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Carbon-carbon bond formation in the reaction of hydrated carbon dioxide radical anions with 3-butyn-1-ol

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Dedicated, in friendship and admiration, to Prof. Dr. Drs. h.c. mult. Helmut Schwarz on the occasion of his 75th birthday.

Abstract

Electrochemical activation of carbon dioxide in aqueous solution is a promising way to use carbon dioxide as a C1 building block. Mechanistic studies in the gas phase play an important role to understand the inherent chemical reactivity of the carbon dioxide radical anion. Here, the reactivity of CO$_2$$^-$($\text{H}_2\text{O}$)$_n$ with 3-butyn-1-ol is investigated by Fourier transform ion cyclotron (FT-ICR) mass spectrometry and quantum chemical calculations. Carbon-carbon bond formation takes place, but is associated with a barrier. Therefore, bond formation may require uptake of several butynol molecules. The water molecules slowly evaporate from the cluster due to the absorption of room temperature black-body radiation. When all water molecules are lost, butynol evaporation sets in. In this late stage of the reaction, side reactions occur including H$^*$ atom transfer and elimination of HOOC$^*$. 

Keywords: carbon dioxide activation; carboxylation of olefins; water cluster; ion-molecule reactions; nanocalorimetry

Highlights

- Hydrated carbon dioxide radical anions attack the triple bond of 3-butyn-1-ol.
- Clear evidence for the formation of a covalent C-C bond is found.
- A barrier in the range of 50 kJ mol$^{-1}$ makes it possible that carbon dioxide radical anions and 3-butyn-1-ol coexist in a cluster with about 50 water molecules for several seconds without reacting.

Graphical abstract
1. Introduction

Carbon dioxide is a promising C1 feedstock [1], and significant effort is currently devoted to closing the carbon cycle in chemical industry by emerging carbon capture and utilization (CCU) technologies [2,3]. Among the numerous routes to carbon dioxide activation [4], electrochemical [5] and photoelectrochemical [6] pathways are the most elegant approaches. The first step in electrocatalytic CO₂ activation is electron transfer to form either the CO₂$$^\text{−}\text{−}$$ radical anion or the hydroxyformyl radical HOCO$$^\text{•}$$ [5]. Both radical species are short lived and difficult to investigate. Due to its charge, the CO₂$$^\text{−}\text{−}$$ radical anion is ideal for mass spectrometric studies in the gas phase, and a considerable body of work is available on its fundamental properties as recently reviewed by Weber [7,8].

While bare CO₂$$^\text{−}\text{−}$$ is metastable [9–11], carbon dioxide [12–14] or water solvated species [15,16] are long lived and can be conveniently studied in molecular beams or ion trapping instruments. Infrared and electronic spectroscopy of metal ions solvated by carbon dioxide has revealed intriguing details on metal to ligand electron transfer [17–33] and intracluster chemical reactions including oxalate formation [34,35] as well as metal insertion into the C-O bond, which has been seen for Ti(CO₂)ₙ [36]. Photoelectron spectroscopy provided detailed information on CO₂ binding in the quinoline-CO₂$$^\text{−}\text{−}$$ complex [37] as well as anionic coinage metal complexes [38]. Co-adsorption of CO₂ and pyridine to Co$$^\text{−}$$ led to strong binding of both ligands to the central metal atom [39]. Photodissociation and photoelectron imaging of CO₂$$^\text{−}\text{−}$$(H₂O)ₙ was reported by Sanov and co-workers [40–42]. For carbon dioxide activation by carbonic anhydrase, a gas-phase model was developed by Schwarz and co-workers [43].

Electron transfer occurs efficiently in bimolecular reactions of CO₂ with (H₂O)ₙ$$^\text{−}$$ [44–50] while reactions of CO₂ with hydrated metal ions M$$^+$$-(H₂O)ₙ, M = Mg, Cr, Co [51–53] are very inefficient. Formation of C-H bonds was observed in the reaction of metal
hydrides with neutral CO₂ [54,55] and in collisions of CO₂•−(H₂O)_n with CH₃SH [56] while collisions with CH₃SSCH₃ provided evidence for C-S bond formation [57]. C-N bond formation has been reported with pyridine [58,59] and NO [60] as well as radical substitution with CH₃I to form CH₃CO₂− [61,62]. However, charge transfer as observed for nitromethane, acetaldehyde and benzaldehyde [63] competes with radical addition. Proton transfer to CO₂•− was observed with strong acids where evidence for HOCO• formation was obtained in reactions of CO₂•−(H₂O)_n with HNO₃ [64].

C-C bond formation is of key importance for the use of CO₂ as C₁ building block, and it has been observed in reactions of CO₂•−(H₂O)_n with methyl acrylate [65] and allyl alcohol [66] as well as in metal-CO₂ complexes with acetaldehyde [67]. Nanocalorimetry and quantum chemical calculations corroborated in all cases that CO₂•− attacks the unsaturated bond. One might expect that the reaction with an organic molecule containing a triple bond should proceed in a similar way. To test this prediction, the reaction of CO₂•−(H₂O)_n with 3-butyn-1-ol is investigated by Fourier transform ion cyclotron (FT-ICR) mass spectrometry and quantum chemical calculations.

2. Experimental and computational methods

The experiments are performed on a modified Bruker/Spectrospin CMS47X FT-ICR mass spectrometer described in detail before [48,49,68]. Hydrated carbon dioxide radical anions CO₂•−(H₂O)_n are generated in an external laser vaporization source [69–71] with a zinc target and traces of H₂O and CO₂ seeded in the helium carrier gas [48]. The charged clusters are transferred via an electrostatic lens system to the ICR cell and stored at room temperature. 3-butyn-1-ol (butynol) is degassed by several freeze-pump-thaw cycles and introduced into the UHV region through a leak valve at a constant pressure of typically 0.6–4 × 10⁻⁸ mbar. The reaction is monitored by
recording a series of mass spectra with increasing reaction delays. Pressure was calibrated following standard procedures [72–74].

The thermochemistry of sequential uptake of butynol is analyzed by nanocalorimetry [48,75,76]. We have shown previously [48] that the average cluster size of reactant and product species evolves in time according to the differential equations (1) and (2). Eq. (1) and the first term in eq. (2) account for black-body radiation induced dissociation (BIRD) of water clusters [77–91], with the linear dependence on cluster size described by $k_f$ [81,86], as well as the contribution of the ionic core to the infrared absorption cross sections described by $N_{0,R}$, $N_{0,P}$. The evaporation of water molecules due to the released reaction enthalpy is accounted for by the second term in eq. (2). Main result of the fit is $\Delta N_{vap}$, the average number of evaporated water molecules. Photodissociation experiments in the groups of Williams [92] and von Issendorff [93] independently established the energy required to evaporate a water molecule from the cluster with $\Delta E_{vap} = 43.3 \pm 3.1 \text{ kJ mol}^{-1}$.

$$dN_R = -k_f(N_R - N_{0,R})dt$$  \hspace{1cm} (1)

$$dN_p = -k_f(N_p - N_{0,p})dt + (N_R - \Delta N_{vap} - N_p)\left(\frac{k_f R}{I_p}\right)dt$$  \hspace{1cm} (2)

The average cluster size $N_R$, $N_P$ as a function of time is extracted from the mass spectra and fitted to the differential equations (1) and (2) with a genetic algorithm. Previous comparisons to literature thermochemistry illustrate that the method works well, provided a sufficient number of data sets is analyzed so that some averaging is possible [49,65,73,94,95].

Observed ions and reactions were analyzed using methods of theoretical chemistry within density functional theory (DFT), employing the B3LYP functional with Grimme’s dispersion correction D2 [96] along with the def2TZVP basis set, further
denoted as B3LYP+D2/def2TZVP. All reported energies were corrected for zero-point energy (ZPE). All calculations were performed in the Gaussian suite of programs [97].

3. Results and Discussion

As observed previously in the reaction of hydrated ions with alcohols [66,98], individual butynol molecules are taken up sequentially, reaction (3) and Figure 1a,b. The square brackets in reaction (3) indicate that it remains open whether C-C bond formation, potentially followed by oligomerization, has taken place or not. After 20 s exposure to the reaction gas, Figure 1c, up to 8 butynol molecules have been taken up, and almost all water molecules are lost due to ligand exchange or BIRD, reaction (4). As soon as all water molecules have evaporated, the more strongly bound butynol molecules follow, reaction (5). The main product after 40 s is \([\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^-\), which slowly reacts to \([\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{H}]^-\), reaction (6). After \( t \sim 130 \) s, \([\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{H}]^-\) is the main product. Reactions (3–6) are similar to the reactions of \( \text{CO}_2^-\text{(H}_2\text{O})_n \) with allyl alcohol [66]. Rate coefficients have been obtained from a kinetic fit of the first four uptake steps, see Figure 2a and Table 1.

\[
\begin{align*}
[\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_m]^-\cdot(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH} & \rightarrow [\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_{m+1}]^-\cdot(\text{H}_2\text{O})_{n-x} + x \text{H}_2\text{O} \\
[\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_m]^-\cdot(\text{H}_2\text{O})_n + h\nu_{IR} & \rightarrow [\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_m]^-\cdot(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} \\
[\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_m]^- + h\nu_{IR} & \rightarrow [\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_{m-1}]^- + \text{C}_4\text{H}_5\text{OH} \\
[\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^- + \text{C}_4\text{H}_5\text{OH} & \rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{H}]^- + \text{C}_4\text{H}_4\text{OH}^* 
\end{align*}
\]

For butynol, however, several additional products are observed after 300 s, Figure 3, namely \([\text{C}_4\text{H}_5\text{O},\text{C}_4\text{H}_5\text{OH}]^-\) at m/z = 139.072, \([\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{C}_2\text{H}_4\text{OH}]^-\) at m/z = 159.077, and \([\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{OH}]^-\) at m/z = 131.031. The kinetic behavior between
100 s and 300 s indicates that the only reaction of \([\text{CO}_2, \text{C}_4\text{H}_5\text{OH}]^-\) competing with reaction (6) is elimination of HOCO•, reaction (7).

\[
[\text{CO}_2, \text{C}_4\text{H}_5\text{OH}]^- + \text{C}_4\text{H}_5\text{OH} \rightarrow [\text{C}_4\text{H}_5\text{O}, \text{C}_4\text{H}_5\text{OH}]^- + \text{HOCO}^+
\]  

The other side products are formed from clusters containing at least two butynol molecules, indicating that a third butynol molecule is required to form a stable bond with the radical fragment, reactions (8), (9). These radical abstraction reactions confirm that at this late stage of the reaction, CO2− is covalently bound to butynol.

**Figure 1:** Mass spectra taken at a) 0 s, b) 5 s and c) 20 s reaction delay at a pressure of 1×10−8 mbar. The cluster size distribution at \(t = 0\) s is in the range of \(n = 31–78\), peaking at \(n = 53\). The sequential uptake of up to 8 butynol molecules, reaction (3), into the \(\text{CO}_2^–(\text{H}_2\text{O})_n\) cluster is observed, with \(m = 8\) represented by the small peak at \(m/z 604.325\). Lines connect species \([\text{CO}_2, (\text{C}_4\text{H}_5\text{OH})_m, (\text{H}_2\text{O})_n]^-\) that differ only in the number of water molecules \(n\).
Table 1: Rate coefficients $k_{abs}$ and nanocalorimetry (number of evaporating water molecules $\Delta N_{vap}$ and absorption energy $\Delta E_{nc}$) of the uptake of butynol by $[\text{CO}_2(\text{C}_4\text{H}_5\text{OH})_m(\text{H}_2\text{O})_n]^{-}$, reaction (3).

<table>
<thead>
<tr>
<th>m</th>
<th>$k_{abs} / 10^{-9}$ cm$^3$ s$^{-1}$</th>
<th>$\Delta N_{vap}$</th>
<th>$\Delta E_{nc} / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.17</td>
<td>1.8 ± 0.3</td>
<td>-73 ± 14</td>
</tr>
<tr>
<td>1</td>
<td>1.16</td>
<td>1.4 ± 0.3</td>
<td>-57 ± 14</td>
</tr>
<tr>
<td>2</td>
<td>1.12</td>
<td>2.5 ± 0.3</td>
<td>-104 ± 15</td>
</tr>
<tr>
<td>3</td>
<td>1.06</td>
<td>3.2 ± 0.3</td>
<td>-137 ± 16</td>
</tr>
<tr>
<td>4</td>
<td>0.98</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2: a) Kinetic and b),c) nanocalorimetric fit of the first three reaction steps ($p_{\text{butynol}} = 1 \times 10^{-8}$ mbar). Reactant ions (black square), uptake of 1$^{\text{st}}$ (red circle), 2$^{\text{nd}}$ (green triangle) and 3$^{\text{rd}}$ (blue diamond) butynol molecule.

$$[\text{CO}_2(\text{C}_4\text{H}_5\text{OH})_2]^{-} + \text{C}_4\text{H}_5\text{OH} \rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{C}_2\text{H}_4\text{OH}]^{-} + [\text{C}_4\text{H}_5\text{OH},\text{CCH}]^{-} \quad (8)$$

$$[\text{CO}_2(\text{C}_4\text{H}_5\text{OH})_2]^{-} + \text{C}_4\text{H}_5\text{OH} \rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{OH}]^{-} + [\text{C}_4\text{H}_5\text{OH},\text{C}_4\text{H}_5]^{-} \quad (9)$$
To investigate further the importance of the C-C bond formation upon uptake of the first butynol molecule, we analyzed the data sets of five independent experimental

Figure 3: Mass spectrum taken after 300 s reaction delay ($P_{\text{butynol}} = 1 \times 10^{-8} \text{ mbar}$).

Table 2: Reaction energies (in kJ/mol) calculated at the B3LYP+D2/def2TZVP level of theory, along with the respective reaction channels (as well as reverse reaction channels, e.g. “–4”) discussed in the text.

<table>
<thead>
<tr>
<th>Reaction No.</th>
<th>Reaction $\setminus n$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(-4)</td>
<td>$\text{CO}_2^-(\text{H}_2\text{O})_n + \text{H}_2\text{O} \rightarrow \text{CO}_2^-(\text{H}<em>2\text{O})</em>{n+1}$</td>
<td>-74</td>
<td>-58</td>
<td>-64</td>
<td>-58</td>
<td>-48</td>
<td>-</td>
</tr>
<tr>
<td>(-5)</td>
<td>$[\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^+(\text{H}_2\text{O})_n + \text{H}_2\text{O} \rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^+(\text{H}<em>2\text{O})</em>{n+1}$</td>
<td>-46</td>
<td>-68</td>
<td>-57</td>
<td>-50</td>
<td>-54</td>
<td>-</td>
</tr>
<tr>
<td>(-5)</td>
<td>$\text{C}_4\text{H}_5\text{OH} + \text{CO}_2^-(\text{H}_2\text{O})_n \rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^-(\text{H}_2\text{O})_n$</td>
<td>-135</td>
<td>-106</td>
<td>-117</td>
<td>-110</td>
<td>-102</td>
<td>-108</td>
</tr>
<tr>
<td>(-5)</td>
<td>$\text{C}_4\text{H}_5\text{OH} + [\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^-(\text{H}_2\text{O})_n \rightarrow [\text{CO}_2,\text{H}_2\text{O},\text{C}_4\text{H}_5\text{OH}]^-(\text{H}_2\text{O})_n$</td>
<td>-137</td>
<td>-172</td>
<td>-159</td>
<td>-159</td>
<td>-165</td>
<td>-166</td>
</tr>
<tr>
<td>(6)</td>
<td>$[\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^+(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH} \rightarrow$</td>
<td>-66</td>
<td>-65</td>
<td>-71</td>
<td>-69</td>
<td>-73</td>
<td>-70</td>
</tr>
<tr>
<td>(6)</td>
<td>$\rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{H}]^+(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH}^+$</td>
<td>-41</td>
<td>-44</td>
<td>-48</td>
<td>-55</td>
<td>-52</td>
<td>-62</td>
</tr>
<tr>
<td>(6)</td>
<td>$[\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^+(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH} \rightarrow$</td>
<td>-49</td>
<td>-48</td>
<td>-51</td>
<td>-45</td>
<td>-50</td>
<td>-48</td>
</tr>
<tr>
<td>(6)</td>
<td>$\rightarrow [\text{CO}_2,\text{C}_4\text{H}_5\text{OH},\text{CCH}]^+(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH}^+$</td>
<td>137</td>
<td>117</td>
<td>129</td>
<td>112</td>
<td>113</td>
<td>113</td>
</tr>
<tr>
<td>(7)</td>
<td>$[\text{CO}_2,\text{C}_4\text{H}_5\text{OH}]^+ + \text{C}_4\text{H}_5\text{OH} \rightarrow$</td>
<td>-17</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(7)</td>
<td>$\rightarrow [\text{C}_6\text{H}_6\text{O},\text{C}_4\text{H}_5\text{OH}]^+ + \text{HO}-\text{C}^-$</td>
<td>-</td>
<td>22</td>
<td>36</td>
<td>36</td>
<td>19</td>
<td>26</td>
</tr>
<tr>
<td>(8)</td>
<td>$[\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_2]^+(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH} \rightarrow$</td>
<td>2</td>
<td>34</td>
<td>17</td>
<td>11</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>(9)</td>
<td>$[\text{CO}_2,(\text{C}_4\text{H}_5\text{OH})_2]^+(\text{H}_2\text{O})_n + \text{C}_4\text{H}_5\text{OH} \rightarrow$</td>
<td>-</td>
<td>22</td>
<td>36</td>
<td>36</td>
<td>19</td>
<td>26</td>
</tr>
</tbody>
</table>
Figure 4: Structures of ions and molecules included in Table 2. For [(C₄H₅OH)ₙ.CO₂]⁻·(H₂O)ₙ, two isomers are shown, with and without a C-C bond formed, with relative energy in kJ/mol. Calculated at the B3LYP+D2/def2TZVP level of theory.
runs with nanocalorimetry [48,49]. A typical fit is shown in Figure 2b,c, all fits are available in the Supporting Information (SI). The number of water molecules evaporating after adsorption of the first butynol molecule, Table 1, is \(\Delta N_{\text{vap}} = 1.8 \pm 0.3\), which corresponds to \(\Delta E_{\text{nc}} = -73 \pm 14\) kJ mol\(^{-1}\). This is close to the \(-69 \pm 43\) kJ mol\(^{-1}\) observed for CO\(_2\)\(^-\) addition to allyl alcohol [66] and significantly below the \(-95 \pm 22\) kJ mol\(^{-1}\) obtained for methyl acrylate [65].

In Table 2, calculated reaction energies for ions with up to five water molecules are collected; Figure 4 contains the respective molecular structures. CO\(_2\)\(^-\) is predicted to bind to the terminal CH moiety of butynol, forming a C-C bond as well as a hydrogen bond between CO\(_2\) and OH groups, with an energy release of 135 kJ/mol for the structure without water molecules. For hydrated structures, the energy decreases to \(~110\) kJ/mol. When the C-C bond is not formed, the energy drops by about 40–50 kJ/mol (see [CO\(_2\),C\(_4\)H\(_5\)OH]\(^-\) isomers without the C-C bond in Figure 4). The adsorption energy without C-C bond formation is then in better agreement with the experimentally obtained value for larger clusters (-73 kJ/mol, Table 1), indicating that CO\(_2\)\(^-\) is predominantly not covalently bound to the butynol molecule. A relaxed scan optimization showed that even when the hydrogen bonding network is in favorable position to form the C-C bond between butynol and CO\(_2\)\(^-\), there is still a barrier of about 35 kJ/mol for the structure with five water molecules (Figure S3). Together with the reorganization energy of this favorable structure relative to the minimum structure displayed in Figure 4, the barrier for C-C bond formation lies in the range of 50 kJ mol\(^{-1}\). The hydration energy of both CO\(_2\)\(^-\) and [CO\(_2\),C\(_4\)H\(_5\)OH]\(^-\) ions for a low number of water molecules is calculated to be similar, \(~50–60\) kJ/mol. In larger clusters, fast evaporation of water molecules, which are bound with only 43.3 kJ/mol, may remove excess energy before C-C bond formation takes place. When almost all water molecules have evaporated due to BIRD and water binding energies increase, also the
remaining clusters undergo C-C bond formation, then activated by room temperature black-body radiation and unreactive collisions with 1-butynol.

For structures with two butynol molecules, two isomers are again considered, with and without a C-C bond between the butynol units (Figure 2). When the C-C bond is formed, the adsorption energy of butynol to $[\text{C}_4\text{H}_5\text{OH},\text{CO}_2]^{--}(\text{H}_2\text{O})_n$ amounts to ~160 kJ/mol for 2–5 water molecules. Without the bond, the energy is reduced to about 60–80 kJ/mol. Judging from the low experimentally measured adsorption energy values collected in Table 1, we might expect that adsorption again takes place preferentially without C-C bond formation. Based on the high adsorption energy obtained within nanocalorimetric measurements, a C-C bond seems to be formed with higher probability upon uptake of the third and fourth butynol molecule, while a fraction of molecules is still expected to bind only through hydrogen bonds.

Next, we discuss reactions with transfer of various fragments ($\text{H}^+$, $\text{OH}^+$, $\text{CCH}^+$, $\text{C}_2\text{H}_4\text{OH}^+$) from a butynol molecule to $[\text{C}_4\text{H}_5\text{OH},\text{CO}_2]^{--}(\text{H}_2\text{O})_n$. The incoming fragment is predicted to adsorb on the exposed carbon atom of $[\text{C}_4\text{H}_5\text{OH},\text{CO}_2]^{--}(\text{H}_2\text{O})_n$ (see Figure 4). Among these reactions, $\text{H}^+$, $\text{OH}^+$ and $\text{CCH}^+$ transfers are calculated to be exothermic with about 50–70 kJ/mol while $\text{C}_2\text{H}_4\text{OH}^+$ transfer is markedly endothermic, with about 110 kJ/mol; in agreement with the experiment, this reaction needs more than one butynol molecule to proceed as we discuss below. All named reactions are relatively insensitive to the degree of hydration.

Reaction (7) with HOCO$^-$ evaporation is predicted to be mildly exothermic with -17 kJ/mol (Table 2), forming a compact $[\text{C}_4\text{H}_5\text{O},\text{C}_4\text{H}_5\text{OH}]^-$ structure shown in Figure 4. Note however that formation of such structure requires certain bond rearrangement, associated with a barrier above the dissociation asymptote. Reactions (8) and (9) start with an ion with several butynol molecules and split another incoming butynol, either to $\text{C}_2\text{H}_4\text{OH}^+$ and $\text{CCH}^+$ or $\text{OH}^+$ and $\text{C}_4\text{H}_5^+$. When modelled with two butynol molecules
in the initial ion, we obtain mildly endothermic reactions for (8,9), see Table 2. On the other hand, in case the two butynol molecules are not bound by a covalent bond, the reaction energy decreases by about 90 kJ/mol as discussed above, making both reactions exothermic.

4. Conclusions

The reaction of CO$_2$$^•$$^-$($\text{H}_2\text{O})_n$ with butynol proceeds via sequential uptake of butynol molecules by the clusters, similar to the previously studied reaction with allyl alcohol. The stability of the long-term products clearly shows that formation of a covalent C-C bond between the carbon dioxide radical anion and butynol takes place. Nanocalorimetry in comparison with quantum chemical calculations indicate that this covalent bond formation does not take place immediately upon uptake of the first molecule. Attack of the triple bond by CO$_2$$^•$$^-$ is associated with a barrier, as revealed by a relaxed potential energy surface scan. This barrier can be overcome when additional butynol molecules are taken up, which heats the cluster for a short time before water evaporation takes place, and room temperature black body radiation. After long reaction delays, side reactions are observed, including H atom transfer and elimination of HOCO$^•$, which arise from the high reactivity of the triple bond of butynol.

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