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# Are the anions $\text{MeO}(\text{CO})_n^-$ ( $n = 1$ and $2$ ) methoxide anion donors in the gas phase? A theoretical investigation

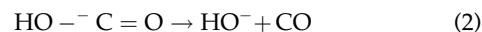
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1. The anions  $\text{CH}_3\text{O}^-\text{CO}$  and  $\text{CH}_3\text{OCO}^-\text{CO}$  are both methoxide anion donors. The processes  $\text{CH}_3\text{O}^-\text{CO} \rightarrow \text{CH}_3\text{O}^- + \text{CO}$  and  $\text{CH}_3\text{OCO}^-\text{CO} \rightarrow \text{CH}_3\text{O}^- + 2\text{CO}$  have  $\Delta G$  values of  $+8$  and  $-68 \text{ kJ mol}^{-1}$ , respectively, at the CCSD(T)/6-311++G(2d, 2p)//B3LYP/6-311++G(2d,2p) level of theory.
2. The reactions  $\text{CH}_3\text{OCOCO}_2^- \rightarrow \text{CH}_3\text{OCO}_2^- + \text{CO}$  ( $\Delta G = -22 \text{ kJ mol}^{-1}$ ) and  $\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{COCH}(\text{O}^-)\text{OCH}_3 + \text{CO}$  ( $\Delta G = +19 \text{ kJ mol}^{-1}$ ) proceed directly from the precursor anions via the transition states  $(\text{CH}_3\text{OCO} \cdots \text{CO}_2)^-$  and  $(\text{CH}_3\text{COCHO} \cdots \text{CH}_3\text{OCO})^-$ , respectively.
3. Anion  $\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3$  undergoes methoxide anion transfer and loss of two molecules of CO in the reaction sequence  $\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}(\text{O}^-)\text{COCO}_2\text{CH}_3 \rightarrow [\text{CH}_3\text{CHO}(\text{CH}_3\text{OCO}^-\text{CO})] \rightarrow \text{CH}_3\text{CH}(\text{O}^-)\text{OCH}_3 + 2\text{CO}$  ( $\Delta G = +9 \text{ kJ mol}^{-1}$ ). The hydride ion transfer in the first step is a key feature of the reaction sequence. Copyright © 2010 John Wiley & Sons, Ltd.

We recently attempted to use oxalyl esters to produce the radical anion  $[\text{O}_2\text{CCO}_2]^-$ , which we intended to convert into neutral  $\text{O}_2\text{CCO}_2$  by charge stripping. This process occurred in poor yield; instead, the negative ion spectra of  $\text{ROC}(=\text{O})\text{CO}_2^-$  ( $\text{R} = \text{Me}$ , *isoPr* and *tertBu*) exhibited base peaks corresponding to the processes  $[(\text{M}-\text{H})^- - \text{CO}]^-$  (S. Dua and J. H. Bowie, unpublished observations). At the time that this work was being carried out, Soldi-Lose *et al.* reported the same process and proposed a mechanism for the rearrangement.<sup>1</sup> Loss of CO from  $[\text{M}-\text{H}]^-$  anions has been observed previously from a variety of esters including phenyl propionates,<sup>2</sup> succinates,<sup>3</sup> pyruvates and hydroxy acetates,<sup>4</sup> and acyloxy acetates.<sup>5</sup> <sup>13</sup>C-Labeling has confirmed loss of <sup>13</sup>CO from anions containing the  $^{-13}\text{CO}_2\text{R}$  moiety.<sup>4,5</sup> In all these cases<sup>1–5</sup> it was proposed that the loss of CO originates from an intermediate containing an alkoxy carbonyl anion  $\text{RO}^-\text{C}=\text{O}$ , rather than via an  $\text{ABC}^- \rightarrow \text{AC}^- + \text{B}$  process proceeding through a three-membered transition state.



The hydroxycarbonyl anion  $\text{HO}^-\text{CO}$  has been observed from the oxalate anion,<sup>6</sup>  $\alpha$ -hydroxycarboxylates<sup>7</sup> and  $[\text{M}-\text{H}]^-$  parent anions of amino acids.<sup>8–11</sup> Loss of CO is the major fragmentation process from the oxalate anion  $\text{HO}_2\text{CCO}_2^-$  (Eqn. (1)),<sup>6</sup> and from the  $(\text{M}-\text{H})^-$  anions of amino acids.<sup>8–11</sup> A theoretical study at the RMP2-FC/6-311++G\*\*//RHF/6-31+G\* level of theory confirmed the hydroxycarbonyl anion to be an hydroxyl anion donor.<sup>12</sup> The process shown in Eqn. (2) requires an energy  $\Delta E$  of  $+71 \text{ kJ mol}^{-1}$  ( $\Delta G = +21 \text{ kJ mol}^{-1}$ ). This reaction is more favourable than hydrogen transfer to form the formate anion (Eqn. (3)), which, although favourable ( $-154 \text{ kJ mol}^{-1}$ ), has a barrier of  $122 \text{ kJ mol}^{-1}$ .<sup>12</sup>

The negative ion spectra of deprotonated (acyloxy)acetates  $[\text{R}^1\text{COO}^-\text{CHCO}_2\text{R}^2]$  ( $\text{R}^1$  and  $\text{R}^2 = \text{alkyl}$ ) indicate a rearrangement to deprotonated acylhydroxyacetates  $[\text{R}^1\text{COCH}(\text{O}^-)\text{CO}_2\text{R}^2]$ , with the rearranged species losing both CO and the elements of  $\text{C}_2\text{O}_2$ .<sup>5</sup> It was suggested that the species losing “ $\text{C}_2\text{O}_2$ ” corresponds to an ion-neutral complex containing the anion  $(\text{R}^2\text{OCO}^-\text{CO})$ .<sup>5</sup>

This paper revisits (a) the methoxycarbonyl anion using theoretical calculations to investigate: (i) the dissociation of  $\text{MeO}^-\text{CO}$  to  $\text{MeO}^-$  and CO, and (ii) the loss of CO from the  $[\text{M}-\text{H}]^-$  anions of two representative systems, the oxalate species  $\text{MeOC}(=\text{O})\text{CO}_2^-$  and the acyloxy acetate anion  $\text{MeCO}_2\text{CHCO}_2\text{Me}$ , and (b) the mechanism for the loss of the elements of “ $\text{C}_2\text{O}_2$ ” from  $\text{MeCO}_2\text{CHCO}_2\text{Me}$ , i.e. to determine whether the species  $\text{MeOCO}^-\text{CO}$  is a methoxide anion donor and whether the neutral loss(es) involved in this process is (are) transient  $\text{C}_2\text{O}_2$ <sup>13</sup> or two molecules of CO.

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<sup>†</sup>Suresh Dua left an academic career in India to come to Australia in the early 1990s. He was a research associate in my research group for more than a decade before moving to the Defence Science and Technology Organisation (Edinburgh, South Australia). He died in early December 2009 after a long battle with serious illness. He is survived by his wife and two children. He was an outstanding organic chemist and a wonderful mentor to my graduate students. A friend and colleague sadly missed. This is the 84th Dua/Bowie paper.

## EXPERIMENTAL

### Mass spectra

Tandem mass spectrometry (MS/MS) spectra were measured (using an electric sector scan) with a VG ZAB 2HF mass spectrometer. Full experimental details have been reported previously.<sup>14</sup> The specific experimental details were as follows: a chemical ionisation slit was used in the ion source, the ionising energy was 70 eV, the source temperature was 150°C, and the accelerating voltage 7 kV. Samples were introduced through the septum inlet (maintained at 100°C) (measured pressure inside the source housing  $5 \times 10^{-7}$  mm Hg). Deprotonation was effected by  $\text{NH}_2^-$  (from  $\text{NH}_3$ ; measured pressure inside the source housing  $1 \times 10^{-5}$  mm Hg). The estimated source pressure was  $10^{-1}$  mm Hg. Helium was used in the second of two collision cells; the pressure of He adjusted so that 90% of the main beam was transmitted through the collision cell. This corresponds to an average of 1.1 to 1.2 collisions per ion.<sup>15</sup> The precursor anion  $\text{MeOC(=O)CO}_2^-$  was produced by an  $\text{S}_{\text{N}}2$  reaction between dimethyloxalate and  $\text{NH}_2^-$  (from  $\text{NH}_3$ ). The acyloxy acetate anion  $\text{MeCO}_2\text{CHCO}_2\text{Me}$  was formed by deprotonation of  $\text{MeCO}_2\text{CH}_2\text{CO}_2\text{Me}$  by  $\text{NH}_2^-$ ; MS/MS data for this anion and those of other (acyloxy)acetates have been reported previously.<sup>5</sup> Fragmentations may occur both inside and outside the collision cell when a voltage of 1000 V is applied to the collision cell. A peak shifted from the normal value is produced by a collision process occurring within the cell, whereas an unshifted peak is due to processes occurring outside the cell.

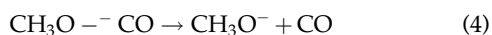
### Computational details

Geometry optimisations were carried out with the Gaussian 03 suite of programs<sup>16</sup> using the Becke B3LYP method<sup>17</sup> with the split-valence 6-311++G(2d,2p) basis set.<sup>18</sup> Stationary points were determined by calculation of the frequencies using analytical gradient procedures, according to the principle of either minima (no imaginary frequencies) or transition states (one imaginary frequency). The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations.<sup>19</sup> Single-point energies for the B3LYP/6-311++G(2d,2p) geometries were determined using the CCSD(T)/6-311++G(2d,2p) level of theory<sup>20</sup> including zero-point energy correction (unscaled).

## RESULTS AND DISCUSSION

### The methoxycarbonyl anion ( $\text{MeO}^-\text{CO}$ )

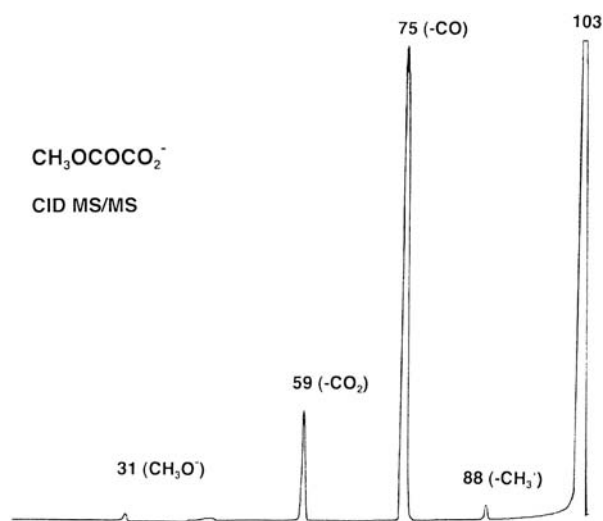
First, let us consider the methoxycarbonyl anion in isolation, and determine how much energy is required to cause it to dissociate to  $\text{MeO}^-$  and CO. Full details of the structure and energies of species involved are contained in Supplementary Table 1 (see Supporting Information). Energies were calculated at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. The process shown in Eqn. (4) has  $\Delta E = 41 \text{ kJ mol}^{-1}$  and  $\Delta G = 8 \text{ kJ mol}^{-1}$ , a process more favourable than the dissociation of the hydroxycarbonyl anion  $\text{HO}^-\text{CO}$  to  $\text{HO}^-$  and CO (Eqn. (2)).



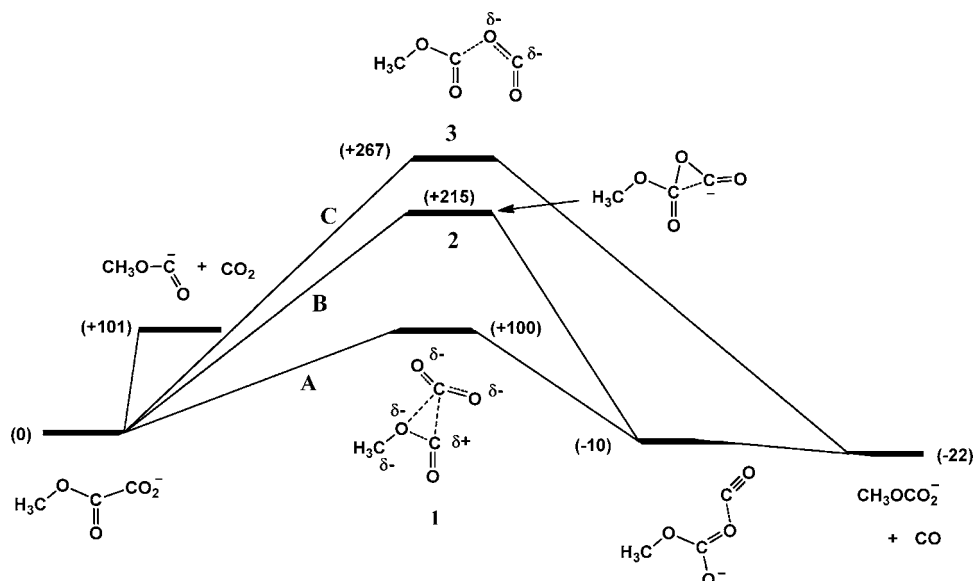
### The $\text{CH}_3\text{OCOCO}_2^-$ system

Soldi-Lose *et al.*<sup>1</sup> have carried out an extensive experimental and theoretical study of the loss of CO from  $\text{ROCOCO}_2^-$  systems ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , *iso*- $\text{C}_3\text{H}_7$  and *tert*- $\text{C}_4\text{H}_9$ ). Although our calculations for the loss of CO from  $\text{CH}_3\text{OCOCO}_2^-$  give the same overall mechanisms as those of Soldi-Lose *et al.*, their calculations at the MP2/6-311++G(3df,3pd)//MP2/6-311++G(d) level of theory show some differences from ours, and one of those differences is of particular importance in the description of the mechanistic pathway for this system. As a consequence, we summarise the results of our joint experimental/theoretical study here.

The collision-induced dissociation (CID) MS/MS data for  $\text{CH}_3\text{OCOCO}_2^-$  are recorded in Fig. 1. The major fragmentation involves loss of CO from the  $[\text{M}-\text{H}]^-$  anion. Minor processes from the  $[\text{M}-\text{H}]^-$  species include decarboxylation (to form  $m/z$  59), together with loss of  $\text{CH}_3^\bullet$  and formation of  $\text{CH}_3\text{O}^-$ . A summary of the theoretical calculations for the loss of CO from  $\text{CH}_3\text{OCOCO}_2^-$  [to form  $m/z$  75 (Fig. 1)] and dissociation to form  $\text{CH}_3\text{O}^-\text{CO}$  ( $m/z$  59) is shown in Fig. 2. Details of the geometries and energies (both  $\Delta E$  and  $\Delta G$  in  $\text{kJ mol}^{-1}$ ) of all the species shown in Fig. 2 are recorded in Supplementary Table 2 (see Supporting Information). The first process shown in Fig. 2 is decarboxylation, which proceeds without barrier to yield  $\text{CH}_3\text{O}^-\text{CO}$  plus  $\text{CO}_2$  ( $\Delta G = +101 \text{ kJ mol}^{-1}$ ). The potential surface for the loss of CO is complex. There are three transition states in which the incipient species  $\text{CH}_3\text{O}^-\text{CO}$  attaches to  $\text{CO}_2$ , and there are no reactive intermediates between the reactant and these transition states at the level of theory used in this study. The lowest energy reaction (A) proceeds through transition state 1 ( $+100 \text{ kJ mol}^{-1}$ ) with the CO lost originating from the  $\text{CH}_3\text{O}^-\text{CO}-$  moiety of transition state 1 (Fig. 2). The initial process forming transition state 1 is depicted in Scheme 1. The two other higher energy transition states (2 and 3) result in the loss of CO from the original  $\text{CO}_2$  with the initial reaction summarised for reactions B and C in Scheme 1.

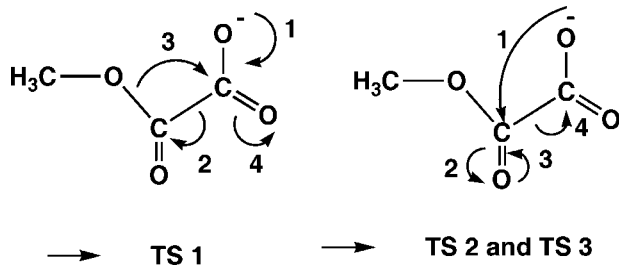


**Figure 1.** CID MS/MS of  $\text{CH}_3\text{OCOCO}_2^-$ . VG ZAB 2HF mass spectrometer. See Experimental section for experimental details.



**Figure 2.** Reaction coordinate profile of the reaction  $\text{CH}_3\text{OCOCO}_2^- \rightarrow \text{CH}_3\text{OCO}_2^- + \text{CO}$ . CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. Details of the geometries and energies of minima and transition states are contained in Supplementary Table 2 (see Supporting Information).

There are two differences between these results and those of Soldi-Lose *et al.* The first involves uncovering a high-energy pathway C (Fig. 2), which is non-competitive in energy terms with process A. The second difference is the more important. In the past we proposed that a reactive intermediate should be formed which is an ion-neutral complex in which  $\text{CH}_3\text{O}^-$  binds to a neutral molecule. In the present case the complex would be  $[\text{CH}_3\text{O}^- \cdot \text{CO}(\text{CO}_2)]$ , but our calculations do not detect this reactive intermediate. In contrast, calculations carried out by Soldi-Lose *et al.*<sup>1</sup> do indicate the presence of such an intermediate, and the authors state that the intermediate is formed without barrier from the reactant anion. At first we thought that this apparent discrepancy between the two results was merely a consequence of using two different levels of theory. *However, this is not so.* Careful reconsideration of this system using the two levels of theory reproduces the results obtained by both research groups. An intermediate is obtained at the level of theory used by Soldi-Lose *et al.* However, the Soldi-Lose intermediate turns out not to be on the reaction coordinate of the process involving the loss of CO [process A (Scheme 1 and Fig. 2)], since an IRC calculation on the Soldi-Lose transition state does not stop at the proposed reactive intermediate, but proceeds directly to the original reactant. It is an intermediate for the reaction  $\text{CH}_3\text{OCOCO}_2^- \rightarrow \text{CH}_3\text{O}^- \cdot \text{CO} + \text{CO}_2$ .



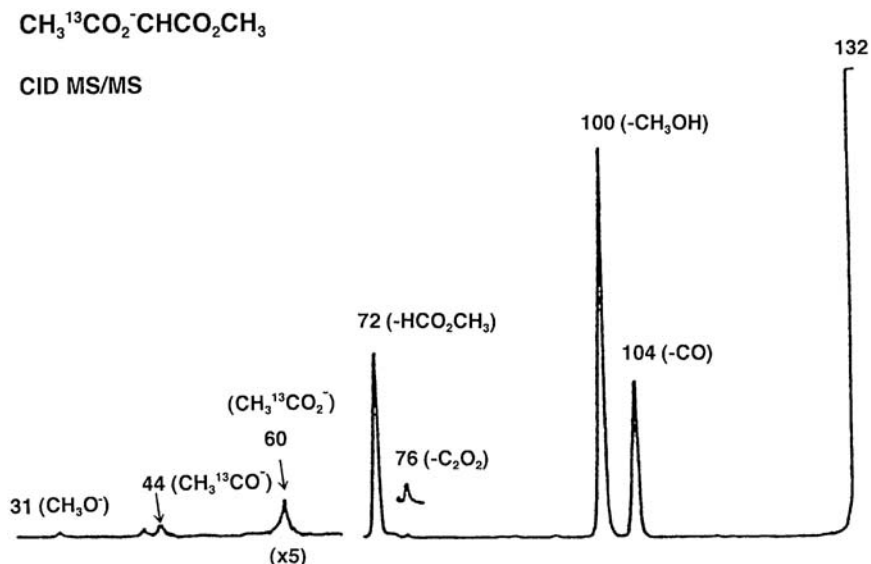
**Scheme 1.**

### The loss of CO from the $\text{CH}_3\text{CO}_2^- \text{CHCO}_2\text{Me}/\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3$ system

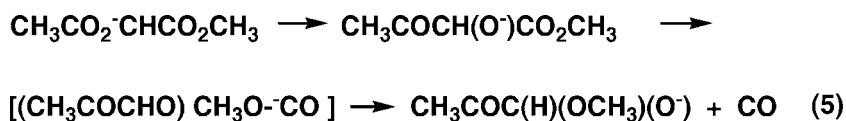
A variety of compounds of this type have been studied experimentally, and the spectrum of a  $^{13}\text{C}$ -labelled derivative (Fig. 3) shows that the CO lost has come from the  $-\text{CO}-\text{OCH}_3$  group.<sup>5</sup> The fragmentation is shown experimentally to be a relatively low-energy process because it occurs mainly in the field-free region of the mass spectrometer between the magnet and the first of the collision cells; i.e. essentially a unimolecular process occurring from an energised ion formed in the ion source, rather than being formed by collisional activation in a collision cell containing an inert gas. The mechanism proposed for the loss of CO is shown in Eqn. (5) of Scheme 2.<sup>5</sup> The proposal involves an initial rearrangement reaction, the product of which fragments to a  $\text{CH}_3\text{O}^- \cdot \text{CO}$  ion-neutral complex which then effects an  $\text{S}_{\text{N}}\text{I}$  reaction followed by loss of CO. A key feature of this mechanism is the proposed intermediacy of the methoxycarbonyl anion-neutral complex.

The results of the computational study of this system are recorded in Figs. 4 and 5, and full details of the geometries and energies of all systems shown in the two figures are listed in Supplementary Tables 3 and 4 (see Supporting Information).

The sequence for the loss of CO is shown in Fig. 4. The rearrangement of 4 to 5 proceeds over a barrier ( $\Delta G = 75 \text{ kJ mol}^{-1}$ ). Once 5 ( $+33 \text{ kJ mol}^{-1}$ ) is formed, the process involving loss of CO is analogous to that of reaction A (Fig. 2). *There is no reactive intermediate formed directly from 5 in this process.* Instead, the reaction proceeds over TS5/6 ( $+109 \text{ kJ mol}^{-1}$ ;  $+76 \text{ kJ mol}^{-1}$  above 5) to ion-neutral complex 6 which dissociates to product anion 7 and CO. The overall process is unfavourable by only  $19 \text{ kJ mol}^{-1}$  at the level of theory used in this study. The maximum energy required for the sequential reaction is only  $109 \text{ kJ mol}^{-1}$ : in agreement with the experimental observation that this process occurs for energised



**Figure 3.** CID MS/MS of  $\text{CH}_3^{13}\text{CO}_2^-\text{CHCO}_2\text{CH}_3$ . VG ZAB 2HF mass spectrometer. See Experimental section for experimental details.

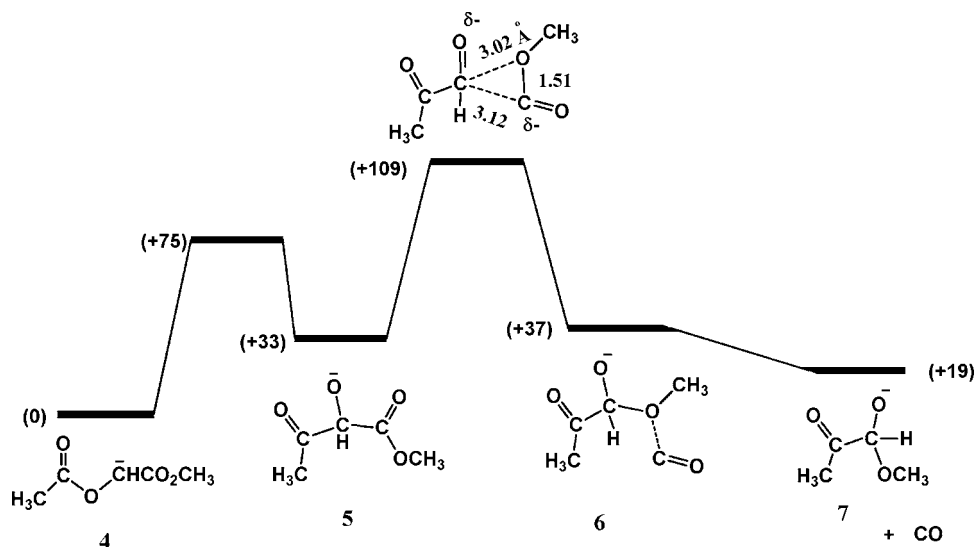


**Scheme 2.**

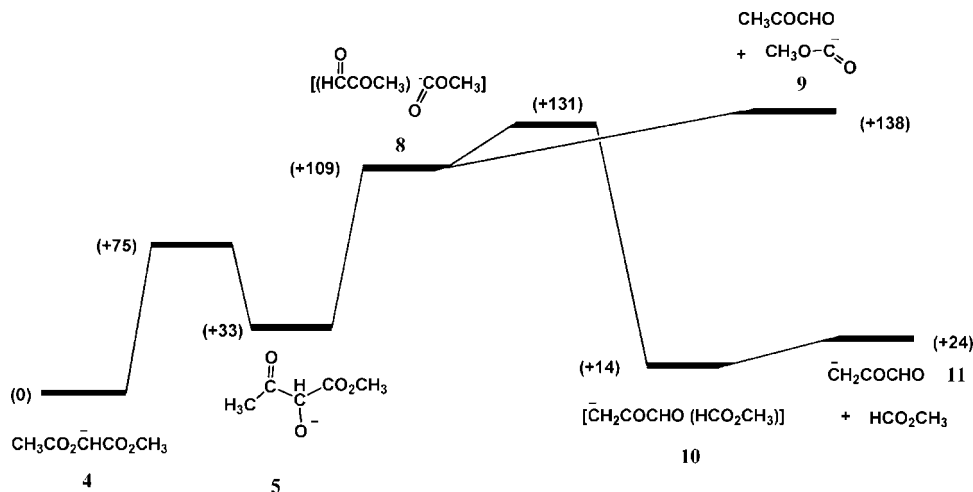
source-formed ions, rather than by bimolecular collisional activation in a collision cell containing an inert gas.

It is instructive to now consider the reactions involving the competitive formation of  $\text{CH}_3\text{O}^-\text{CO}$  ( $m/z$  59) and  $[(\text{M}-\text{H})^--\text{HCO}_2\text{CH}_3]$  in this system and to compare these with the loss of CO considered above. We mentioned above that the loss of

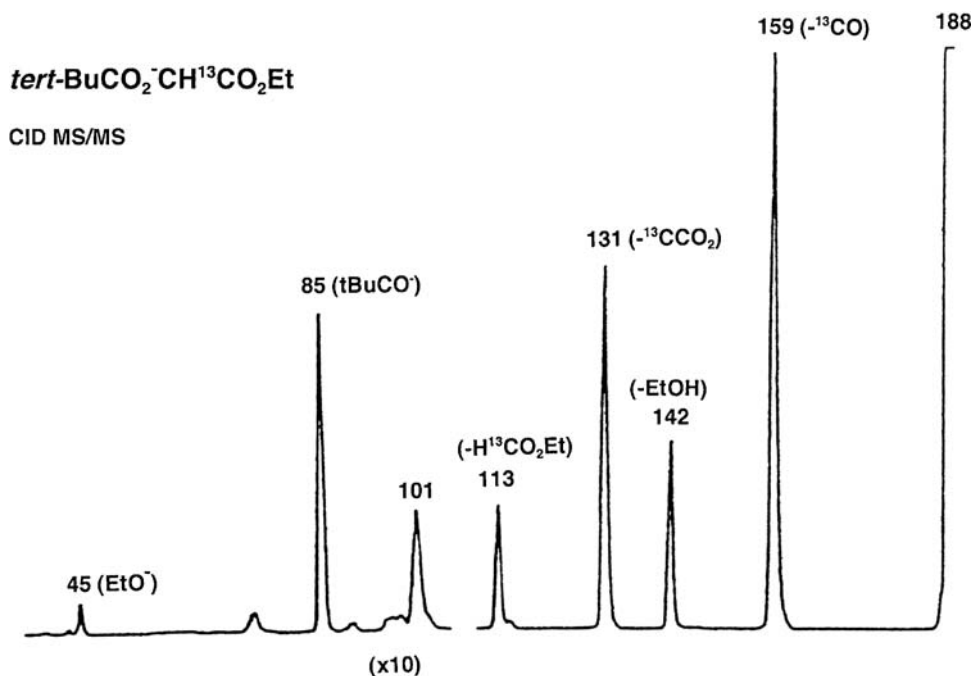
CO occurred mainly in the field-free region preceding the first collision cell. A similar experiment for these two processes mentioned above shows almost equal formation of both ions in the field-free region and in the collision cell, suggesting that these processes require more excess energy than that shown in Fig. 4 for loss of CO. The two reactions are



**Figure 4.** Reaction coordinate profile of the reaction  $\text{CH}_3\text{CO}_2^-\text{CHCO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{COCH}(\text{O}^-)(\text{OCH}_3) + \text{CO}$ . CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. Details of the geometries and energies of minima and transition states are contained in Supplementary Table 3 (see Supporting Information).



**Figure 5.** Reaction coordinate profiles of the reactions  $\text{CH}_3\text{CO}_2\text{CHCO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{COCHO} + \text{CH}_3\text{O}^-\text{CO}$  and  $\text{CH}_3\text{CO}_2\text{CHCO}_2\text{CH}_3 \rightarrow ^-\text{CH}_2\text{COCHO} + \text{HCO}_2\text{CH}_3$ . CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. Details of the geometries and energies of minima and transition states are contained in Supplementary Table 4 (see Supporting Information).

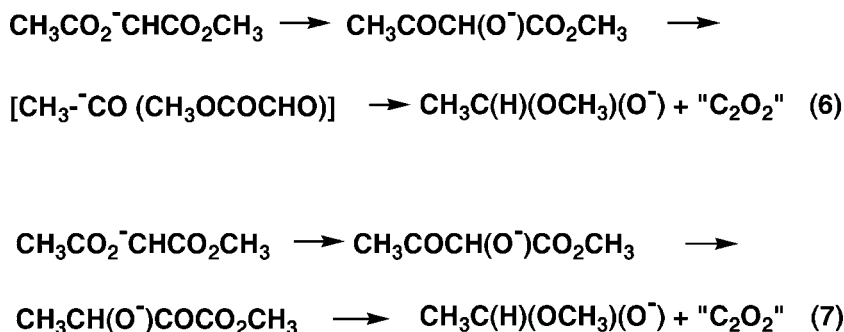


**Figure 6.** CID MS/MS of  $\text{tert-BuCO}_2\text{CH}^{13}\text{CO}_2\text{Et}$ . VG ZAB 2HF mass spectrometer. See Experimental section for experimental details.

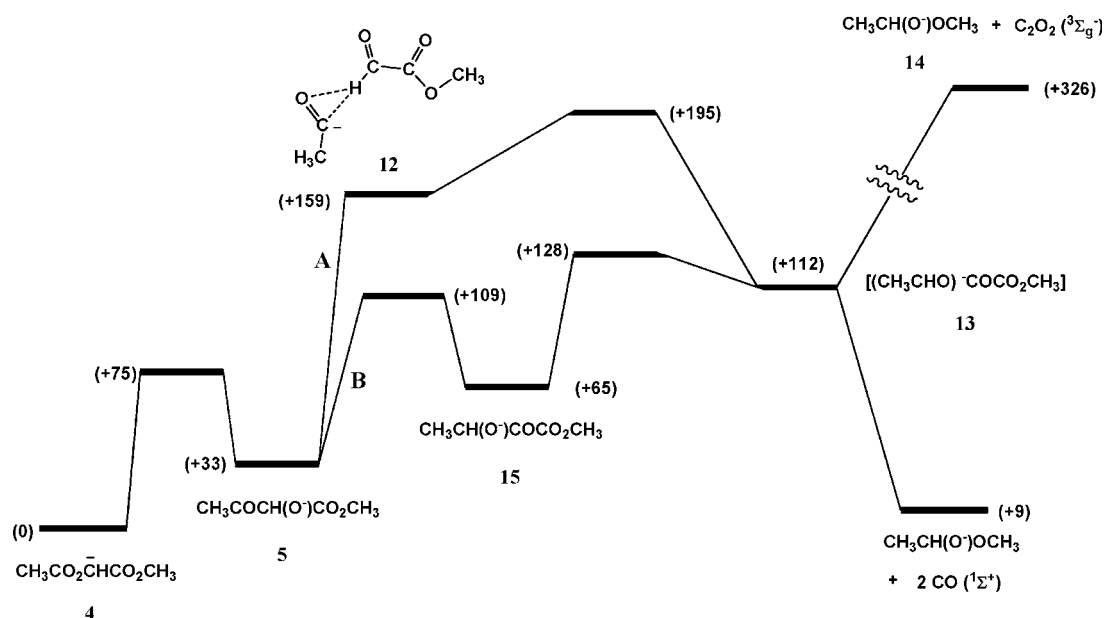
shown in Fig. 5 with full details of geometries and energies listed in Supplementary Table 4 (see Supporting Information). Most of the data contained in Fig. 5 are self explanatory. Of particular interest is that there is a reactive intermediate (8) formed in this sequence. It is formed without apparent barrier from 5. The key finding is that ion-neutral complex 8 is quite different from that we were expecting to be involved in the loss of CO. In this case, ion-neutral complex 8 is an H-bonded species which does not lose CO: rather, it either decomposes competitively to  $\text{CH}_3\text{O}^-\text{CO}$  (9) and  $\text{CH}_3\text{COCHO}$  (+138  $\text{kJ mol}^{-1}$ ), or effects proton transfer with-

in the complex to proceed through TS8/10 (+131  $\text{kJ mol}^{-1}$ ) to ion-neutral complex 10 which dissociates to  $\text{HCO}_2\text{CH}_3$  and  $^-\text{CH}_2\text{COCHO}$  (11) (+24  $\text{kJ mol}^{-1}$ ).<sup>a</sup> Both these processes require more excess energy than that involving loss of CO, in agreement with the experimental data that these fragmentations occur in both the field-free region (before the first collision cell) and in the first collision cell of the mass spectrometer.

<sup>a</sup>Decomposition to give  $\text{HCO}_2\text{CH}_3$  and  $\text{CH}_3\text{CO}^-\text{CO}$  is less favourable ( $\Delta G$  for this process from 4 is +112  $\text{kJ mol}^{-1}$ ).



Scheme 3.



**Figure 7.** Reaction coordinate profiles of the reactions  $\text{CH}_3\text{CO}_2^-\text{CHCO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}(\text{O}^-)\text{OCH}_3 + 2\text{CO}$ . CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory. Details of the geometries and energies of minima and transition states are contained in Supplementary Table 5 (see Supporting Information).

### The loss of "C<sub>2</sub>O<sub>2</sub>" from the [M-H]<sup>−</sup> anion of the CH<sub>3</sub>CO<sub>2</sub><sup>−</sup>CHCO<sub>2</sub>CH<sub>3</sub>/CH<sub>3</sub>COCH(O<sup>−</sup>)CO<sub>2</sub>CH<sub>3</sub> system

The loss of the elements of C<sub>2</sub>O<sub>2</sub> from the [M-H]<sup>−</sup> anion of an acyloxy acetate is illustrated in Fig. 6. The following experimental data follow from the original study: (i) <sup>13</sup>C-labelling shows that the two carbons eliminated are the central C and the carbonyl C of the −CO<sub>2</sub> alkyl group, and (ii) the loss of "C<sub>2</sub>O<sub>2</sub>" only occurs when the central carbanion bears a hydrogen substituent, and (iii) the process is of relatively low energy, since 90% of the product anions are formed in the field-free region before the first collision cell.<sup>5</sup> When we first reported the occurrence of this process we were interested in the structure of the product anion, not the structure of the neutral lost in the process. Since the original paper was published, it has been shown that C<sub>2</sub>O<sub>2</sub> is likely to be unstable during the reaction conditions,<sup>13</sup> so the fragmentation may produce two CO molecules. The mechanism of this unusual process will now be probed for the prototypical system CH<sub>3</sub>CO<sub>2</sub><sup>−</sup>CHCO<sub>2</sub>CH<sub>3</sub>.

Two plausible mechanisms which may account for the loss of the elements of C<sub>2</sub>O<sub>2</sub> are shown in Scheme 3. A prerequisite for both proposals is that the carbanion centre of the initial [M-H]<sup>−</sup> ion bears a hydrogen substituent. The mechanism proposed in the original paper involves a deprotonation occurring within an ion-neutral complex [Eqn. (6)],<sup>5</sup> but the mechanism shown in Eqn. (7) must also be considered. The key step in Eqn. (7) involves a 1,2-H<sup>−</sup> transfer within CH<sub>3</sub>COCH(O<sup>−</sup>)CO<sub>2</sub>CH<sub>3</sub> to generate intermediate CH<sub>3</sub>CH(O<sup>−</sup>)COCO<sub>2</sub>CH<sub>3</sub> which may yield the required products. Both the sequences shown in Scheme 3 have been examined theoretically. The results of this investigation are summarised in Fig. 7, with full details of the energies and geometries of the species shown in Fig. 7 listed in Supplementary Table 5 (see Supporting Information).

It can be seen in Fig. 7 that the deprotonation mechanism [route A (Fig. 7) and Eqn. (6) (Scheme 3)] is the less energetically favourable of the two processes with an energy of +195 kJ mol<sup>−1</sup> required to surmount transition state 12/13. In contrast, the hydride transfer mechanism [route B (Fig. 7)

and Eqn. (7) (Scheme 3)] requires a maximum energy of  $+128 \text{ kJ mol}^{-1}$ . The key step is the hydride transfer (5 to 15) ( $+76 \text{ kJ mol}^{-1}$  from 5). This is followed by formation of anion-neutral complex 13.

Does loss of the elements of  $\text{C}_2\text{O}_2$  from 13 involve elimination of ethylene dione ( $\text{O}=\text{C}=\text{C}=\text{O}$ ) or two molecules of CO? The background  $\text{C}_2\text{O}_2$  story is long and complex and is fully described elsewhere.<sup>13,20,21</sup> There appear to be a number of  $\text{C}_2\text{O}_2$  isomers: a Van der Waals molecule (possible with a T-shaped structure of low ionisation energy<sup>22</sup>), singlet and triplet OCCO with the triplet being the ground state<sup>13,20,21,23,24</sup> with a calculated ionisation energy of ca.  $9.2 \text{ eV}$ ,<sup>21</sup> and a further isomer of unknown structure with an ionisation energy of  $12.24 \text{ eV}$ .<sup>25</sup> It might be expected that the  $^3\Sigma_g^-$  ground state of OCCO should be stable,<sup>26</sup> since decomposition of this species to two molecules of CO is forbidden. However, triplet OCCO has not been observed experimentally. Schröder *et al.*<sup>13</sup> explain this anomaly by proposing that the triplet ground state spin inverts to the singlet (S/T gap is computed to be  $43.2 \text{ kJ mol}^{-1}$  at the G2 level of theory<sup>21</sup> with T to S crossing taking  $0.5 \text{ ns}^{13}$ ). The singlet may undergo allowed decomposition to two molecules of CO. Ethylene dione is designated as an intrinsically short-lived molecule.<sup>13</sup>

The scenario shown in Fig. 7 is straightforward. Methoxide anion addition to the carbonyl carbon within anion-neutral complex 13 occurs with loss of two molecules of CO in a reaction unfavourable by only  $9 \text{ kJ mol}^{-1}$ . Competitive elimination involving triplet  $\text{C}_2\text{O}_2$  is not an option since the reaction from 13 is unfavourable by  $+214 \text{ kJ mol}^{-1}$ . We conclude that  $(\text{CH}_3\text{OCO}^-\text{CO})$  is a methoxide anion donor within ion-neutral complex 13 and that the formation of  $\text{CH}_3\text{O}^-$  is accompanied by the loss of two molecules of CO. The isolated reaction  $(\text{CH}_3\text{OCOCO})^- \rightarrow \text{CH}_3\text{O}^- + 2\text{CO}$  is favourable, with  $\Delta G = -68 \text{ kJ mol}^{-1}$  at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory.

## CONCLUSIONS

- Both  $\text{CH}_3\text{O}(\text{CO})_n^-$  ( $n=1$  and  $2$ ) are methoxide anion donors. Calculations at the CCSD(T)/6-311++G(2d,2p)//B3LYP/6-311++G(2d,2p) level of theory indicate: (i) anion  $\text{CH}_3\text{O}^-\text{CO}$  may decompose to  $\text{CH}_3\text{O}^-$  and CO ( $\Delta G = +8 \text{ kJ mol}^{-1}$ ) while  $\text{CH}_3\text{OCO}^-\text{CO}$  fragments to  $\text{CH}_3\text{O}^-$  and  $2\text{CO}$  in a favourable reaction ( $\Delta G = -68 \text{ kJ mol}^{-1}$ ).
- Anions  $\text{CH}_3\text{OCOCO}_2^-$  and  $\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3$  eliminate CO via transition states  $[(\text{CH}_3\text{O}^-\text{CO})\text{CO}_2]$  and  $[(\text{CH}_3\text{O}^-\text{CO})\text{CH}_3\text{COCHO}]$ . The loss of CO is synchronous; there are no reactive intermediates between the reactants and these transition states in the reaction coordinates.
- Anion  $\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3$  eliminates two molecules of CO to form  $\text{CH}_3\text{CH}(\text{O}^-)\text{OCH}_3$ . A plausible process (in contrast to the less likely deprotonation reaction proposed in the initial report<sup>13</sup>) is reaction sequence  $\text{CH}_3\text{COCH}(\text{O}^-)\text{CO}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}(\text{O}^-)\text{COCO}_2\text{CH}_3 \rightarrow [\text{CH}_3\text{CHO}(\text{CH}_3\text{OCO}^-\text{CO})] \rightarrow \text{CH}_3\text{C}(\text{H})(\text{OCH}_3)(\text{O}^-) + 2\text{CO}$ . A key step in this reaction sequence is the 1,2 hydride transfer reaction shown in the first step of the reaction.

## SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

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## REFERENCES

- Soldi-Lose H, Schröder D, Schwarz H. *Int. J. Mass Spectrom.* 2008; **270**: 68.
- Bowie JH, Stringer MB, Hayes RN, Raftery MJ, Currie GJ, Eichinger PCH. *Spectros. Int. J.* 1985; **4**: 277.
- Raftery MJ, Bowie JH. *Aust. J. Chem.* 1987; **40**: 711.
- Eichinger PCH, Hayes RN, Bowie JH. *J. Chem. Soc. Perkin Trans. 2* 1990; 1815.
- Eichinger PCH, Hayes RN, Bowie JH. *J. Am. Chem. Soc.* 1991; **113**: 1949.
- O'Hair RAJ, Bowie JH, Hayes RN. *Rapid Commun. Mass Spectrom.* 1988; **2**: 275.
- Bialecki JB, Axe FU, Attygalle AB. *J. Mass Spectrom.* 2009; **44**: 252.
- Voigt D, Schmidt J. *Biomed. Mass Spectrom.* 1978; **5**: 44.
- Kulik W, Heerma W. *Biomed. Envir. Mass Spectrom.* 1988; **15**: 419.
- Eckersley M, Bowie JH, Hayes RN. *Int. J. Mass Spectrom. Ion. Proc.* 1989; **93**: 199.
- Bowie JH. *Mass Spectrom. Rev.* 1990; **9**: 349.
- Sheldon JC, Bowie JH. *J. Am. Chem. Soc.* 1990; **112**: 2424.
- Schröder D, Schwarz H, Dua S, Blanksby SJ, Bowie JH. *Chem. Eur. J.* 1998; **4**: 2550.
- Stringer MB, Bowie JH, Holmes JL. *J. Am. Chem. Soc.* 1986; **108**: 3888.
- Holmes JL. *Org. Mass Spectrom.* 1985; **20**: 169.
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T, Kudin TN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Topyota K, Fukuda R, Hasegawa J, Ishida M, Makajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Know JE, Hratchian HP, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifffors S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Latham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA. *Gaussian 03 Revision C.02*, Gaussian, Inc.: Wallingford, CT, 2004.
- Becke AD. *Phys. Rev. A* 1988; **38**: 3098. Lee CT, Yang WT, Parr RG. *Phys. Rev. B* 1988; **37**: 785.
- Gonzalez C, Schlegel HB. *J. Chem. Phys.* 1989; **90**: 2154. Gonzalez C, Schlegel HB. *J. Phys. Chem.* 1990; **94**: 5523.
- Dunning TH. *J. Chem. Phys.* 1989; **90**: 1007. Raghavachari K, Trucks GW, Pople JA, Headgordon M. *Chem. Phys. Lett.* 1989; **157**: 479. Woon DE, Dunning TH. *J. Chem. Phys.* 1993; **98**: 1358.
- Talbi T, Chandler GS. *J. Phys. Chem. A* 2000; **104**: 5872.
- Maclagen RAR. *THEOCHEM* 2005; **713**: 107.
- Van den Bout PA, Steed JM, Bernstein LS, Klemperer W. *Astrophys. J.* 1979; **234**: 503.
- Haddon RC, Poppinger D, Radom L. *J. Am. Chem. Soc.* 1975; **97**: 1645.
- Raine GP, Schaefer HF, Haddon RC. *J. Am. Chem. Soc.* 1983; **105**: 194.
- Mahnert J, Baumgärtel, Weitzel K-M. *J. Chem. Phys.* 1995; **103**: 7016.
- Korkin AA, Balkova A, Bartlett RJ, Boyd RJ, Schleyer P von R. *J. Phys. Chem.* 1996; **100**: 5702.