

Diagnostic fragmentations of adducts formed between carbanions and carbon disulfide in the gas phase. A joint experimental and theoretical study†

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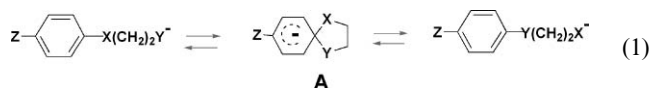
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Selected carbanions react with carbon disulfide in a modified LCQ ion trap mass spectrometer to form adducts, which when collisionally activated, decompose by processes which in some cases identify the structures of the original carbanions. For example (i) $\text{C}_6\text{H}_5^- + \text{CS}_2 \rightarrow \text{C}_6\text{H}_5\text{CS}_2^- \rightarrow \text{C}_6\text{H}_5\text{S}^- + \text{CS}$, occurs through a 3-membered ring *ipso* transition state, and (ii) the reaction between $\text{C}_6\text{H}_5\text{CH}_2^-$ and CS_2 gives an adduct which loses H_2S , whereas the adduct(s) formed between *o*- $\text{CH}_3\text{C}_6\text{H}_4^-$ and CS_2 loses H_2S and CS . Finally, it is shown that decarboxylation of $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CO}_2^-$ produces the β -phenylethyl anion ($\text{PhCH}_2\text{CH}_2^-$), and that this thermalized anion reacts with CS_2 to form $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CS}_2^-$ which when energized fragments specifically by the process $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CS}_2^- \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{S})\text{SH} \rightarrow [(\text{C}_6\text{H}_5\text{CH}_2\text{CH}=\text{C}=\text{S})-\text{SH}] \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CCS}^- + \text{H}_2\text{S}$. Experimental findings of processes (ii) and (iii) were aided by deuterium labelling studies, and all reaction profiles were studied by theoretical calculations at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory unless indicated to the contrary.

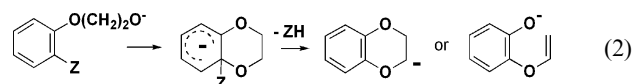
Introduction

A classical (condensed phase) Smiles rearrangement¹ is shown in eqn (1). This nucleophilic *ipso* attack normally requires an electron withdrawing group (e.g. nitro, sulfonyl or halogen) either in the *ortho* or *para* position on the aromatic ring; generally X is a good leaving group, Y is a strong nucleophile and Z is shown as a *para* substituent in eqn (1). The anionic Smiles rearrangement has been used extensively synthetically (see e.g.^{2–9} for some recent examples), and radical Smiles rearrangements have also been reported.^{10–14} The Truce–Smiles rearrangement (involving attack of a carbanion centre at an *ipso* electrophilic centre) has also been used as a synthetic method.^{15,16}



The gas phase Smiles rearrangement has not been studied in such depth as that in the condensed phase. The Smiles rearrangement occurs in the gas phase without the necessity for activation

of the aromatic ring by electron-withdrawing groups. Heavy atom (¹³C and ¹⁸O) labelling shows that the product ion PhO^- from $\text{PhO}(\text{CH}_2)_2\text{O}^-$ and products PhO^- and PhS^- from $\text{PhS}(\text{CH}_2)_2\text{O}^-$ are formed exclusively from Smiles intermediates **A** ($\text{X} = \text{Y} = \text{O}$ or $\text{X} = \text{S}$, $\text{Y} = \text{O}$).¹⁷ [For the degenerate process where $\text{X} = \text{Y} = \text{O}$, calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory indicate that *ipso* intermediate **A** ($\Delta E = +285 \text{ kJ mol}^{-1}$) is reached via a transition state 289 kJ mol^{-1} above $\text{PhO}(\text{CH}_2)_2\text{O}^-$].¹⁸ In contrast, the formation of PhO^- from $\text{PhO}(\text{CH}_2)_3\text{O}^-$ occurs by competitive Smiles (85%) and $\text{S}_{\text{N}}1$ reactions (15%), while PhO^- is formed from $\text{PhO}(\text{CH}_2)_4\text{O}^-$ solely by an $\text{S}_{\text{N}}1$ process.¹⁷ ¹⁸O Labelling shows that when there is a substituent in the *ortho* position, the gas phase Smiles rearrangement competes with an *ortho* cyclization process as shown in eqn (2).¹⁹ The classical $[\text{PhNO}_2]^-$ to $[\text{PhONO}]^-$ gas phase rearrangement is probably an *ipso* process,²⁰ and gas-phase Smiles processes have been proposed for 2-hydroxybenzyl-*N*-pyrimidinylamine,²¹ phenoxy-*N*-phenyl acetamide anions,²² deprotonated 2-(4,6-dimethoxypyrimidine-2-yl)sulfonyl-*N*-phenylbenzamide²³ and other systems.^{24–26}



We wished to revisit our gas-phase *ipso* rearrangement studies in order to determine whether reactions of CS_2 with aryl carbanions give adducts *cf.*^{27,28} which undergo collision-induced cleavages [perhaps *ipso* (Smiles) rearrangements] diagnostic of the structures of the reacting carbanions. The systems we have chosen to react with CS_2 are (a) the phenyl anion, (b) the isomers PhCH_2^- and [*ortho*- $\text{CH}_3\text{C}_6\text{H}_4^-$] and (c) the β -phenylethyl anion ($\text{PhCH}_2\text{CH}_2^-$) together with some other isomeric anions C_8H_6^- . In (c), we wished to determine whether the reaction with CS_2 can settle the old debate^{29–31} as to whether the β -phenylethyl anion is stable or

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† Electronic supplementary information (ESI) available: Tables S1 and S1(a): Anion geometries and energies of reaction pathway for the CS_2 addition to the singlet phenyl anion. Tables S2 and S2(a): Anion geometries and energies of reaction pathway for the collision induced dissociation of the singlet PhCOS^- anion. Tables S3 and S3(a): Anion geometries and energies for the possible reaction pathway for the CS_2 addition to the singlet Benzyl anion. Tables S4 and S4(a): Anion geometries and energies of reaction pathway for the interconversion of the singlet anion *o*- $\text{CH}_3(\text{C}_6\text{H}_4)^-$ to singlet PhCH_2^- . Tables S5 and S5(a): Anion geometries and energies of reaction pathway for the interconversion of the singlet $\text{PhCH}_2\text{CH}_2^-$. Tables S6 and S6(a): Potential energy surface for the dissociation of the singlet $\text{PhCH}_2\text{CH}_2\text{CS}_2^-$ anion. Tables S7 and S7(a): Potential energy surface of dissociation of the singlet $\text{PhCH}_2\text{CH}_2\text{CO}_2^-$ anion. See DOI: 10.1039/b916477d

undergoes side chain rearrangement *via* an *ipso*, or some other intermediate.

Results and discussion

1. Reaction of the phenyl anion with CS₂

The phenyl anion was formed in the LCQ mass spectrometer by decarboxylation of the benzoate anion.³² Reaction of C₆H₅[−] with CS₂ forms C₆H₅CS₂[−] and collisional activation of this species gives C₆H₅S[−] (*m/z* 109) as the only observable fragment ion. Reduction in the pressure of the CS₂ reagent gas in this system results in the detection of a minor peak corresponding to *m/z* 77 (C₆H₅[−]) accompanying *m/z* 109.

Since anions can react with CS₂ in the gas phase either at C or S,³³ the collision induced negative ion mass spectrum of deprotonated dithiobenzoic acid (C₆H₅CS₂H) was measured using a Waters QTOF2 mass spectrometer operating in negative ion electrospray ionization mass spectrometry (ESI MS/MS) mode. We chose the QTOF2 (rather than the LCQ) for this purpose since the QTOF2 uses an efficient gas collision CID MS/MS process for accelerated ions, whereas the LCQ uses a less efficient collisional process in the mass analyser. Two fragment ions, *m/z* 77 [C₆H₅[−] 100%] and *m/z* 109 [C₆H₅S[−] 64%] were observed. This is consistent with the adduct of the ion molecule reaction being C₆H₅CS₂[−] and suggests that fragment anion C₆H₅[−] is produced in the LCQ, but reacts immediately with CS₂ on formation.

In order to compare the reactions of C₆H₅CS₂[−] with those of oxygen analogues, we have measured the negative ion CID ESI MS/MS of [C₆H₅COS][−] and C₆H₅CO₂[−] using a Waters QTOF2 mass spectrometer. The spectrum of [C₆H₅COS][−] shows *m/z* 77 (100%), 93 (C₆H₅O[−] 15%) and 109 (C₆H₅S[−] 55%), while that of the benzoate anion gives *m/z* 77 (C₆H₅[−]) as the only fragment anion. So C₆H₅CO₂[−] does not undergo the *ipso* rearrangement, whereas [C₆H₅COS][−] undergoes two competitive *ipso* rearrangements.

The reaction coordinate profiles of the possible *ipso* rearrangements described above have been investigated at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. All relative energies indicated in the text and in the Figures are Δ*G* (free energy) values (as requested by a reviewer rather than Δ*E*). The supplementary tables list both Δ*E* and Δ*G* values. Results for the *ipso* processes of C₆H₅CS₂[−] and C₆H₅COS[−] are summarized in Fig. 1 and 2, with full details of geometries and energies listed in supplementary tables 1 and 2.[†] No *ipso* intermediates are identified in any case. In the case of C₆H₅CS₂[−] (Fig. 1), reaction proceeds through an *ipso* transition state (+316 kJ mol^{−1}) to [C₆H₅SCS][−], which is energized and may decompose to C₆H₅S[−] and CS in an overall endothermic reaction (+193 kJ mol^{−1}).[‡]

The two competitive rearrangements of [C₆H₅COS][−] are shown in Fig. 2. Formation of C₆H₅S[−] and CO is endothermic (+26 kJ mol^{−1}) proceeding *via* an *ipso* transition state (+300 kJ mol^{−1}). In comparison, the competitive formation of C₆H₅O[−] and CS is more endothermic (+245 kJ mol^{−1}) with a transition state marginally higher in energy (at +306 kJ mol^{−1}).

[‡] A reviewer has asked whether electron detachment of the precursor anion competes with the *ipso* rearrangement to form C₆H₅S[−]. The electron affinity of C₆H₅CS₂[−] is calculated to be 3.345 eV (332 kJ mol^{−1}) [using the G3B3 level of theory (see Experimental section)] so the process shown in Fig. 1 is more energetically favourable than electron loss.

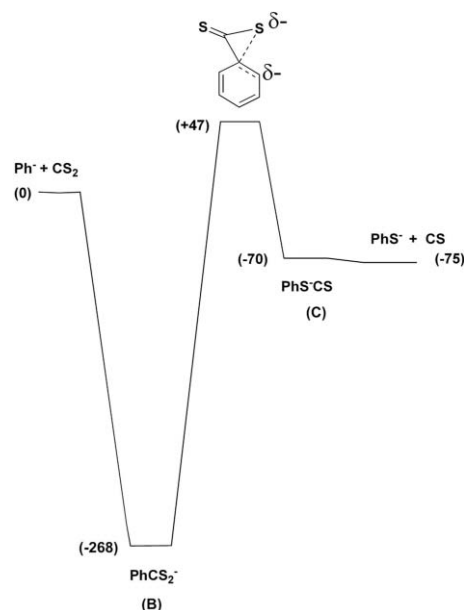


Fig. 1 The *ipso* rearrangement of PhCS₂[−]. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies (Δ*G*) in kJ mol^{−1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 1.[†]

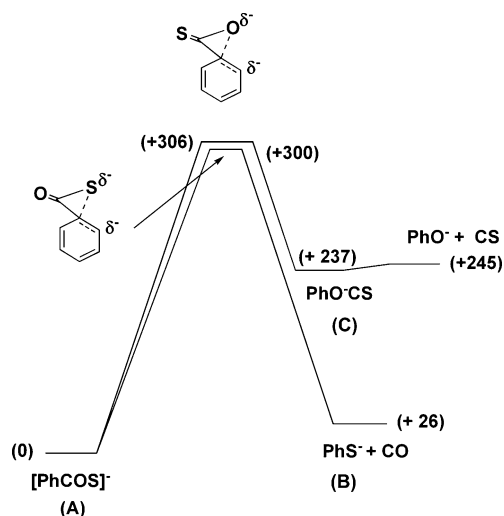


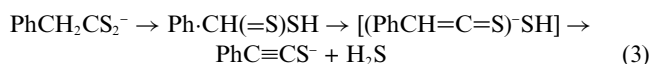
Fig. 2 The *ipso* rearrangements of [PhCOS][−]. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p)] level of theory. Relative free energies in kJ mol^{−1}. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 2.[†]

The theoretical results are consistent with experiments, where the relative abundance of the peak due to C₆H₅S[−] is greater than that of C₆H₅O[−].

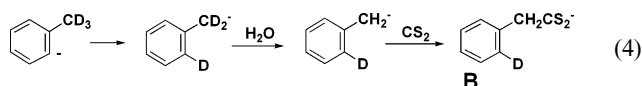
2. Reactions of the benzyl and *ortho*-tolyl anions with CS₂

The reactions of these two anions with CS₂ give adducts whose characteristic fragmentations differentiate between the structures of the original reacting carbanions. The precursors of the two anions were produced following electrospray ionization of phenylacetic acid and *ortho*-toluic acid to yield the two carboxylate anions which were decarboxylated following collisional activation

to yield the benzyl and *ortho*-tolyl anions respectively. The reaction of these two anions with CS₂ gave adducts whose fragmentations were probed using the CID MS4 scanning procedure. Decomposition of PhCH₂CS₂⁻ gave only one fragmentation, yielding a pronounced peak corresponding to the [PhCH₂CS₂⁻ - H₂S]⁻ ion (*m/z* 133). When this procedure was repeated with the D labelled species PhCD₂⁻, the adduct PhCD₂CS₂⁻ lost only D₂S. This process is shown in eqn (3): decomposition of PhCH₂CS₂⁻ gives PhCCS⁻ and H₂S, an endothermic process (+120 kJ mol⁻¹) at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory (see Supplementary Table 3†).



The situation with the *ortho*-tolyl anion is more complex: the adduct formed with CS₂ when collisionally activated shows competitive losses of H₂S and CS. The loss of CS is simply the *ipso* rearrangement (*cf.* Fig. 1) of the expected adduct *ortho*-CH₃C₆H₄CS₂⁻. But how is H₂S lost? This was uncovered when the reaction between the D labelled *ortho*-CD₃C₆H₄⁻ and CS₂ was studied. The decarboxylation process formed *ortho*-CD₃C₆H₄⁻ and if this anion was allowed to react immediately with CS₂, the adduct lost only CS by a standard *ipso* rearrangement. If, in contrast, the *ortho*-CD₃C₆H₄⁻ anion was allowed to remain in the trap for 10 microseconds, it back exchanged two D for H (reaction with residual H₂O from the electrospray ionization process). This ion formed an adduct with CS₂ which, on collisional activation, lost H₂S exclusively. This can only be due to the process shown in eqn (4): namely D transfer to the *ortho* position followed by D/H exchange of the two remaining benzylic deuteriums by water (a process of the type first reported by DePuy *et al.*^{27,28}) to yield the D₁ adduct **B** which then loses H₂S (see eqn (4) and *cf.* eqn (3)). The interconversion of the *ortho*-tolyl and benzyl anions is an exothermic process (-53 kJ mol⁻¹) with a barrier of 179 kJ mol⁻¹ at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory (see Fig. 3 and Supplementary table 4†).



3. The reactions of the β-phenylethyl anion and other isomers with CS₂

The question as to whether the β-phenylethyl anion (PhCH₂CH₂⁻) is stable has been a matter of debate for almost 20 years. Nibbering *et al.*³⁰ presented data which showed that the β-phenylethyl anion rearranges to the cyclised *ipso* form on collisional activation in a conventional mass spectrometer, while Squires and Graul³¹ proposed that the β-phenylethyl anion was stable in a flowing afterglow instrument, because the ion formed by decarboxylation of PhCH₂CH₂CO₂⁻ was thermalised by the helium carrier gas, and had a gas phase basicity (Δ*G*^o_{acid}) of 1699 ± 13 kJ mol⁻¹, a value consistent with that expected for PhCH₂CH₂⁻.

The reaction coordinate calculations [at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory] of relevant C₈H₇⁻ isomers provide some interesting results (see Fig. 4 and Supplementary table 5†). First, PhCH₂CH₂⁻ (**A**) can undergo a 1,2-H transfer over a transition state (+145 kJ mol⁻¹) to yield Ph⁻CHCH₃ (**D**) in an exothermic reaction (-104 kJ mol⁻¹). Second,

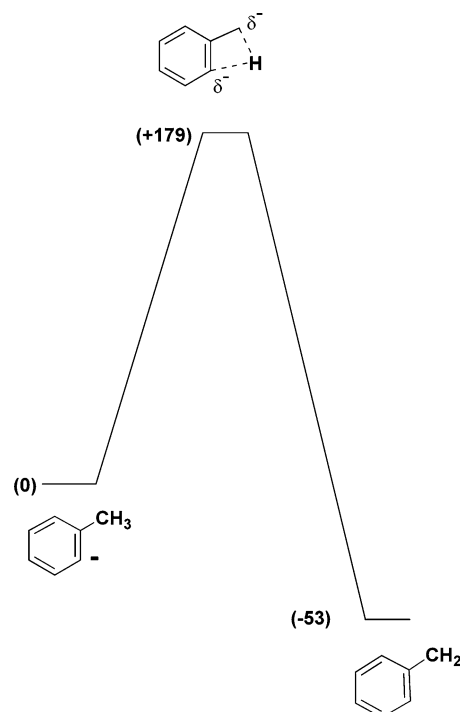


Fig. 3 The interconversion of the benzyl and *ortho*-tolyl anion. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. Relative free energies in kJ mol⁻¹. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 4.†

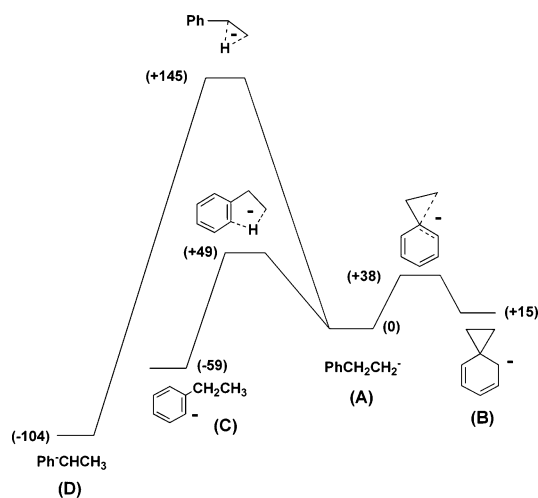


Fig. 4 The interconversions of PhCH₂CH₂⁻ (**A**), Ph⁻CHCH₃ (**D**), *ortho*-C₂H₅-C₆H₄⁻ (**C**) and the cyclised species (**B**). Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. Relative free energies in kJ mol⁻¹. Full details of geometries and energies of minima and transition states are recorded in Supplementary table 5.†

PhCH₂CH₂⁻ can H⁺ transfer from the *ortho* position to give *ortho*-C₂H₅C₆H₄⁻ (**C**) [barrier (+49 kJ mol⁻¹), reaction exothermic (-59 kJ mol⁻¹)]. However, the electron affinity of PhCH₂CH₂⁻ at the G3B3 level of theory is calculated to be 0.215 eV (21 kJ mol⁻¹), so these two H transfer processes are unfavourable compared with electron loss from PhCH₂CH₂⁻. Finally, the data shown in Fig. 4 indicates that the conversion of PhCH₂CH₂⁻ (**A**) to the cyclic isomer (**B**) is endothermic (+15 kJ mol⁻¹) and has a modest barrier

to the transition state of 38 kJ mol^{-1} . This interconversion and electron loss from $\text{PhCH}_2\text{CH}_2^-$ should therefore be competitive. These theoretical data are consistent with previous studies, namely (i) Nibbering *et al.* finding rearrangement of $\text{PhCH}_2\text{CH}_2^-$ on collisional excitation,³⁰ and (ii) Squires and Graul suggesting that $\text{PhCH}_2\text{CH}_2^-$ is stable when the ion is efficiently thermalized by the helium carrier gas in the flowing afterglow drift tube.³¹

The collision induced mass spectrum of the adduct formed between “ $\text{PhCH}_2\text{CH}_2^-$ ” (by decarboxylation of $\text{PhCH}_2\text{CH}_2\text{CO}_2^-$) and CS_2 shows pronounced loss of H_2S . The analogous spectra of $\text{Ph}(\text{CH}_3)\text{CHCS}_2^-$ and *ortho*- $\text{C}_2\text{H}_5\text{-C}_6\text{H}_4\text{-CS}_2^-$ do not exhibit loss of H_2S . *Ortho*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4\text{-CS}_2^-$ eliminates CS by the standard *ipso* rearrangement (data not shown but *cf.* Fig. 1)], while $\text{Ph}(\text{CH}_3)\text{CHCS}_2^-$ yields $\text{Ph}(\text{CH}_3)\text{CH}^-$ at low CS_2 pressures. It can therefore be concluded that $\text{PhCH}_2\text{CH}_2^-$ neither isomerizes to Ph^-CHCH_3 nor to *ortho*- $\text{C}_2\text{H}_5\text{C}_6\text{H}_4^-$ prior to or during reaction with CS_2 in the LCQ mass spectrometer.

The two D labelled species $\text{PhCH}_2\text{CD}_2\text{CS}_2^-$ and $\text{PhCD}_2\text{CH}_2\text{CS}_2^-$ were formed in the Waters QTOF2 mass spectrometer [by deprotonation under electrospray ionization of $\text{PhCH}_2\text{CD}_2\text{CS}_2\text{H}$ and $\text{PhCD}_2\text{CH}_2\text{CS}_2\text{H}$ in methanol]. These two dithiocarboxylate anions are those which would be formed by the ion molecule reactions between the appropriately D-labelled β -phenylethyl anion and CS_2 in the LCQ spectrometer. CID MS/MS of $\text{PhCH}_2\text{CD}_2\text{CS}_2^-$ shows loss of D_2S (see Fig. 5), while $\text{PhCD}_2\text{CH}_2\text{CS}_2^-$ loses H_2S . Loss of H_2S from $\text{PhCH}_2\text{CH}_2\text{CS}_2^-$ has been shown by *ab initio* calculations to occur as shown in Fig. 6 (also Supplementary table 6†).

The two D labelled species “ $\text{PhCD}_2\text{CH}_2^-$ ” and “ $\text{PhCH}_2\text{CD}_2^-$ ” were prepared by decarboxylation of their respective carboxylate anions in the LCQ mass spectrometer. If these anions interconvert

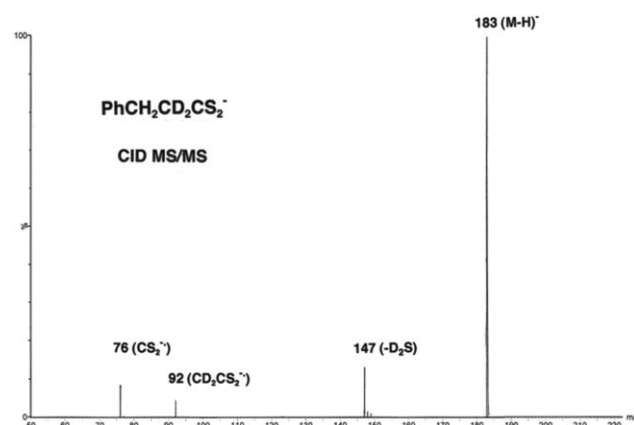


Fig. 5 The CID MS/MS of $\text{PhCH}_2\text{CD}_2\text{CS}_2^-$ using electrospray ionization with a Waters QTOF2 mass spectrometer. The collisional activation process in the QTOF2 produces more energized anions than those formed in the LCQ. Thus the peaks observed at m/z 92 and 76 in Fig. 5 are not observed in Fig. 7. Since H_2S is lost exclusively from $\text{PhCD}_2\text{CH}_2\text{CS}_2^-$, the small peaks at m/z 148 and 149 (losses of HDS and H_2S respectively) shown in this Figure are produced by undefined reactions favoured by the operation of a primary deuterium isotope effect occurring for the loss of D_2S from $\text{PhCH}_2\text{CD}_2\text{CS}_2^-$.

through the D_2 analogue of cyclic (B) (Fig. 4) prior to or during reaction with CS_2 , the subsequent losses of $\text{H}_2\text{S} : \text{D}_2\text{S}$ should be the same from both labelled adducts (assuming no deuterium isotope effect is operating). If there is no cyclization then specific losses of H_2S and D_2S should be observed, as seen in the QTOF2 spectra described above. The LCQ data are as follows. The adduct formed from “ $\text{PhCD}_2\text{CH}_2^-$ ” and CS_2 loses H_2S , while that from

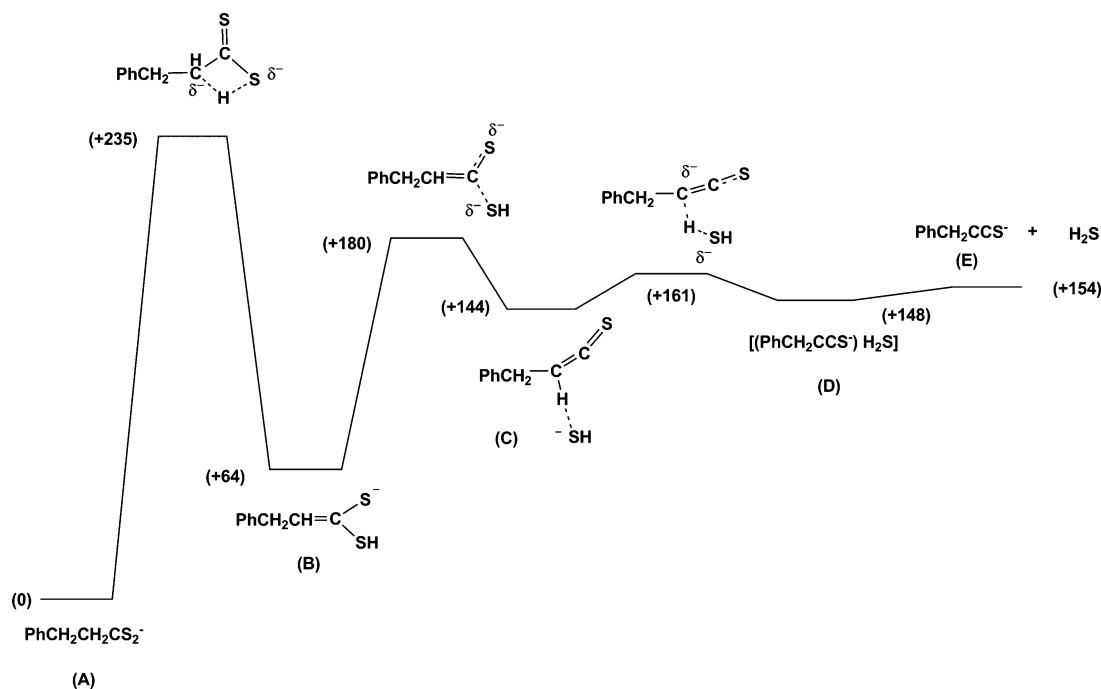


Fig. 6 Reaction coordinate profile for the dissociation of $\text{PhCH}_2\text{CH}_2\text{CS}_2^-$ to $\text{PhCH}_2\text{CCS}^- + \text{H}_2\text{S}$. Energies at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory. Relative free energies in kJ mol^{-1} . Full details of geometries and energies of minima and transition states are recorded in Supplementary table 6.† The reaction $\text{PhCH}_2\text{CH}_2^- + \text{CS}_2 \rightarrow \text{PhCH}_2\text{CH}_2\text{CS}_2^-$ is exothermic by 330 kJ mol^{-1} .

"PhCH₂CD₂⁻" and CS₂ loses D₂S (see Fig. 7). The spectrum shown in Fig. 7 does not change when the trapping time of the reactant ion is increased to 10 μsec.

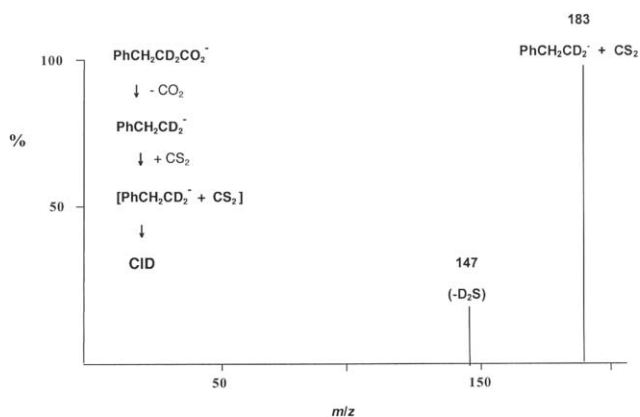


Fig. 7 The CID MS/MS/MS/MS scan of "PhCH₂CD₂CS₂⁻" formed by the reaction of CS₂ with "PhCH₂CD₂⁻" (formed from PhCH₂CD₂CO₂⁻). Electrospray ionization of PhCH₂CD₂CO₂H using a modified³⁶ Finnigan LCQ mass spectrometer.

The decarboxylation reaction shown in eqn (5) is calculated to be endothermic (+231 kJ mol⁻¹) at the UCCSD(T)/6-31+G(d,p)//B3LYP/6-31+G(d,p) level of theory (see Supplementary table 7†). Thus PhCH₂CH₂CO₂⁻ on collisional activation must produce a precursor with sufficient energy (231 kJ mol⁻¹) in order to effect decarboxylation. Collisional processes will produce energized precursor ions with a range of excess energies. The consequence of this is that some product ions PhCH₂CH₂⁻ may have excess energy. The theoretical results shown in Fig. 4 indicate that PhCH₂CH₂⁻ (**A**) needs only 38 kJ mol⁻¹ of excess energy in order to effect conversion to *ipso* species **B**. The experiments already carried out for the reactions of PhCH₂CD₂⁻ and PhCD₂CH₂⁻ with CS₂ show that there is no evidence of the *ipso* anion (**B**) (see Fig. 4) reacting with CS₂ during the ion molecule reaction, or of **B** being involved in an equilibrium process with **A** preceding or accompanying the ion molecule reaction with CS₂. This indicates that only thermalised ions **A** (or more correctly, anions with less than 38 kJ mol⁻¹ of excess energy) are reacting with CS₂ in the LCQ ion trap (*cf.* Gronert^{34,35}).

Conclusions

1. The reaction between C₆H₅⁻ and CS₂ in the gas phase gives an adduct C₆H₅CS₂⁻ which, when energized, rearranges *via* an *ipso* transition state to yield C₆H₅S⁻ and CS.
2. The respective reactions between C₆H₅CH₂⁻ and *ortho*-CH₃C₆H₅⁻ with CS₂ give adducts which can be readily distinguished by their collision induced dissociations; *i.e.* the adduct with C₆H₅CH₂⁻ loses H₂S, while that with *ortho*-CH₃C₆H₅⁻ loses both H₂S and CS₂, and
3. Decarboxylation of C₆H₅CH₂CH₂CO₂⁻ gives C₆H₅CH₂CH₂⁻ which reacts with CS₂ without rearrangement, to yield C₆H₅CH₂CH₂CS₂⁻.

Experimental

Mass spectrometry

All ion molecule reactions were carried out using electrospray ionization with a Finnigan LCQ ion trap mass spectrometer, modified³⁶ to allow ion-molecule reactions to be carried out by the incorporation of additional inlets for introduction of an extra reagent gas or liquid (in this case CS₂). The reagent CS₂ was injected into the system by syringe at a rate of 5 mL min⁻¹. Typical electrospray conditions involved a needle potential of 4.0 to 5.0 kV and a heated capillary temperature of 180 °C. Ions undergoing ion-molecule reactions in the LCQ have been essentially shown to be at room temperature.^{34,35} These experiments were investigated using the MS_n capability of the LCQ instrument. As an example, CID of C₆H₅CO₂⁻ to C₆H₅⁻ and CO₂ utilises an MS/MS scan, reaction of C₆H₅⁻ with CS₂ (MS/MS/MS) and finally, decomposition of the C₆H₅⁻ plus CS₂ adduct utilises an MS/MS/MS/MS scan.

Electrospray CID MS/MS spectra of ArCO₂⁻, ArCOS⁻ and ArCS₂⁻ anions were measured using a Waters QTOF2 hybrid orthogonal acceleration time-of-flight mass spectrometer (Waters/Micromass, Manchester, UK) with a mass range to *m/z* 10,000. The QTOF2 is fitted with an electrospray (ES) source in an orthogonal configuration with a Z-spray interface. Samples were dissolved in acetonitrile–water (1 : 1 v/v) and infused into the ES source at a flow rate of 5 mL min⁻¹. Experimental conditions were as follows: capillary voltage 3.1 kV, source temperature 80 °C, desolvation temperature 150 °C, and cone voltage 50 V. Tandem mass spectrometry (MS/MS) data were acquired using argon as the collision gas and the collision energy was set to give maximum fragmentation.

Theoretical methods

Geometry optimizations were carried out with the B3LYP/6-31+G(d,p) basis set [energies at UCCSD(T)/6-31+G(d,p) within the GAUSSIAN 03 suite of programs.³⁷ Stationary points were characterized as either minima (no imaginary frequencies) or transition states (one imaginary frequency) by calculation of the frequencies using analytical gradient procedures. The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations.³⁸ The calculated frequencies were also used to determine zero-point vibrational energies.

The G3B3 level of theory³⁹ was used to calculate electron affinities (the difference in energy between the appropriate anion and the corresponding radical). Three levels of theory were used for chosen standards CH₃CO₂⁻ and HCO₂⁻. The computed values obtained were compared with experimental values as shown below:-

Level of theory CH₃CO₂⁻ HCO₂⁻
 Experimental 3.470 eV⁴⁰ 3.541 eV⁴¹
 G2⁴² 3.499 eV 3.715 eV
 G3B3 3.319 eV 3.555 eV
 UCCSD//B3LYP 3.082 eV 3.474 eV

The G3B3 level of theory was used for calculating the following electron affinities because of reasonable accuracy (see above) and efficiency of computer time usage:- PhCS₂⁻ 3.345 eV and PhCH₂CH₂⁻ 0.215 eV.

All calculations were carried out using the South Australian Partnership for Advanced Computing (SAPAC) Facility.

Materials/synthesis

The following were purchased from Sigma-Aldrich and were used without purification: (i) argon gas, carbon disulfide, benzoic acid, thiobenzoic acid, phenylacetic acid, *ortho*-toluic acid, 1-phenylpropionic acid, 2-phenylpropionic acid, *ortho*-ethylbenzoic acid, and 1,2-dibromobenzene; (ii) CD₃I (*d*₃ > 99.5%).

Dithiobenzoic acid was made by a standard Grignard reaction between bromobenzene and carbon disulfide⁴³ [(M – H)[–] *m/z* 153; m.p. dec. > 200 °C; lit.⁴⁴ 208 °C].

Dithiophenyl acetic acid (benzene ethane dithioic acid) was prepared by a standard Grignard reaction using benzyl chloride and carbon disulfide.⁴³ (yield 57%; m.p. 17–19 °C, lit.⁴⁵ 20 °C

***o*-Methyl(*d*₃)benzoic acid** [m.p. 103–104 °C (lit.⁴⁶ 104–105 °C; *d*₃ = 99.5%)] was made by a Grignard sequence using *d*₃-methyl iodide (*d*₃ = 99.5%) and commencing with the diethylacetal of *o*-bromobenzaldehyde.⁴⁷

2,2-Dideuterophenylacetic acid [m.p. 77–78 °C (lit.⁴⁸ 78 °C; *d*₂ = 95%)] was prepared by two cycles of exchange of phenylacetic acid with deuterium oxide using a standard method.⁴⁸

2-Phenyl-2,2-dideutero-1-bromoethane. 2,2-dideuterophenylacetic acid was treated with lithium aluminium hydride in tetrahydrofuran (THF) at 0° by a standard method⁴⁹ giving 2-phenyl-2,2-dideuteroethanol (90% yield after vacuum distillation; *d*₂=95%), which was treated with bromine and triphenyl phosphine in dichloromethane by a standard method,⁵⁰ to give 2-phenyl-2,2-dideutero-1-bromoethane as a colourless oil after vacuum distillation (yield 65%; *d*₂ = 95%).

2-Phenyl-1,1-dideutero-1-bromoethane. Phenylacetic acid was treated with lithium aluminium deuteride in THF at 0° by a standard method⁴⁹ giving 2-phenyl-1,1-dideuteroethanol as a colourless oil (after vacuum distillation) (yield 91%; *d*₂ = 98%), which was treated with bromine and triphenyl phosphine in dichloromethane by a standard method⁵⁰ to give 2-phenyl-1,1-dideutero-1-bromoethane as a colourless oil (after vacuum distillation) (yield 83%; *d*₂ = 98%).

2,2-Dideutero-3-phenylpropionic acid. 2-Phenyl-1,1-dideutero-1-bromoethane in THF was allowed to react (by a standard Grignard reaction⁵¹) with magnesium in THF under reflux, followed by addition of solid carbon dioxide to give 2,2-dideutero-3-phenylpropionic acid [m.p. 46–48 °C (lit.⁴⁷ 47–48 °C); yield 62%; *d*₂ = 98%].

3,3-Dideutero-3-phenylpropionic acid. 2-Phenyl-2,2-dideutero-1-bromoethane in THF was allowed to react with magnesium in THF under reflux.⁵¹ Addition of solid CO₂ gave 3,3-dideutero-3-phenylpropionic acid [m.p. 46–48 °C (lit.⁴⁷ 47–48 °C); yield 65%; *d*₂ = 95%].

2,2-Dideutero-3-phenylpropane dithiolic acid. 2-Phenyl-1,1-dideutero-1-bromoethane in THF was allowed to react with Mg in THF, followed by addition of CS₂ and a catalytic amount of CuCl (in THF) at –50 °C.⁴³ Workup gave 2,2-dideutero-3-phenylpropanedithiolic acid as an unstable red–orange oil [(M – H)[–] *m/z* 183; 23% yield; *d*₂ = 98%] which was used immediately in

the gas phase ion chemistry experiments to form PhCH₂CD₂CS₂[–] in the QTOF2 mass spectrometer.

3,3-Dideutero-3-phenylpropane dithiolic acid. 2-Phenyl-2,2-dideutero-1-bromoethane in THF was allowed to react with Mg in THF, followed by addition of CS₂ and a catalytic amount of CuBr in THF at –50 °C.⁴³ 3,3-Dideutero-3-phenylpropanedithiolic acid was isolated as an unstable red–orange oil [(M – H)[–] *m/z* 183; 25% yield, *d*₂ = 95%]. This was used immediately in the gas phase experiment in the QTOF2 to form PhCD₂CH₂CS₂[–].

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