub>H<sub>11</sub><sup>•</sup> + O<sub>2</sub> reaction has been proposed.<sup>19,32,55</sup> The most significant reaction channels were used here to formulate the reaction manifold for the corresponding distonic ion **E** (Scheme 6).

In the present study, the mass spectra arising from the ion-molecule reaction of the isolated 4-carboxylatocyclohexyl radical (E) with dioxygen at reaction times ranging from 30 to 5000 ms are shown in Figure 2a. On the basis of these data and previous measurements<sup>30</sup> of background dioxygen concentrations in the ion trap of  $3.0 \times 10^9$  molecules cm<sup>-3</sup>, a secondorder rate constant for the loss of the precursor ion of  $1.8 \times$  $10^{-10}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> can be derived, representing an overall reaction efficiency of 30%. Figure 2a reveals an abundant product ion at m/z 158 that is observed to increase in abundance at longer reaction times. The CID spectrum of mass-selected m/z 158 (Figure 2b) reveals very little loss of dioxygen at m/z126 and is thus consistent with a covalently bound alkylperoxyl radical structure rather than any nonspecific ion-dipole adduct that would be expected to dissociate to reactants upon collisional activation. Two other abundant product ions are also observed in the reaction of 4-carboxylatocyclohexyl radical E with dioxygen (Figure 2a). These ions appear at m/z 125 and 141

that correspond in mass to neutral losses of HO<sub>2</sub><sup>•</sup> (33 Da) and HO<sup>•</sup> (17 Da), respectively, and are consistent with several of the pathways in the reaction manifold shown in Scheme 6. The assignments of these ions are aided by the equivalent mass spectrum obtained in the presence of <sup>18</sup>O<sub>2</sub> that shows a 4 Da shift in the mass of the cyclohexylperoxyl radical (*m*/*z* 162), a 2 Da shift (*m*/*z* 143) consistent with the loss of H<sup>18</sup>O<sup>•</sup> and no shift in the *m*/*z* 125 ion as expected following loss of H<sup>18</sup>O<sup>•</sup> (Figure S2, Supporting Information). Importantly, these labeling data confirm that reaction products resulting from addition of oxygen and loss of either hydroxyl or hydroperoxyl radicals do not involve participation of carboxylate oxygens, thus indicating that the charged moiety is a spectator to the observed free radical reactivity.

Branching ratios for the three major competitive reaction channels were estimated from the data in Figure 2a to be 32%, 11%, and 54% for the product ions m/z 158, 141, and 125, respectively with the remaining 3% made up of minor products. These data confirm that all three are primary reaction products and no significant secondary products were identified (e.g., secondary additions of O<sub>2</sub>). Considering the major reaction pathway in the first instance, the formation of the 3-cyclohexenecarboxylate anion (J) at m/z 125, could arise from either direct H-atom abstraction by molecular oxygen from the cyclohexyl radical or dissociation of the nascent cyclohexylperoxyl radical (I) via concerted elimination (Scheme 6i) or via the intermediacy of the 2-hydroperoxlcyclohexyl radical (M, Scheme 6ii). The observation of a significant abundance of the m/z 125 ion in the CID spectrum (Figure 2b) of isolated 4-carboxylatocyclohexylperoxyl radical (I) confirms that the cyclohexene product ion (J) can be formed from dissociation of the peroxyl radical. This observation is consistent with previous theoretical studies that suggest that HO<sub>2</sub> production occurs via the alkylperoxyl radical intermediate and that direct H-atom abstraction (cf. reaction 6) is not a significant process at low temperatures.9

The reaction product ion at m/z 141 is found to be the minor product with a branching ratio of 11%. The CID spectrum of m/z 158 (Figure 2b) confirms that this ion can also be formed directly from the isolated cyclohexylperoxyl radical precursor (I) via loss of the HO<sup>•</sup> radical. Previous work has suggested at least five mechanistic possibilities to account for this observation, and these are outlined in Scheme 6. To probe these possibilities, deuterium labeling was undertaken to establish the site(s) of hydrogen abstraction from the cyclohexane backbone in generation of the HO<sup>•</sup> radical. Using 1,4-dideuterio-1,4cyclohexanedicarboxylic acid as a precursor, the 4-carboxylato-1,4-dideuteriocyclohexyl radical anion was generated at m/z 128.



**Figure 1.** Mass spectra obtained following isolation of isomeric carboxylatocyclohexyl radical anions at m/z 126 in the presence of (a, b, c) O<sub>2</sub> and (d, e, f) NO. Reactions of (a, d) 4-carboxylatocyclohexyl **E**, (b, e) 3-carboxylatocyclohexyl **F**, and (c, f) 1-carboxylatocyclohexyl **H** are shown. It should be noted that adventitious oxygen is always present in the ion trap<sup>29,30</sup> so competing reactions are also observed in the NO spectra (d, e, f).

**SCHEME 5** 



**SCHEME 6** 



Reaction of this isotopologue with dioxygen produced major products at m/z 160, 143, and 127 corresponding to the labeled cyclohexylperoxyl radical, with subsequent loss of HO<sup>•</sup> and HO<sub>2</sub><sup>•</sup>, respectively (Figure 2c). Loss of DO<sup>•</sup> at m/z 142 in this spectrum was observed to be minor compared to HO<sup>•</sup> loss at m/z 143; this suggests deuterium abstraction from the 1- and 4-positions in the dissociation of the peroxyl radical is a minor pathway. The same trend is also observed in the CID spectrum of the mass-selected peroxyl radical anions at m/z 160 (Figure 2d). These data are consistent with unimolecular dissociation of the 4-carboxylatocyclohexylperoxyl radical anion (I) via loss of HO<sup>•</sup> that does not result in significant formation of either the cyclohexanone **R** or the 1,4-epoxycyclohexane **Q** (Scheme 6ix and Scheme 6viii).

Figure 3 compares the CID spectrum of the m/z 141 ion formed from reaction of 4-carboxylatocyclohexyl radical anion (Figure 3a) and dioxygen with the CID spectra of authentic 4-oxocyclohexanecarboxylate (R, Figure 3c) and 3,4-epoxycyclohexanecarboxylate (L, Figure 3b) anions formed by negative ion electrospray ionization of the corresponding carboxylic acids. The fragment ions observed at m/z 99 and 71 in the CID spectrum of the 4-oxocyclohexanecarboxylate anion (R, Figure 3c) are absent in Figure 3a indicating that the ketone is not a product of the reaction of the charge labeled cyclohexyl radical with O<sub>2</sub>. This observation is consistent with the deuterium labeling data (vide supra). The fragment ions observed in the CID spectrum of the 3,4-epoxycyclohexanecarboxylate anion (L, Figure 3b) show a greater similarity to the m/z 141 formed from reaction (Figure 3a); however, there are significant differences, particularly in the observation of a fragment ion at



Figure 2. (a) Stack plot representation of the mass spectra acquired of the mass-selected 4-carboxylatocyclohexyl radical anion (E, *m/z* 126) in the presence of oxygen at reaction times ranging from 30 to 5000 ms (MS<sup>3</sup>, *m/z* 86 → 126 → ○). (b) CID spectrum of mass-selected *m/z* 158 ions formed from the ion-molecule reaction of the 4-carboxylatocyclohexyl radical anion (E, *m/z* 126) with dioxygen (MS<sup>4</sup>, *m/z* 86 → 126 → 158 → ○). (c) Mass spectrum acquired from the reaction of the mass-selected 4-carboxylato-1,4-dideuterocyclohexyl radical anion (*m/z* 128) in the presence of dioxygen with a reaction time of 5000 ms (MS<sup>3</sup>, *m/z* 87 → 128 → 160). (d) CID spectrum of mass-selected *m/z* 160 formed from the ion-molecule reaction of the 4-carboxylato-1,4-dideutericyclohexyl radical anion (*m/z* 128) with dioxygen (MS<sup>4</sup>, *m/z* 86 → 128 → 160). (d) CID spectrum of mass-selected *m/z* 160 formed from the ion-molecule reaction of the 4-carboxylato-1,4-dideutericyclohexyl radical anion (*m/z* 128) with dioxygen (MS<sup>4</sup>, *m/z* 87 → 128 → 160).



**Figure 3.** CID spectra of isolated m/z 141 ions formed from (a) the reaction of 4-carboxylatocyclohexyl radical anion (**E**) with O<sub>2</sub>, (b) deprotonation of authentic [3,4]-epoxycyclohexanecarboxylic acid and (c) deprotonation of 4-oxocyclohexanecarboxylic acid. All spectra are recorded under the same conditions using a normalized collision energy of 25 (arbitrary units).

m/z 61 in the latter spectrum, which is not observed in the former. Furthermore, the fragment ion abundances differ significantly between the two spectra, with the reaction product (Figure 3a) appearing significantly more labile than the authentic epoxide product (Figure 3b) when provided with equivalent collision energy. These data show that while the ion population at m/z 141 arising from the reaction of the charge labeled cyclohexyl radical (E) with dioxygen may include 3,4-epoxycyclohexanecarboxylate anions (L), this is clearly not the exclusive product of this reaction. Given this evidence, a contribution from the 2,4-epoxycyclohexanecarboxylate anion (**O**) seems likely but the presence of this isomer could not be established unequivocally due to the unavailability of the requisite precursor compound. Scheme 6vi also suggests a possible ring-opened isomer N might also be present but this is excluded on the basis of computation data (vide infra).

According to Scheme 6, the observation of the epoxide product ions at m/z 141 implies that 2- and 3-hydroperoxylcyclohexyl radicals (**M** and **K**, respectively) are intermediates in the reaction. The presence of these rearranged 'QOOH radicals was investigated by isolating the ion at m/z 158 in the presence of dioxygen. Significantly, no reaction of these ions was observed even at reaction times up to 5 s (data not shown). The absence of product ions resulting from the further addition of O<sub>2</sub> or formation of the carbonate radical anion supports the notion that carboxylatohydroperoxylcyclohexyl radical anions such as **M**, **K**, and **P** ('QOOH) are not stable intermediates under the conditions of these experiments and the ion population at m/z 158 can be exclusively assigned to 4-carboxylatocyclohexylperoxyl radical (**I**).

**Reaction Coordinate Calculations.** Calculation of the reaction coordinate diagram for the reaction of the 4-carboxylatocyclohexyl radical anion (E) with dioxygen was undertaken at the B3LYP/6-31+G(d) level of theory, and the results are illustrated in Figure 4. Full details of the structure and energetics of the stationary points depicted on this potential energy diagram are provided as Supporting Information (Table S2). Addition of dioxygen to the 4-carboxylatocyclohexyl radical anion (E) can give rise to two geometric isomers with the carboxylate anion and peroxyl radical moieties bound to the same ( $I_Z$ ) or opposite ( $I_E$ ) faces of the cyclohexane ring. While these diastereomeric peroxyl radicals are calculated to be within 0.2 kcal mol<sup>-1</sup>, they can result in different chemistries and different reaction energetics as illustrated in Figure 4a,b.

Computations predict that rearrangement of the nascent peroxyl radical (I) via hydrogen atom transfer can proceed without additional activation energy from all positions except the  $\alpha$ -carbon of the peroxyl moiety itself (Scheme 6ix). The latter abstraction results in concerted formation of 4-oxocyclohexanecarboxylate anion (R) via a 4-centered transition state that lies either +4.3 or +3.1 kcal mol<sup>-1</sup> above the entrance channel for rearrangement from the  $I_Z$  and  $I_E$  isomers, respectively. The presence of this barrier explains why this otherwise exothermic product channel  $(-61 \text{ kcal mol}^{-1})$  is not observed experimentally. Both pathways for the observed elimination of HO<sub>2</sub><sup>•</sup>, either via a concerted mechanism (Scheme 6i) or via the intermediate 2-hydroperoxylcyclohexyl radical (M, Scheme 6iii), are found to be energetically accessible. Transition structures for concerted elimination of HO<sub>2</sub><sup>•</sup> from  $I_Z$  and  $I_E$  are located some -4.2 and -6.6 kcal mol<sup>-1</sup>, below the entrance channel, while the most energetic transition states for the stepwise process are found at -0.4 and -4.2 kcal mol<sup>-1</sup>. The calculations thus give no clear indication as to whether the concerted or stepwise mechanism is more likely responsible for the experimental observation of HO2 loss. Transition states for rearrangement via 1,4-, 1,5-, or 1,6-hydrogen atom transfer are calculated to lie between -0.4 and -13.6 kcal mol<sup>-1</sup> below the entrance channel. While all the resulting hydroperoxylcyclohexyl radicals (K, M, and P, Scheme 6) are found to be minima on the potential energy surface, all are further connected to energetically accessible pathways for subsequent reaction via epoxide formation with concomitant loss of the HO' radical. The accessibility of such pathways is consistent with the fact that no secondary addition of O2 was observed experimentally as might be expected if such 'QOOH isomers are present in the ion population at m/z 158. Interestingly, the calculations do not provide a clear prediction as to the most likely structure(s) of the product ion arising from loss of HO<sup>•</sup> at m/z 141. In particular, the 1,4-epoxycyclohexane carboxylate ( $\mathbf{Q}_E$ ) is found to be energetically accessible with among the lowest energy transition states for both the 1,6-hydrogen atom transfer  $(-9.1 \text{ kcal mol}^{-1})$ and subsequent epoxide formation  $(-12.2 \text{ kcal mol}^{-1})$ . It should be noted, however, that this product can only be formed from the trans-peroxyl radical ( $I_E$ , see Figure 4b) while both 2,4and 3,4-epoxycyclohexane carboxylates (O and L, respectively) can be formed from both cis and trans isomers (Figure 4a,b). Furthermore, from symmetry there are four near-equivalent paths (2 for cis and 2 for trans) for formation of the 2,4- and 3,4epoxycyclohexane carboxylates compared to only a single pathway for formation of the low energy 1,4-epoxyocylcohexane carboxylate ( $\mathbf{Q}_E$ ). The resulting low probability for this reaction may account for the fact that no experimental evidence (based on deuterium-labeling) was obtained for this otherwise energetically competitive exit channel. Finally the calculated  $\beta$ -scission pathway (Scheme 6vi) for the 3-hydroperoxycyclohexyl radical (K) was found to have a transition state significantly above the entrance channel ( $\pm 11.5$  kcal mol<sup>-1</sup>, Figure 4a). This result suggests that the ring opened aldehyde isomer is an unlikely contributor to the ion population at m/z 141.

The carboxylate charge tag is an obvious point of difference between the distonic radical anion studied here and the archetypal neutral radical system. Interestingly, however, the calculated energies for the reaction of dioxygen and the 4-carboxylatocyclohexyl radical (E) are in generally good agreement with previous computations of the analogous neutral cyclohexyl radical reaction.<sup>19,32</sup> For example, addition of dioxygen to the charge-tagged cyclohexyl radical to form the peroxyl radical was found to be exothermic by -37 kcal mol<sup>-1</sup> (Figure 4), which is equal to the value for the corresponding neutral radical reaction using a G2(MP2)' approach.<sup>19</sup> Furthermore, the barriers to rearrangement of the 4-carboxylatocyclohexyl radical via hydrogen atom transfer range between -0.4and -13.6 kcal mol<sup>-1</sup> compared with -2.1 and -10.1 kcal mol<sup>-1</sup> for rearrangement on the neutral radical potential surface. The relative order of the barrier heights for 1,4-, 1,5-, and 1,6hydrogen atom transfer and 1,4-hydrogen transfer with concerted elimination of HO<sub>2</sub><sup>•</sup> are consistent those calculated by Silke et al., namely, 1,5-hydrogen atom transfer (to form  $\mathbf{K}$ ) < 1,6hydrogen atom transfer (to form  $\mathbf{P}$ ) < concerted elimination of  $HO_2^{\bullet}$  (to form J) < 1,4-hydrogen atom transfer (to form M).<sup>32</sup> This differs slightly from the findings of Knepp et al. who report a lower activation energy for concerted elimination of HO<sub>2</sub><sup>•</sup> with respect to 1,6-hydrogen atom transfer.<sup>19</sup> The resulting hydroperoxylcyclohexyl radical isomers computed in the present study (K, M, and P, Scheme 6) range in energy between -15.6 and -23.1 kcal mol<sup>-1</sup> below the entrance channel, with the lowest of these minima being identified as the 1-carboxylato-4hydroperoxylcyclohexyl radical (P, Scheme 6). This contrasts with calculations of the analogous neutral surface where the 3-hydroperoxylcyclohexyl radical and 2-hydroperoxylcyclohexyl radical are calculated as the lowest energy 'QOOH structures.<sup>19,32</sup> This is not surprising, however, as the presence of the carboxylate moiety in the 1-carboxylato-4-hydroperoxylcyclohexyl radical (P) provides for resonance delocalization that is absent in the neutral system.

## Conclusion

Overall the reaction products observed for charge-tagged 4-carboxylatocyclohexyl radical anions (E) in the ion trap mass spectrometer closely mirror those observed in previous experimental studies of the corresponding cyclohexyl radicals, namely reactions resulting in the elimination of HO<sub>2</sub><sup>•</sup> and HO<sup>•</sup>.<sup>19,33</sup> Furthermore, there is a satisfying agreement between the computed reaction coordinate diagram for the distonic radical





**Figure 4.** Reaction coordinate diagram for the reaction of the 4-carboxylatocyclohexyl radical anion (**E**) with  $O_2$  where all energy values are presented as kcal mol<sup>-1</sup>. Addition of  $O_2$  can occur from either the face of the cyclohexyl moiety resulting in cis- and trans-isomers of the 4-carboxylatocyclohexylperoxyl radical anion. The rearrangements are calculated for both the (a) the cis-isomer  $I_Z$  and (b) the trans-isomer  $I_E$ . All calculations were performed at the B3LYP/6-31+G(d) level of theory and include unscaled ZPE corrections. Full structure and energies for stationary points are provided as Supporting Information (Tables S2).

anion and previous theoretical investigations of the neutral system. The congruence in the chemistry of E and its neutral counterpart provide further confidence in the use of the distonic radical anions as probes of neutral reactivity. Observation of the 4-carboxylatocyclohexylperoxyl radical anion (I) at m/z 158, provides direct evidence for the formation of a stabilized cyclohexylperoxyl radical in the gas phase and is consistent with the recent detection of the analogous neutral cyclohexylperoxyl radical by cavity ring-down spectroscopy.56 The absence of further reactivity of this ion with dioxygen indicates the absence of isomeric hydroperoxylcyclohexyl radicals (e.g., K, M, and P), often referred to as 'QOOH radicals, in the ion population. This is a significant observation, as these elusive radicals are thought to be involved in low temperature chain branching reactions because of the ability to add a second dioxygen. If these intermediate species are formed under the conditions of our experiment (2.5 mTorr and 307 K), they rapidly decompose via loss of HO<sup>•</sup> and HO<sub>2</sub><sup>•</sup>. The ability to synthesize and isolate a model alkylperoxyl radical as described here provides a novel pathway to probe the gas phase reactivity of these otherwise elusive species. This approach offers promise for the study of the bimolecular reactions of peroxyl radicals as well as their gas phase photochemistry.

Finally, the reaction of this distonic alkyl radical with dioxygen gives rise to characteristic products: the addition of O<sub>2</sub> (+32 Da) and neutral losses of HO<sup>•</sup> (+15 Da) and HO<sub>2</sub><sup>•</sup> (-1 Da). Such diagnostic gas phase chemistry constitutes a mass spectral fingerprint for not only the verification of distonic radical character but also characterization of the structure of the radical itself. As such, this study supports other recent suggestions that dioxygen is an effective probe reagent for elucidating the structure of the radical ions arising from contemporary mass spectrometric techniques (e.g., electron transfer dissociation and photodissociation).<sup>28,57</sup>

Acknowledgment. B.B.K. is supported through an Australian Postgraduate Award. D.G.H. and S.J.B. acknowledge the financial support of the Australian Research Council (DP0452849 and DP0986628) and the University of Wollongong. S.J.B. and B.B.K. thank the Australian Partnership for Advanced Computing (ANU, Canberra) for a generous allocation of resources under the Merit Allocation Scheme. We acknowledge Professor Paul Wenthold and Dr. Adam Trevitt for helpful discussions and the late Mr. Larry Hick whose technical ability and friendship are sorely missed.

Supporting Information Available: CID mass spectra and lists of geometric parameters and electronic and zero-point energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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JP9073398