Is the Collision Induced Loss of Methanol from Deprotonated 4-Methoxybut-1-yne in the Gas Phase a Charge Remote Reaction?

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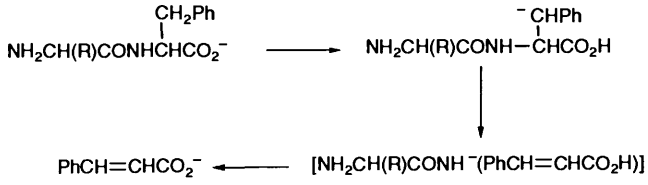
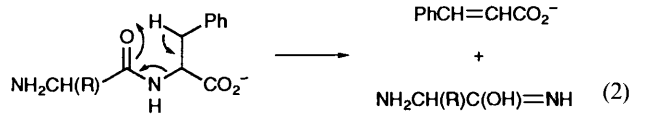
The collision induced loss of methanol from deprotonated 4-methoxybut-1-yne occurs by at least two mechanisms, *viz.* (*a*) a stepwise cyclization–deprotonation–ring opening process involving the acetylenic π electrons, and (*b*) a 1,2-elimination process which may either be (*i*) a process in which cyclisation involving the π electrons and loss of methanol are synchronous, or (*ii*) a 'remote' concerted process which does not involve the acetylenic centre.

Even-electron organic anions dissociate primarily by loss of neutral molecules. The basic fragmentation types have been reviewed, and are proposed to involve the anion centre.[1–3] Losses of radicals also occur: such reactions are generally minor and produce stabilized radical anions.[4] However there has been much interest recently in the possible operation of 'charge remote' processes for negative ions, *i.e.* fragmentations which occur remote from and uninfluenced by the centre of charge in the anion.[5,6] While there can be no doubt that such fragmentations could occur if competing pathways are of higher energy, we have had difficulty in authenticating their operation for simple organic negative ions. Take the fragmentations of the $(M-H)^-$ ions of dipeptides as examples; some of the basic fragmentations could occur either following proton transfers [*e.g.* reaction (1)] or by remote mechanisms [*e.g.* reaction (2)], and it is difficult to differentiate between such mechanistic possibilities.[7]



(1)



(2)

Recently, we have chosen to study anion systems where loss of a neutral molecule by simple fragmentation is unfavourable. We hoped that these anions, upon collisional activation, would either decompose by 'remote' fragmentation or by some rearrangement of the skeleton of the system. Deprotonated prop-2-ynyl (propargyl) methyl ether fits this prerequisite since the acetylenic moiety should 'isolate' the negative charge and restrict normal fragmentation. This system loses methanol on collision activation to yield the major daughter anion, however we have shown that this is not a 'remote' reaction but one which proceeds through the intermediacy of a vinylidene carbene complex [see reaction (3)].[8]

$$MeO{-}CH_2{-}C{\equiv}C^- \longrightarrow [MeO^-(CH_2{=}C{=}C{:})] \longrightarrow C_3H^- + MeOH \quad (3)$$

The mechanism shown in reaction (3) cannot apply if the chain length of the ether is increased by one methylene group; *i.e.* to $MeOCH_2CH_2C{\equiv}C^-$. We now report the results of an investigation of this and cognate systems, and we seek the answers to two questions; *viz.* (*i*) does $MeOCH_2CH_2C{\equiv}C^-$ eliminate methanol under conditions of collisional activation, and (*ii*) if so, is the loss of methanol a 'remote' reaction?

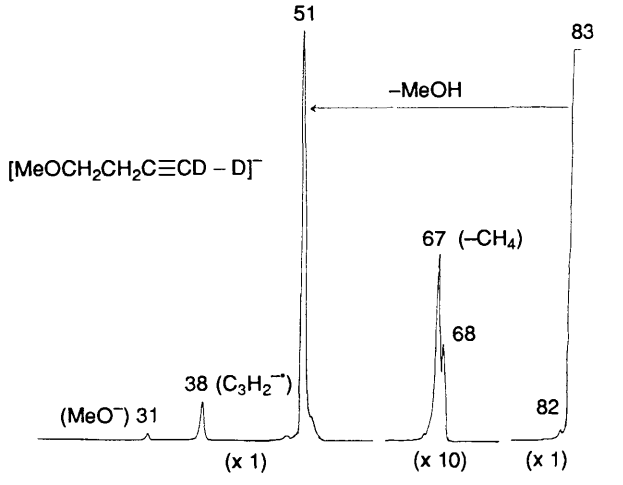


Fig. 1 Collision induced mass spectrum (MS–MS) of $[MeOCH_2CH_2C{\equiv}CD - D]^-$, VG ZAB 2HF instrument; for experimental conditions, see Experimental section

Table 1 Collision induced mass spectra of $MeOCD_2CH_2C{\equiv}C^-$ and $MeOCH_2CD_2C{\equiv}C^-$

Ion (*m/z*)	Spectrum [*m/z* (loss or formation) relative abundance]
$[MeOCD_2CH_2C{\equiv}CD - D]^-$ (*m/z* 85)	84 (H•) 18, 83 (H_2, D•) 3, 68 (CH_3D) 5, 53 (MeOH) 100, 52 (MeOD) 34, 38 [($C_3H_2^{\bullet-}$)] 17, 31 [(MeO^-)] 3
$[MeOCH_2CD_2C{\equiv}CH - H]^-$ (*m/z* 85)	84 (H•) 18, 83 (H_2, D•) 8, 69 (CH_4) 20, 53 (MeOH) 92, 52 (MeOD) 100, 40 [($C_3D_2^{\bullet-}$)] 28, 38 [($C_3H_2^{\bullet-}$) 2, 31 [(MeO^-)] 5

Results and Discussion

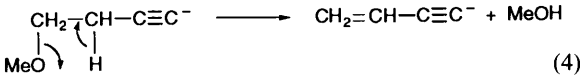
The collision induced mass spectrum (MS–MS) of deprotonated 4-methoxybut-1-yne is shown in Fig. 1, while those of two deuteriated derivatives are recorded in Table 1. The spectrum shown in Fig. 1 is dominated by loss of methanol to form product ion *m/z* 51. The collision induced and charge reversal spectra of this ion are presented in Table 2 and identify the

Table 2 Comparison of the charge reversal (positive ion) mass spectra of the $C_4H_3^-$ product ion from $MeOCH_2CH_2C{\equiv}C^-$ and authentic $CH_2{=}CH{-}C{\equiv}C^-$ [a]

Ion	Spectrum [*m/z* (loss or formation) relative abundance]
$C_4H_3^-$ (*m/z* 51)	51 (parent) 42, 50 ($H^\bullet$) 100, 49 (2 H) 38, 48 (3 H) 5, 39 (C) 3, 38 ($CH^\bullet$) 9, 37 (CH_2) 24, 36 ($CH_3^\bullet$) 12, 27 (C_2) 6, 26 ($C_2H^\bullet$) 7, 25 (C_2H_2) 5, 24 ($C_2H_3^\bullet$) 4, 14 [$(CH_2^{\bullet+})$] 2, 13 [(CH^+)] 1, 12 [(C^+)] 2
$CH_2{=}CH{-}C{\equiv}C^-$ (*m/z* 51)	51 (parent) 34, 50 ($H^\bullet$) 100, 49 (2 H) 36, 48 (3 H) 5, 39 (C) 3, 38 ($CH^\bullet$) 8, 37 (CH_2) 21, 36 ($CH_3^\bullet$) 12, 27 (C_2) 6, 26 ($C_2H^\bullet$) 6, 25 (C_2H_2) 4, 24 ($C_2H_3^\bullet$) 6, 14 [$(CH_2^{\bullet+})$] 2, 13 [(CH^+)] 1, 12 ($C^{\bullet+}$) 2

[a] The collision induced mass spectra (MS–MS) of the $C_4H_3^-$ ions only show peaks corresponding to losses of $H^\bullet$ and H_2.

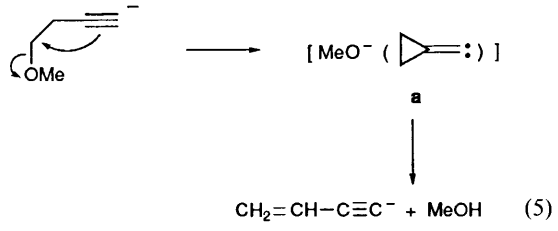
structure of *m/z* 51 to be $CH_2{=}CH{-}C{\equiv}C^-$ by comparison with an authentic anion synthesised by an unambiguous route. How do we interpret these data?



(4)

The first mechanistic possibility is the 'remote' process shown in reaction (4): a synchronous reaction proceeding through a four-centred transition state. The other possible 'remote' reaction involves a synchronous 1,1-elimination, but this seems unlikely since the activation energy for such a process would be prohibitive (*cf.* ref. 9).

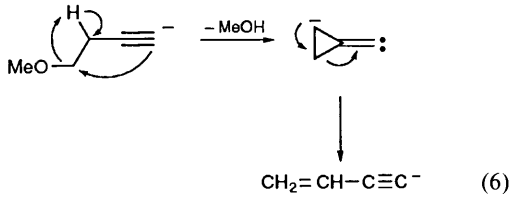
Another rationale involves the cyclization–elimination shown in sequence (5). This reaction involves the intermediacy of an



(5)

alkylidene carbene–methoxide anion complex **a**. (There is both experimental[10,11] and theoretical evidence[12] that the neutral vinylidene carbene shown in **a** is a stable species. For example, the reaction between bromomethylenecyclopropane and solid potassium *tert*-butoxide proceeds through the methylenecyclopropane carbene to produce 1-*tert*-butoxymethylenecyclopropane as the major product together with the minor rearrangement product 1-*tert*-butoxycyclobutene.)[10]

There are several scenarios to consider in this situation, *viz.* (*i*) the incipient methoxide anion of ion complex **a**, acting as a powerful base, is free to deprotonate at either of the equivalent methylene groups of the ring, and/or (*ii*), the leaving MeO^- group deprotonates at the position adjacent to that to which it was initially bound (a 1,2-elimination), either by a stepwise process [sequence (5)], or one in which the elimination of MeOH is concerted [see sequence (6)]. Fragmentation of **a**



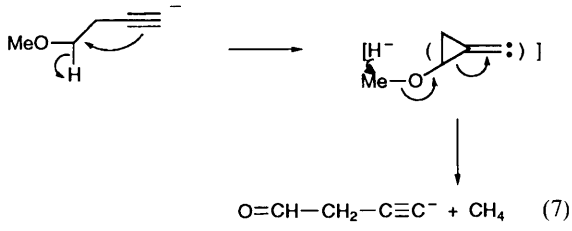
(6)

via either stepwise mechanism of sequence (5) is, in principle, possible: examples of deprotonation within ion complexes at different positions[13] and at adjacent positions[14,15] have been reported.

Deuterium labelling may help to differentiate these possibilities. Consider the results that would be expected from $MeOCD_2CH_2C{\equiv}C^-$ and $MeOCH_2CD_2C{\equiv}C^-$ for the possible mechanisms outlined above. (*i*) If 'remote' reaction (4) is operative, $MeOCD_2CH_2C{\equiv}C^-$ should eliminate MeOH and $MeOCH_2CD_2C{\equiv}C^-$ should lose MeOD. (*ii*) If the MeO^- ion is able to deprotonate either of the equivalent methylene groups of the neutral carbene in **a**, then the ratio of MeOH to MeOD loss should be the same for each of the labelled precursors. (*iii*) If the MeO^- group deprotonates at the position adjacent to that to which it was initially bound (a 1,2-elimination), either by a stepwise process [reaction (5)], or one in which the elimination of MeOH is concerted [reaction (6)], $MeOCD_2CH_2C{\equiv}C^-$ and $MeOCH_2CD_2C{\equiv}C^-$ will respectively lose MeOH and MeOD exclusively.

The results outlined in Table 1 for the deuteriated analogues indicate the situation to be more complex than any of the individual possibilities outlined above: $MeOCD_2CH_2C{\equiv}C^-$ and $MeOCH_2CD_2C{\equiv}C^-$ lose MeOH and MeOD in the respective ratios 3:1 and 1:1. We believe that the observations that $MeOCD_2CH_2C{\equiv}C^-$ loses some MeOD and $MeOCH_2CD_2C{\equiv}C^-$ loses some MeOH, can only be accommodated by a stepwise process proceeding through **a** [sequence (5)] in which the MeO^- species is able to deprotonate at either methylene position. However, the major loss of MeOH from $MeOCD_2CH_2C{\equiv}C^-$ and MeOD from $MeOCH_2CD_2C{\equiv}C^-$ must involve a competing 1,2-elimination with an appreciable deuterium kinetic isotope effect. This could be explained by a remote fragmentation [sequence (4)], and/or a stepwise cyclisation–elimination [sequence (5)] and/or the corresponding concerted process [sequence (6)]. The available evidence does not distinguish these possibilities.

The only other fragmentation shown in Fig. 1 of particular interest, is loss of methane. Labelling studies are consistent with the mechanism proposed in eqn. (7): a process which has some



(7)

analogy with that shown in eqn. (5) and a related process which occurs for prop-2-ynyl methyl ether.[8]

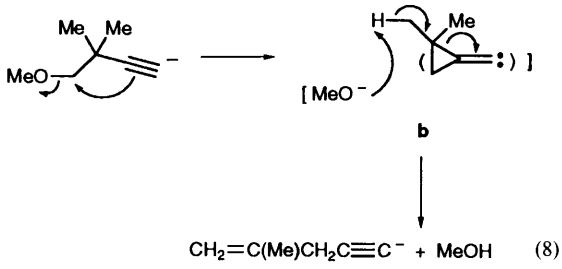
The evidence presented above indicates that there are three possible mechanisms for the 1,2-elimination of methanol from $MeOCH_2CH_2C{\equiv}C^-$. One of those possibilities is a concerted process which does not involve the anion centre, *i.e.* a 'remote' fragmentation. Let us now (*i*) synthesize a cognate anion in which a remote 1,2-elimination of methanol cannot occur and (*ii*) determine how its collision-induced fragmentations differ from those shown in Fig. 1. The molecule we have chosen to study is 4-methoxy-3,3-dimethylbut-1-yne, and the collision induced mass spectra of its deprotonated form and of a labelled analogue are listed in Table 3.

The base peak in the spectrum of $MeOCH_2C(Me)_2C{\equiv}C^-$ is again produced by loss of methanol. The spectrum of $MeOCD_2C(Me)_2C{\equiv}C^-$ shows losses of MeOH and MeOD in the ratio 4:1. We believe that the loss of MeOD can only occur by a cyclization process analogous to that shown in reaction (5), *i.e.* through ion complex **b** [see reaction (8)] (we have attempted to identify the product ion of this minor but important process:

Table 3 Collision induced mass spectra (MS–MS) of $MeOCH_2C(Me)_2C{\equiv}C^-$ and a deuterium labelled derivative

Ion (*m/z*)	Spectrum [*m/z* (loss or formation) relative abundance]
$MeOCH_2C(Me)_2C{\equiv}C^-$ (*m/z* 111)	95 (CH_4) 14, 79 (MeOH) 100, 66 ($MeOCH_2^{\bullet}$) 30, 65 (MeOMe) 39
$MeOCD_2C(Me)_2C{\equiv}C^-$ (*m/z* 113)	97 (CH_4) 12, 81 (MeOH) 100, 80 (MeOD) not resolved but < 40,[a] 66 ($MeOCD_2^{\bullet}$) 15, 65 ($MeOCHD_2$) 14

[a] Losses of MeOH and MeOD for source decompositions are in the ratio 100:26.



$$CH_2{=}C(Me)CH_2C{\equiv}C^- + MeOH \quad (8)$$

unfortunately, its abundance is too small to obtain suitable collisional activation and charge reversal spectra). Whether the competing loss of MeOH (which involves deprotonating a methyl substituent), is stepwise [see sequence (8)], or is concerted accompanying cyclization, is not known.

In conclusion, we propose that at least a portion of the methanol lost from deprotonated 4-methoxybut-1-yne and a dimethylated derivative occurs following cyclisation–deprotonation–ring opening involving acetylenic π electrons. There is a competitive process for the unsubstituted compound which formally involves 1,2-elimination of methanol. It is possible that this could involve a 'remote' reaction, but an alternative scenario is that shown in reaction (6). This reinforces our contention of how difficult it is to substantiate unequivocally a 'remote' dissociation of an organic negative ion.

Experimental

Collisional activation (CA) and charge reversal (CR, positive ion)[16] mass spectra (MS–MS) were determined with a VG ZAB 2HF[17] instrument. Full experimental details have been reported previously.[18] Specific details were as follows: a chemical ionization slit was used in the ion source, the ionizing energy was 70 eV, the ion source temperature was 50 °C, and the accelerating voltage was 7 kV. Liquids were introduced through the septum inlet at 50 °C, and gases through a specially designed gas inlet system (pressure of sample 5×10^{-7} Torr; 1 Torr = 133.322 Pa). Deprotonation was effected using HO^- (from H_2O: source pressure 1×10^{-5} Torr). The estimated source pressure was 10^{-1} Torr. Argon was used in the second collision cell (measured pressure, outside the cell, 2×10^{-7} Torr), giving a 10% reduction in the main beam, equivalent to single collision conditions.

But-3-en-1-yne[19] and 4-methoxybut-1-yne[20] were prepared by reported procedures.

[1-^{2}H]4-*Methoxybut-1-yne*. To 4-methoxybut-1-yne[20] (1.0 g) in anhydrous diethyl ether (20 cm^3) was added methyl lithium in diethyl ether (1.4 m, 8.5 cm^3) dropwise, at −78 °C. The mixture was allowed to stir at this temperature for 30 min, and deuterium oxide (0.5 cm^3) was added. Fractional distillation gave [1-^{2}H]4-methoxybut-1-yne (80% yield).

[4,4-$^2H_2$]4-*Methoxybut-1-yne*. But-3-ynoic acid[21] (2.0 g) was reduced[22] with lithium aluminium deuteride in refluxing tetrahydrofuran (THF) to give [1,1-$^2H_2$]but-3-ynol (1.1 g, 67%), which was methylated[20] with dimethyl sulfate to yield [4,4-$^2H_2$]4-methoxybut-1-yne (0.7 g, 55%).

[3,3-$^2H_2$]4-*Methoxybut-1-yne*. Methoxymethyl acetate (5.0 g) was reduced[22] with lithium aluminium deuteride to give [1,1-$^2H_2$]methoxyethanol (1.9 g, 50%). The alcohol was tosylated and subsequently converted[23] to the corresponding iodide (1.47 g, 35%). The iodide (0.75 g) was allowed to react with lithium acetylenide–ethylenediamine complex in dimethyl sulfoxide,[24] to yield [3,3-$^2H_2$]4-methoxybut-1-yne (0.18 g, 55%).

3,3-*Dimethyl*-4-*methoxybut*-1-*yne*. Dimethylbut-3-ynol[25] (1.0 g) was methylated[15] with methyl iodide in diethyl ether to give 3,3-dimethyl-4-methoxybut-1-yne (0.77 g, 69%; b.p. 78–80 °C/760 mmHg): $\delta_H(CDCl_3$; 200 MHz) 1.25 (6 H, s), 2.2 (1 H, s), 3.4 (3 H, s) and 3.55 (2 H, s) (MS, $M^{\bullet+}$, 112.0888; $C_7H_{12}O$ requires *M*, 112.0888).

[4,4-$^2H_2$]3,3-*Dimethyl*-4-*methoxybut*-1-*yne*. 2,2-Dimethylbut-3-ynoic acid[26] (1.5 g) was reduced[22] with lithium aluminium deuteride in refluxing THF to produce [1,1-$^2H_2$]-2,2-dimethylbut-3-ynol (0.78 g, 58%), which was methylated[15] with methyl iodide in diethyl ether to give [4,4-$^2H_2$]3,3-dimethyl-4-methoxybut-1-yne (0.57 g, 65%).

Acknowledgements

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References

1 J. H. Bowie, in *Mass Spectrometry Specialist Reports*, The Chemical Society, London, 1989, **10**, 145.
2 J. H. Bowie, *Mass Spectrom. Rev.*, 1990, **9**, 349.
3 J. H. Bowie, in *Experimental Mass Spectrometry*, ed. D. H. Russell, Plenum Press, New York, 1994, pp. 1–38.
4 P. C. H. Eichinger and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, 1991, **110**, 123.
5 J. Adams, *Mass Spectrom. Rev.*, 1990, **9**, 141.
6 M. L. Gross, *Int. J. Mass Spectrom. Ion Processes*, 1992, **118/119**, 137.
7 R. J. Waugh and J. H. Bowie, *Rapid Commun. Mass Spectrom.*, 1994, **8**, 169.
8 S. Dua and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1994, 543.
9 J. C. Sheldon, J. H. Bowie and D. E. Lewis, *Nouv. J. Chim.*, 1988, **12**, 269.
10 K. L. Erickson and S. B. Gordon, *J. Org. Chem.*, 1973, **38**, 1431.
11 T. Bassler and M. Hanack, *Tetrahedron Lett.*, 1971, 2171.
12 Y. Apeloig, R. Schreiber and P. J. Stang, *Tetrahedron Lett.*, 1980, 411.
13 M. J. Raftery and J. H. Bowie, *Int. J. Mass Spectrom. Ion Processes*, 1987, **79**, 267.
14 S. Dua, A. P. Pollnitz and J. H. Bowie, *J. Chem. Soc., Perkin Trans. 2*, 1993, 2235.
15 S. Dua, R. B. Whait, M. J. Alexander, R. N. Hayes, A. T. Lebedev, P. C. H. Eichinger and J. H. Bowie, *J. Am. Chem. Soc.*, 1993, **115**, 5709.
16 J. H. Bowie and T. Blumenthal, *J. Am. Chem. Soc.*, 1975, **97**, 2959.
17 VG ZAB 2HF, VG Analytical, Manchester, UK.
18 M. B. Stringer, J. L. Holmes and J. H. Bowie, *J. Am. Chem. Soc.*, 1986, **108**, 3888.
19 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 2nd edn., 1988, p. 178.
20 W. R. Jackson, P. Perlmutter and A. J. Smallridge, *Aust. J. Chem.*, 1988, **41**, 251.
21 L. Brandsma and H. P. Verkinijsse, in *Allenes and Cumulenes—A Laboratory Manual*, Elsevier, Amsterdam, 1981, p. 49.
22 A. Burger, L. Turnbull and J. G. Dinwiddie, *J. Am. Chem. Soc.*, 1950, **72**, 5512.
23 J. Defaye, M. Naumberg and T. Reyners, *J. Heterocycl. Chem.*, 1969, **6**, 229.
24 W. N. Smith and D. F. Beumel, *Synthesis*, 1974, 441.
25 F. Barbot and Ph. Miginiac, *J. Organometallic Chem.*, 1992, **440**, 249.
26 M. A. Schexnayder and P. S. Engel, *J. Am. Chem. Soc.*, 1975, **97**, 4825.

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