Gas-Phase Syntheses of Three Isomeric C_5H_2 Radical Anions and Their Elusive Neutrals. A Joint Experimental and Theoretical Study

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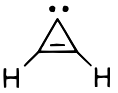
Three different radical anions of the empirical formula C_5H_2 have been generated by negative ion chemical ionization mass spectrometry in the gas phase. The isomers $C_4CH_2^{\bullet-}$, $C_2CHC_2H^{\bullet-}$, and $HC_5H^{\bullet-}$ have been synthesized by unequivocal routes and their connectivities confirmed by deuterium labeling, charge reversal, and neutralization reionization experiments. The results also provide evidence for the existence of neutrals C_4CH_2, C_2CHC_2H, and HC_5H as stable species; this is the first reported observation of C_2CHC_2H. Ab initio calculations confirm these structures to be minima on the anion and neutral potential energy surfaces.

Introduction

Since the discovery of the cyclic carbene C_3H_2 (**1**) in interstellar and circumstellar environments, interest in the generation and characterization of carbenes of the form C_nH_2 has increased.[1,2] Cyclic C_3H_2, together with its isomers and charged analogues, has been the subject of intensive investigation in recent years. Matrix-trapping experiments have characterized the neutrals cyclopropenylidene (**1**), propargylene (**2**), and propadienylidene (**3**),[3] while mass spectrometry has probed the molecular cations of **1**−**3**[4] and the molecular anions of **2** and **3**.[5] A number of theoretical studies have also been reported pertaining to these elusive systems,[6] and it is of interest to note that small unsaturated carbon species such as these have been proposed to act as negative charge carriers in some ion chemistry processes that occur in interstellar and circumstellar clouds.[7]



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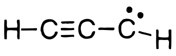

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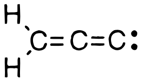

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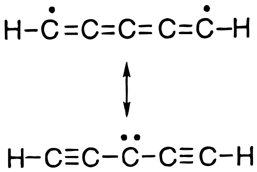
Some isomers of neutral C_5H_2 have also been described. Pentadiynylidene (**4**) has been trapped in a neon matrix and characterized by its electronic spectrum,[8] while pentatetraenylidene (**5**) and ethynylcyclopropenylidene (**6**) have been identified in a molecular beam using Fourier transform microwave spectroscopy.[9] The stabilities of **4**, **5**, and **6** have been studied using various ab initio methods,[10] and a thorough investigation of the C_5H_2 potential surface at high level has revealed two further stable isomers of C_5H_2, viz. ethynylpropadienylidene (**7**) and 3-(dihydrovinylidene)cyclopropene (**8**).[11]



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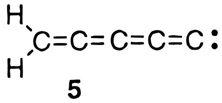

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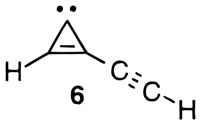

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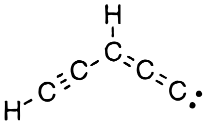

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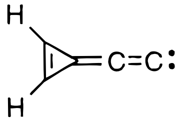

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Even-numbered cumulenes C_nH_2 ($n = 2, 4$) have been studied by mass spectrometric techniques.[12,13] In these cases, radical anions of the type C_nCH_2 ($n = 1, 3$) were formed in the gas phase by negative ion chemical ionization of appropriate precursors. Comparison of the charge reversal (CR)[14] and neutralization reionization (NR)[15] spectra of these radical anions with the mass spectra of acetylene ($HC_2H^{\bullet+}$) and diacetylene ($HC_4H^{\bullet+}$) radical cations show the CR and NR data to be surprisingly diagnostic.[12,13] The spectra of $C_3CH_2^{\bullet-}$ shows fragments $C_mCH_2^{\bullet+}$ (where $m = 1$ and 2), while these fragmentations are minimal for the $HC_4H^{\bullet+}$ isomer (the C_2H_2 system also shows this trend[12]). Similarly, we have found that the CR spectra of C_5H^- and $C_2CHC_2^-$ are also diagnostic as far as connectivity is concerned.[16,17] Thus it is possible that if we can generate other isomeric cumulene radical anions (e.g., $C_5H_2^{\bullet-}$, the subject matter of this paper), such species may also be distinguishable by CR and/or NR techniques, with the latter also providing an indication of the stability of the corresponding neutral.

In this paper, methodologies for the generation of the three radical anions of **4**, **5**, and **7** are described, as are the means by which the isomers may be distinguished. Generation of these radical anions provides access to the corresponding neutrals and cations by NR or photoelectron spectroscopic[18] techniques. Further, we describe the results of an ab initio study of the structures and relative energies of the three anions together with their neutral and cationic counterparts.

Experimental Section

A. Mass Spectrometric Methods. CR and NR spectra were measured using a two-sector reversed geometry VG ZAB 2HF spectrometer. This instrument and the typical experimental conditions of negative ion chemical ionization (NICI) have been

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described in detail elsewhere.[19] The instrument has been recently upgraded (by inclusion of two collision cells between the magnetic and electric sectors) in order to allow the measurement of NR spectra. Spectra were generated in the following manner. Samples were placed in glass capillaries, which were drawn to a fine point and inserted into the chemical ionization source via the solid inlet probe, in order to produce a measured pressure of 5×10^{-6} Torr, inside the source housing. Typical ionization conditions were source temperature, 200 °C; ionizing energy, 70 eV (tungsten filament); accelerating voltage, −7 kV. All slits were fully open in order to minimize mass discrimination effects due to energy resolution.[20] The reagent ions HO^-, DO^-, and CH_3O^- were generated, respectively, from substrates H_2O, D_2O, and CH_3OH (introduced through the heated septum inlet) to give an operating pressure inside the source housing of ca. 5×10^{-5} Torr, and thus an estimated pressure inside the ion source of close to 0.1 Torr. Negative ion chemical ionization of the sample either effected (i) deprotonation or dedeuteration as appropriate or (ii) desilylation of a neutral trimethylsilated substrate by the method developed by DePuy and co-workers.[21] Neutralization of the anion beam in the first collision cell was achieved by collision with oxygen gas at a typical pressure of 5×10^{-6} Torr: this reduces the main beam to 80% of its initial value, producing essentially single-collision conditions in the collision cell.[22] Residual ions were removed using the deflector electrode, with neutrals passing into the second cell where they were reionized to the corresponding cation under identical conditions to those used in the first cell. The spectra were collected by reversing the polarity of the electric sector voltage and scanning the sector voltage. CR spectra were measured under the same conditions as those used for NR spectra, except that the deflector electrode is grounded. Although this CR method does increase the likelihood of double collisions, it allows direct comparison between NR and CR spectra.[23] All spectra were repeated a minimum of three times in order to establish their reproducibility.

B. Syntheses of Precursor Molecules. *Methyl (5-Trimethylsilyl)penta-2,4-diynyl Ether [*$TMSC{\equiv}CC{\equiv}CCH_2OCH_3$*].* A solution of trimethylsilylbutadiyne lithiate was prepared by dropwise addition of methyllithium−lithium bromide complex (1.7 cm^3, 1.5 M solution in ether) to a stirred solution of bis(trimethylsilyl)butadiyne (0.5 g) in anhydrous tetrahydrofuran (20 cm^3), at 0 °C, under a nitrogen atmosphere.[24] The resultant mixture was stirred at 0 °C for 15 min, warmed to 20 °C and stirred for 2 h, and cooled to 0 °C, and freshly distilled chloromethyl methyl ether (0.23 cm^3) was added dropwise; the mixture was stirred at 20 °C for 12 h. The reaction mixture was cooled to 0 °C, quenched with aqueous ammonium chloride (saturated, 10 cm^3), and extracted with diethyl ether (3×20 cm^3); the ethereal extract was separated, washed with water (20 cm^3) and sodium chloride (saturated, 10 cm^3), and dried ($MgSO_4$). The solvent was then removed in vacuo to yield methyl (5-trimethylsilyl)penta-2,4-diynyl ether (0.36 g, 87%), $[M-H^+]^- = 165.0725$. $C_9H_{14}OSi$ requires 165.0736. ^1H NMR (200 MHz, $CDCl_3$) δ 0.16 (s, 9H), 3.36 (s, 3H), 4.13 (s, 2H).[25]

[1,1-D_2]-5-Trimethylsilylpenta-2,4-diyn-1-ol [$TMSC{\equiv}CC{\equiv}CCD_2OH$*]*[26a,b] was prepared by a standard procedure[26c] except that [D_2]paraformaldehyde was used in place of the unlabeled reagent. Yield = 83%. $D_2 > 99\%$.

[3-D_1]Penta-1,4-diyn-3-ol [$HC{\equiv}CCD(OH)C{\equiv}CH$*]* was prepared by a standard procedure[27] except that methyl [D_1]formate was used in place of ethyl formate. Yield = 73%. $D_1 = 98\%$.

[1,5-D_2]Penta-1,4-diyn-3-ol [$DC{\equiv}CCH(OH)C{\equiv}CD$*].* 1,5-Bis(trimethylsilyl)penta-1,4-diyn-3-ol[28] (1.5 g) in anhydrous tetrahydrofuran (20 cm^3) was added dropwise over 0.5 h to a stirred solution of potassium fluoride (1.0 g) in deuterium oxide (1 cm^3), at 0 °C, under a nitrogen atmosphere. The solution was then stirred at 25 °C for 12 h, before being dried ($MgSO_4$). Removal of the solvent in vacuo gave [1,5-D_2]penta-1,4-diyn-3-ol (0.31 g, 76%, $D_2 = 85\%$).

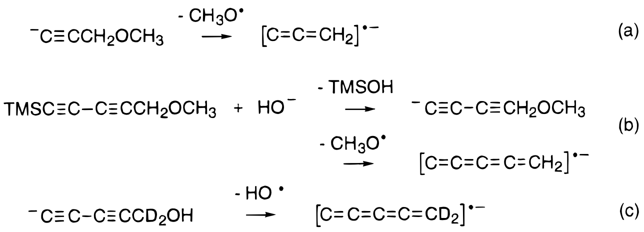
(1-Trimethylsilyl)penta-1,4-diyn-3-ol [$TMSC{\equiv}CCH(OH)C{\equiv}CH$*].* Ethynylmagnesium bromide (0.74 cm^3, 0.5 M in anhydrous tetrahydrofuran) was added dropwise under nitrogen to a stirred solution of (3-trimethylsilyl)propynal[29] (0.03 g), in anhydrous tetrahydrofuran (10 cm^3), at 0 °C, the mixture was stirred for 12 h at 25 °C, cooled to 0 °C, quenched with aqueous ammonium chloride (saturated, 10 cm^3) at 0 °C, and extracted with diethyl ether (3×20 cm^3). The organic extract was washed with water (20 cm^3) and sodium chloride (saturated 10 cm^3) and dried ($MgSO_4$), and the solvent was removed in vacuo to yield (1-trimethylsilyl)penta-1,4-diyn-3-ol, (0.03 g, 80%). $[M-H^+]^- = 151.0565$. $C_8H_{10}OSi$ requires 151.0579. ^1H NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 9H), 2.52 (d,1H), 2.90 (br, 1H), 5.10 (d,1H).

Methyl 3-[1,5-Bis(trimethylsilyl)]penta-1,4-diynyl Ether [$TMSC{\equiv}CCH(OCH_3)C{\equiv}CTMS$*].* Freshly distilled dichloromethyl methyl ether (1.61 cm^3) in anhydrous tetrahydrofuran (20 cm^3) was added dropwise to a stirred solution of trimethylsilylethynylmagnesium bromide[28] (7.83 g) in tetrahydrofuran (100 cm^3) over 0.5 h, at 0 °C, under a nitrogen atmosphere, and the reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched with aqueous ammonium chloride (saturated, 50 cm^3) and extracted with diethyl ether (3×50 cm^3), the ethereal extract was separated, washed with water (20 cm^3) and aqueous sodium chloride (saturated, 20 cm^3), and dried ($MgSO_4$). The solvent was removed in vacuo and the crude product purified by distillation at reduced pressure ($bp_{0.07}$ 76−80 °C) to yield methyl-3-[1,5-bis(trimethylsilyl)]penta-1,4-diynyl ether (1.74 g, 24%). $[M^{\bullet +}] = 238.1192$. $C_{12}H_{22}OSi_2$ requires 238.1209. ^1H NMR (200 MHz, $CDCl_3$) δ 0.19 (s, 18 H), 3.40 (s, 3H), 4.89 (s, 1H).

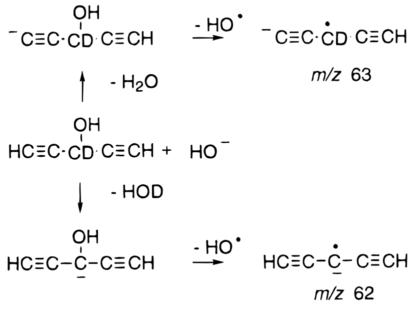
Methyl 3-[1,5-D_2]Penta-1,4-diynyl Ether [$DC{\equiv}CCH(OCH_3)C{\equiv}CD$*].* This preparation was carried out by the same procedure outlined for the corresponding alcohol; using methyl-3-[1,5-bis(trimethylsilyl)]penta-1,4-diynyl ether (0.75 g) gave methyl-3-[1,5-D_2]penta-1,4-diynyl ether (0.17 g, 59%, $D_2 > 97\%$).

C. Computational Methods. Geometry optimizations were carried out with the Becke 3LYP method[30] using the 6-31G level (GAUSSIAN 94[31]). 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. The calculated frequencies were also used to determine the zero-point vibrational energies, which were then scaled[32] by 0.9804 and used as a zero-point energy correction for the electronic energies calculated at this and higher levels of theory. More accurate energies for the B3LYP/6-31G geometries were determined with the CCSD(T)[33] method, using the Dunning aug-cc-pVDZ[34] basis set, within the MOLPRO package.[35] The described computational method was tested using C_2H_2 (**3**) giving a computed electron affinity of 1.67 eV compared with the experimentally determined 1.794 ± 0.025 eV.[18a] Calculations involving GAUSSIAN 94 geometry optimization were carried out using both PC and Unix machines. MOLPRO single-point energy

SCHEME 1



SCHEME 2



calculations were carried out with both the Cray J 932 computer at the Konrad-Zuse-Zentrum (Berlin) and the Power Challenge Super Computer at the Super Computing Centre (Canberra).

Results and Discussion

Synthesis of Isomeric C_5H_2 Radical Anions and Their Neutrals. *Experimental Confirmation of Connectivity.* Our initial approach to this problem followed earlier work on the collision-induced dissociation (CID) behavior of $^-C{\equiv}CCH_2OCH_3$.[36] This anion decomposes in a number of ways including major loss of $CH_3O^\bullet$ to yield $C_2CH_2^{\bullet-}$ (see sequence a, Scheme 1). The analogous process from $^-C{\equiv}CC{\equiv}CCH_2OCH_3$ should give $C_4CH_2^{\bullet-}$ (the radical anion of **5**). The precursor anion is formed by the reaction between methyl (5-trimethylsilyl)penta-2,4-diynyl ether and HO^- in the ion source of the mass spectrometer; this ion then undergoes facile metastable decomposition to yield a pronounced peak (*m/z* 62) corresponding to an ion of formula $C_5H_2^{\bullet-}$ (sequence b, Scheme 1). This anion must be $C_4CH_2^{\bullet-}$ unless either hydrogen or carbon rearrangement accompanies or precedes the formation of the ion. To support this assignment the corresponding deuterium analogue $C_4CD_2^{\bullet-}$ has also been synthesized: in this case from precursor anion $^-C{\equiv}CC{\equiv}CCD_2OH$ (sequence c, Scheme 1) formed by the reaction between $TMSC{\equiv}CC{\equiv}CCD_2OH$ and HO^-, followed by loss of hydroxide radical.

We next effected the synthesis of $HC_5H^{\bullet-}$ (the radical anion of neutral **4**). In principle, $HC_5H^{\bullet-}$ can be formed from anion $[HC{\equiv}C{-}C(OH)C{\equiv}CH]^-$ following loss of $HO^\bullet$ and indeed reaction of $HC{\equiv}CCD(OH)C{\equiv}CH$ and $DC{\equiv}CCH(OH)C{\equiv}CD$ with HO^- in the ion source yielded $C_5H_2^{\bullet-}$ (*m/z* 62, Scheme 2)[37a,b] and $C_5D_2^{\bullet-}$ (*m/z* 64), respectively. These isotopomers should have the desired HC_5H (also DC_5D) connectivity provided that no hydrogen (or deuterium) rearrangement precedes or accompanies formation of the anion. Coincident to the synthesis of the desired species, C_5HD (*m/z* 63) radical anions were observed as products, in the source reactions of both labeled precursors.[37c] This could occur via loss of $HO^\bullet$ from the ions $[C{\equiv}C{-}CD(OH)C{\equiv}CH]^-$ and $[C{\equiv}C{-}CH(OH)C{\equiv}CD]^-$, thus suggesting $C_2CDC_2H^{\bullet-}$ (*m/z* 63, Scheme 2) and $C_2CHC_2D^{\bullet-}$, respectively, to be the structures of the observed ions. To further investigate this novel connectivity, the precursor $TMSC{\equiv}CCH(OH)C{\equiv}CH$ was ionized under the same conditions and in a process analogous to sequence b of Scheme 1 yielded a peak of *m/z* 62, corresponding to $C_2CHC_2H^{\bullet-}$, the radical anion of **7**.

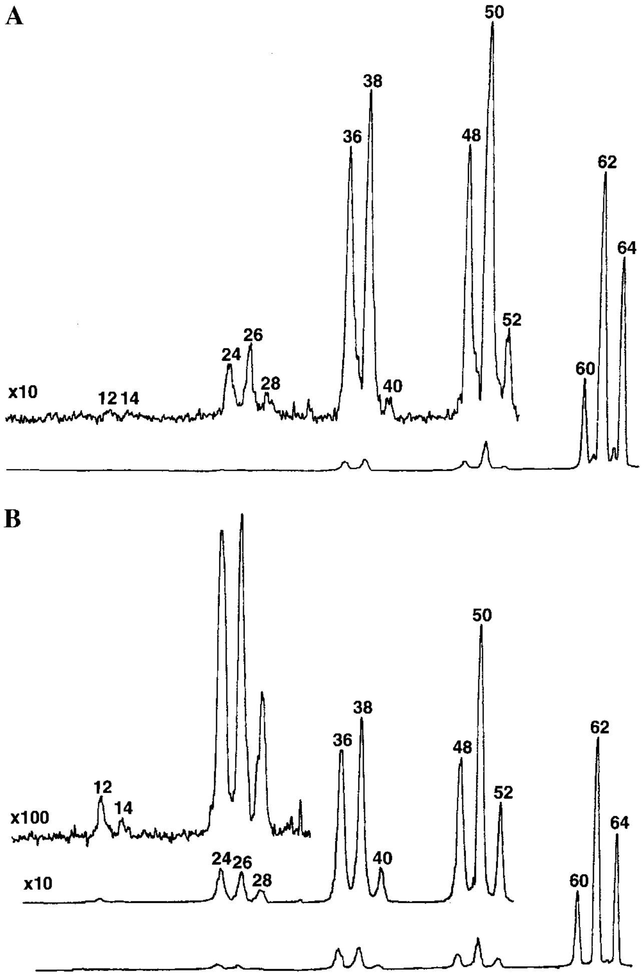


Figure 1. $^-NR^+$ (O_2, 80% T, O_2, 80% T) spectra of *m/z* 64 from (a, top) $DC{\equiv}CCH(OH)C{\equiv}CD$, giving $DC_5D^{\bullet-}$ and (b, bottom) $TMSC{\equiv}CC{\equiv}CCD_2OH$, giving $C_4CD_2^{\bullet-}$. These spectra both show fragment ions of the forms $C_nD_2^{\bullet+}$, $C_nD^{\bullet+}$, and $C_n^{\bullet+}$(where $n = 1{-}5$).

Despite the simple logic of the formation of these isomeric radical anions, further evidence is needed to confirm their connectivities. The conventional negative ion CA spectra of these isomers show only losses of $H^\bullet$ and H_2 and thus do not differentiate the isomers. In contrast, the CR and NR spectra may be used as probes of structure. Consider first the deuterated isomers $DC_5D^{\bullet-}$ and $C_4CD_2^{\bullet-}$ (the radical anions of deuterated **4** and **5**, respectively). Their CR spectra are listed in Table 1, while the NR spectra are illustrated, for comparative purposes, in Figure 1. Both sets of spectra show peaks corresponding to $C_nD_2^{\bullet+}$, C_nD^+, and $C_n^{\bullet+}$ ($n = 1{-}5$), confirming the empirical assignments made for the parent anions. Closer inspection of the spectra of the isomer $DC_5D^{\bullet-}$ reveals a low abundance of peaks corresponding to fragments $C_mD_2^{\bullet+}$ ($m = 2{-}4$).[38] This seems intuitive for the anticipated DC_5D structure given that formation of these ions must occur through loss of carbon with deuterium migration. This contrasts markedly to the spectrum of $C_4CD_2^{\bullet-}$ where the corresponding peaks (see, e.g., Figure 1) show a relative intensity more than twice that observed for $DC_5D^{\bullet-}$. While it is difficult to compare these spectra directly with those of the third labeled isomer, it is useful to compare the results from the two isotopomers $C_2CDC_2H^{\bullet-}$ and $C_2CHC_2D^{\bullet-}$ (Table 1). If we consider here the CR spectra, both show the

TABLE 1: Charge Reversal (CR) and Neutralization Reionization (NR) Spectra for the Three $C_5H_2^{\bullet-}$ Isomers, [D_1] and [D_2] Analogues

precursor	fragmentations: *m/z* (intensity relative to base peak)
	m/z 64 from $DC\equiv CCH(OH)C\equiv CD$
$DC_5D^{\bullet-}$	**CR** 64(88), 62(100), 60(34), 52(2), 50(27), 48(6), 40(0.3), 38(7.5), 36(3.5), 28(0.1), 26(1), 24(0.6), 16(<0.02), 14(<0.1), 12(<0.1)
	NR 64(70), 62(100), 60(31), 52(2), 50(14), 48(7), 40(0.5), 38(8), 36(7), 28(0.7), 26(2), 24(1.3), 16(<0.02), 14(0.2), 12(0.2)
	m/z 64 from $TMSC\equiv CC\equiv CCD_2OH$
$C_4CD_2^{\bullet-}$	**CR** 64(49), 62(100), 60(33), 52(14), 50(23), 48(11), 40(3), 38(8), 36(5), 28(0.3), 26(0.7), 24(0.8), 16(<0.02), 14(<0.02), 12(0.1)
	NR 64(58), 62(100), 60(33), 52(5), 50(14), 48(7), 40(2), 38(9), 36(8), 28(0.6), 26(1.5), 24(1.5), 16(<0.02), 14(0.1), 12(0.2)
	m/z 63 from $DC\equiv CCH(OCH_3)C\equiv CD$
$C_2CHC_2D^{\bullet-}$	**CR** 63(68), 62(100), 61(48), 60(27), 51(11), 50(7.5), 49(9), 48(7.5), 39(5.5), 38(5), 37(8), 36(6), 27(0.5), 26(1.4), 25(1), 24(1.4), 15(<0.02), 14(<0.1), 13(<0.02), 12(0.2)
	NR 63(97), 62(100), 61(69), 60(66), 51(8), 50(9), 49(11), 48(15), 39(4), 38(13), 37(15), 36(23), 27(<0.02), 26(3), 25(<0.02), 24(6), 15(<0.02), 14(<0.02), 13(<0.02), 12(<0.02)
	m/z 63 from $HC\equiv CCD(OH)C\equiv CH$
$C_2CDC_2H^{\bullet-}$	**CR** 63(71), 62(100), 61(35), 60(7), 51(3), 50(11), 49(8), 48(2.5), 39(1.5), 38(7), 37(7), 36(4.5), 27(0.2), 26(0.9), 25(1.5), 24(1), 15(<0.02), 14(<0.02), 13(<0.1), 12(<0.1)
	NR 63(73), 62(100), 61(47), 60(9), 51(3), 50(14), 49(10), 48(4), 39(4), 38(11), 37(16), 36(10), 27(1), 26(3), 25(4), 24(4), 15(<0.02), 14(<0.02), 13(<0.02), 12(<0.02)
	m/z 62 from $HC\equiv CCD(OH)C\equiv CH$
$HC_5H^{\bullet-}$	**CR** 62(87), 61(100), 60(25), 50(0.8), 49(9.5), 48(4), 38(0.2), 37(3), 36(2), 26(0.03), 25(0.25), 24(0.2), 14(<0.02), 13(<0.02), 12(<0.1)
	NR 62(76), 61(100), 60(44), 50(1), 49(6), 48(4), 38(0.5), 37(3.5), 36(4), 26(0.15), 25(0.6), 24(0.75), 14(<0.02), 13(<0.02), 12(<0.1)
	m/z 62 from $TMSC\equiv CC\equiv CCH_2OCH_3$
$C_4CH_2^{\bullet-}$	**CR** 62(60), 61(100), 60(26), 50(10), 49(21), 48(14), 38(2), 37(9), 36(6), 26(0.4), 25(0.9), 24(1), 14(<0.02), 13(<0.02), 12(0.25)
	NR 62(62), 61(100), 60(36), 50(3), 49(11), 48(9), 38(1), 37(8), 36(8), 26(0.5), 25(1.5), 24(2), 14(<0.02), 13(<0.02), 12(<0.02)
	m/z 62 from $TMSC\equiv CCH(OH)C\equiv CH$
$C_2CHC_2H^{\bullet-}$	**CR** 62(56), 61(100), 60(27), 50(6), 49(10.5), 48(7), 38(2), 37(5), 36(5), 26(0.5), 25(0.8), 24(1), 14(<0.02), 13(<0.1), 12(0.15)
	NR 62(54), 61(100), 60(34), 50(3), 49(7), 48(6), 38(0.7), 37(3.5), 36(4.5), 26(0.3), 25(0.6), 24(1), 14(<0.02), 13(<0.02), 12(0.15)

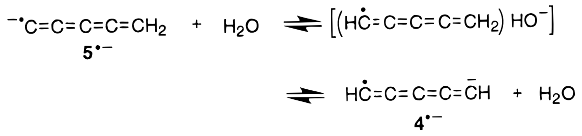
isotopically analogous fragment ions to those already discussed, namely, $C_nDH^{\bullet+}$, C_nD^+, C_nH^+, and $C_n^{\bullet+}$ (where $n = 1-5$). Significantly, however, in the spectrum of $C_2CHC_2D^{\bullet-}$ the losses of $CD^\bullet$ and $C_2D^\bullet$ predominate over losses of $CH^\bullet$ and $C_2H^\bullet$ while the opposite is observed for $C_2CDC_2H^{\bullet-}$. This would be in accord with the assigned connectivities, with the terminal CH/D unit lost preferentially to that at the central position, where some rearrangement or migration would be required. In particular, the comparison of the two different monolabeled $C_5HD^{\bullet-}$ ions unambiguously demonstrates that the radical anion formed has two nonequivalent hydrogen atoms, thus excluding structures HC_5H and C_4CH_2.

The CR spectra of the unlabeled analogues $HC_5H^{\bullet-}$, $C_4CH_2^{\bullet-}$, and $C_2CHC_2H^{\bullet-}$ are illustrated in Figure 2. These spectra show the same trends as do those of their labeled counterparts (cf. Table 1). The CR spectrum of $HC_5H^{\bullet-}$ shows low abundance peaks from ions $C_mH_2^{\bullet+}$ ($m = 2-4$): in contrast, such peaks are more abundant in the CR spectrum of $C_4CH_2^{\bullet-}$. The CR spectrum of the final isomer (Figure 2c) is hardly characteristic, appearing quite similar to that of $C_4CH_2^{\bullet-}$. However, the propensity for $CH^\bullet$ and $C_2H^\bullet$ loss from this structure, established previously from the labeled ions, is consistent with the major losses observed in this spectrum.

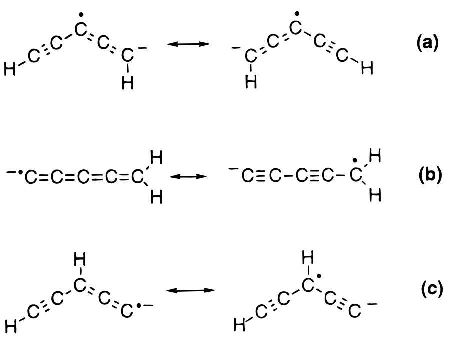
The experimental results discussed to date do not exclude the possibility of some interconversion of the initially formed radical anions. Mechanisms that might lead to isomerization include (i) intramolecular hydride transfer around the C_5-carbon skeleton (i.e., 1,2-H, 1,3-H, and 1,5-H shifts), (ii) cyclization followed by ring opening of the carbon skeleton, and (iii) intermolecular base-catalyzed proton transfer. The first two possibilities are energetically unfavorable. Given the high degree of unsaturation of the carbon chain, the barriers involved in forming the strained intermediates and transition states will be considerable. Examples of such rearrangement processes have been investigated computationally and will be discussed in the theoretical section of this paper. The third possibility is summarized in Scheme 3. This has been discounted by labeling studies which show that isotopic abundances of the product radical anions do not change in the presence of deuterated CI reagent gases in the ion source of the mass spectrometer (i.e., precursors ionized in the presence of either D_2O or H_2O show the same isotopic ratios for each of the $C_5H_2^{\bullet-}$ isomers). Mechanisms for isomerization are thus either energetically unfavorable or inconsistent with labeling data.[39] We conclude that the data presented indicates that $HC_5H^{\bullet-}$, $C_4CH_2^{\bullet-}$, and $C_2CHC_2H^{\bullet-}$ are generated as discrete species and that isomerization of these species is unfavorable under the experimental conditions.

There are abundant peaks corresponding to parent cations (survivor ions) in all of the NR spectra. In addition, the NR and CR spectra of each C_5H_2 radical anions are very similar (see Table 1). This suggests (i) a structural continuity between anion, neutral, and cation, since rearrangement of the neutral during the NR experiment should yield a spectrum quite distinct from that obtained from the vertical CR transition,[23] and (ii) favorable Franck−Condon overlap linking the three surfaces.[40]

SCHEME 3



SCHEME 4



We propose that the three neutral species **4**, **5**, and **7** have been generated successfully and that they are stable species on the time scale of the neutralization reionization experiment (ca. 10^{-6} s).

Theoretical Studies. Energy minima corresponding to $HC_5H^{\bullet-}$, $C_4CH_2^{\bullet-}$ and $C_2CHC_2H^{\bullet-}$ on the radical anion surface are shown in Figure 3 while their relative energies, along with those of the corresponding neutrals and cations, are summarized in Table 2. Consideration of these structures in traditional valence bond terms is by no means trivial as can be seen from the geometries given. Resonance hybrid contributors can be written which give a classic organic chemistry perspective of these species (Scheme 4). The C_{2v} geometry of $HC_5H^{\bullet-}$ can be rationalized by the structure $[HC{=}C{=}C{=}C{=}CH]^{\bullet-}$ together with some contribution from resonance structures a (Scheme 4).[41] The cumulenic nature of this species is best illustrated by the similarities between adjacent bond lengths, for example, the bonds C_1-C_2 and C_2-C_3 are 1.28 and 1.31 Å respectively, and also the sp^2 nature of the terminal C_5-H bonds (1.08 Å). This contrasts markedly with the diyne type structure of the triplet ground-state neutral ($^3\Sigma_g$, **4**, Table 3), where the bonds C_1-C_2 and $H-C_1$ are 1.25 and 1.06 Å, characteristic of sp-hybridized carbons. Interestingly the geometry of the singlet excited state ($^1A'$, **4**, Table 3) contains both cumulenic and acetylenic functionality. Hence, the geometry of the singlet more closely approximates that of the anion. Owing to the fact that electron transfers in CR and NR experiments can be considered to occur as vertical processes, electron detachment is expected to yield the excited singlet state of the neutral species.[15,40] The optimized structures for $C_4CH_2^{\bullet-}$ (C_{2v}) and $C_2CHC_2H^{\bullet-}$ (C_s) may be described as shown in b and c, respectively (Scheme 4). For $C_4CH_2^{\bullet-}$ the difference in the length of alternate carbon−carbon bonds is more pronounced suggesting a contribution from the localized acetylide ion to the hybrid, while the C−H bond lengths and angles, 1.09 Å and 122°, are characteristically sp^2, implying genuine cumulene character. For $C_2CHC_2H^{\bullet-}$ also, the structure suggests contributions from both localized acetylide as well as cumulenic representations. Both $C_4CH_2^{\bullet-}$ and $C_2CHC_2H^{\bullet-}$ are structurally similar to their respective singlet ground-state neutrals (**5** and **7**, Table 3), indicating that these are likely to be the species accessed in the NR experiments. The geometrical data for the neutral C_5H_2 isomers discussed here are listed in Table 3. The B3LYP structures show excellent agreement with the recent work of Seburg and co-workers,[11] who optimized the ground-state neutral geometries of these three C_5H_2 isomers at the CCSD(T) level.[42]

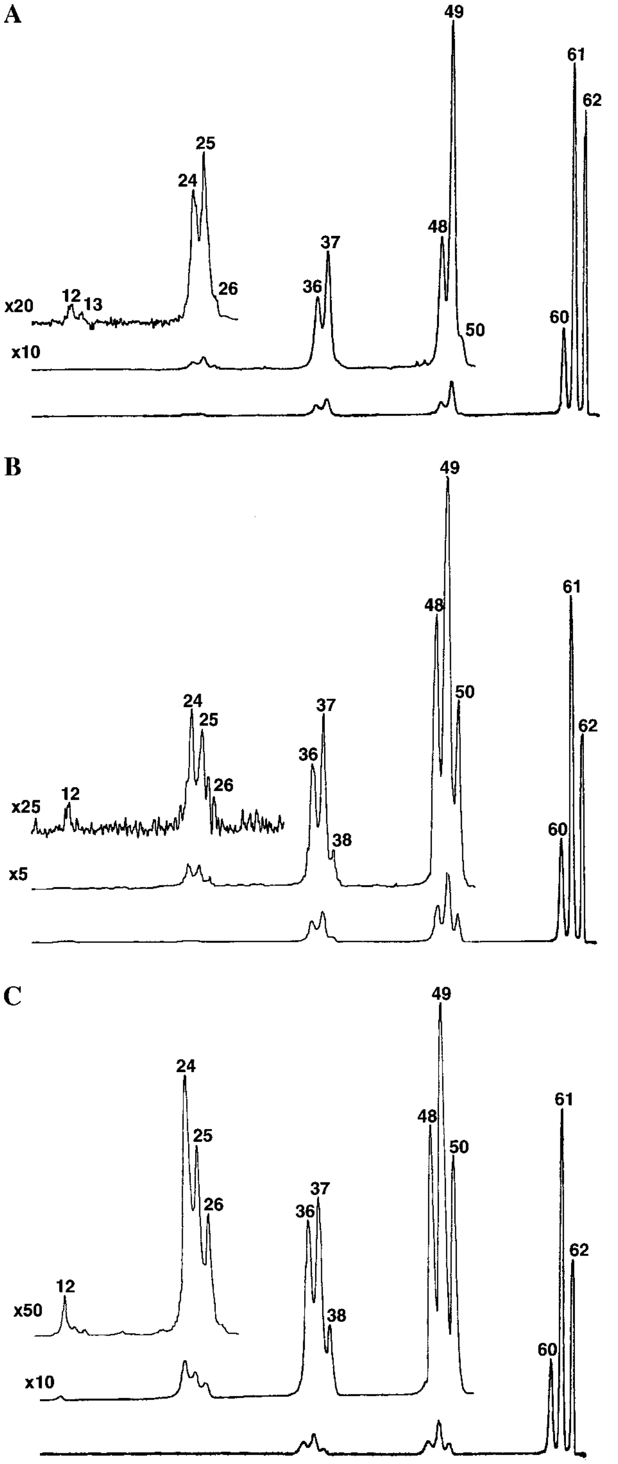


Figure 2. $^{-}CR^{+}$ (O_2, 80% T, O_2, 80% T) spectra of *m/z* 62 from (a, top) $HC{\equiv}CCD(OH)C{\equiv}CH$, giving $HC_5H^{\bullet-}$, (b, middle) $TMSC{\equiv}CC{\equiv}CCH_2OCH_3$, giving $C_4CH_2^{\bullet-}$, and (c, bottom) $TMSC{\equiv}CCH(OH)C{\equiv}CH$, giving $C_2CHC_2H^{\bullet-}$. These spectra each show fragment ions of the forms $C_nH_2^{\bullet+}$, $C_nH^{\bullet+}$, and $C_n^{\bullet+}$ (where $n = 1-5$).

The relative energies of the anions (Table 2) show $C_4CH_2^{\bullet-}$ is more stable than $HC_5H^{\bullet-}$ by 12.9 kcal mol^{-1} at the level of theory indicated. This is the reversal of the trend for the corresponding neutrals but is similar to that observed previously by Ikuta[6b] for the analogous C_3H_2 radical anions, where $C_2CH_2^{\bullet-}$ was found to be more stable than $HC_3H^{\bullet-}$ by 15.8 kcal mol^{-1}. The isomer $C_2CHC_2H^{\bullet-}$ is 6.2 kcal mol^{-1} less stable than

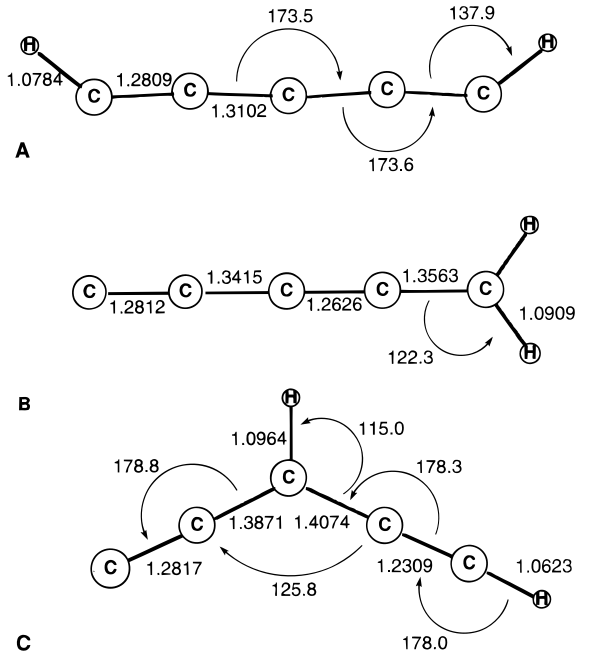


Figure 3. Optimized geometries for the three C_5H_2 radical anion isomers, $\mathbf{4}^{\bullet-}$, $\mathbf{5}^{\bullet-}$, and $\mathbf{7}^{\bullet-}$. All optimizations were carried out at the B3LYP/6-31G level of theory, with bond lengths given in angstroms and angles in degrees.

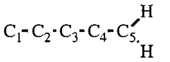
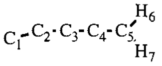
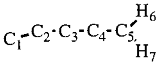
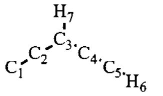
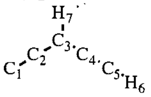
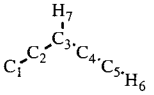
TABLE 2: Energies of Anions, Neutrals, and Cations of Connectivities 4 (HC_5H), 5 (C_4CH_2), and 7 (C_2CHC_2H)[a]

		electronic energy (au) CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G	zero-point energy[b] (au) B3LYP/6-31G	relative energies[c] (kcalmol^{-1})
$\mathbf{4}^{\bullet-}$	$^2B_1$	−191.034 43	0.036 71	12.9
4	$^3\Sigma_g$	−190.981 30	0.039 28	47.8
4	$^1A_1$	−190.958 06	0.038 49	61.9
$\mathbf{4}^{\bullet+}$	$^2\Pi_g$	−190.682 74	0.041 61	236.6
$\mathbf{5}^{\bullet-}$	$^2B_1$	−191.058 79	0.040 63	0.0
5	$^1A_1$	−190.972 71	0.041 87	54.8
5	$^3A''$	−190.931 65	0.039 48	79.1
$\mathbf{5}^{\bullet+}$	$^2A'$	−190.630 81	0.040 42	268.4
$\mathbf{7}^{\bullet-}$	$^2A''$	−191.047 89	0.039 64	6.2
7	$^1A'$	−190.971 36	0.042 06	55.8
7	$^3A''$	−190.902 62	0.041 26	98.4
$\mathbf{7}^{\bullet+}$	$^2A'$	−190.588 37	0.042 73	296.5
TS5$^{\bullet-}$/7$^{\bullet-}$		−190.915 23	0.033 58	85.8
TS4$^{\bullet-}$/6$^{\bullet-}$		−190.940 83	0.033 20	69.5

[a] The energies of **TS5$^{\bullet-}$/7$^{\bullet-}$** and **TS4$^{\bullet-}$/6$^{\bullet-}$** from the radical anion surface are also included. [b] Zero-point energy scaled by 0.9804.[32] [c] Includes zero-point energy correction.

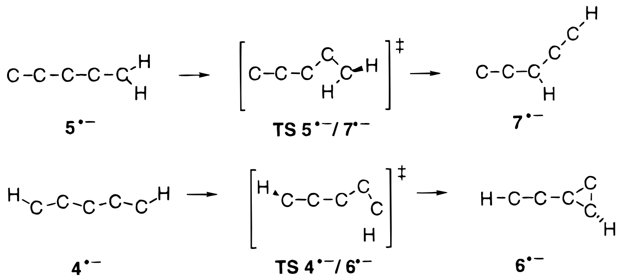
$C_4CH_2^{\bullet-}$. The computational results allow estimation of the adiabatic electron affinities (EA) of the three neutrals HC_5H, C_4CH_2, and C_2CHC_2H: these are 1.51, 2.38, and 2.15 eV, respectively.[43] The possibility of isomerization of these radical anions has also been investigated computationally. Two typical examples are shown in Scheme 5, which represent the two types of processes previously discussed, namely, a 1,3-hydride shift (**TS5$^{\bullet-}$/7$^{\bullet-}$**) and a three-membered ring formation (**TS4$^{\bullet-}$/6$^{\bullet-}$**).[45] These rearrangements have activation barriers of 85.8 and 56.5 kcal mol^{-1}, respectively (Table 2), suggesting that these processes are much more energy demanding than electron loss and as such unlikely to be observed under the experimental conditions. The latter process yields $\mathbf{6}^{\bullet-}$ which is not discussed here, except to make the point that further energetic isomerization would obviously be required for complete conversion to either $C_4CH_2^{\bullet-}$ or $C_2CHC_2^{\bullet-}$.

TABLE 3: Optimized Geometries for C_5H_2 Neutral and Radical Cation Isomers Corresponding to the Anions of Interest[a]

neutral ground state	neutral excited state	cation
4 ($D_{\infty h}$) $^3\Sigma_g$	**4** (C_S) $^1A'$	$\mathbf{4}^{\bullet+}$ ($D_{\infty h}$) $^2\Pi_g$
$H-C_1-C_2-C_3-C_4-C_5-H$	$H_7{}C_1-C_2-C_3-C_4-C_5-H_6$	$H-C_1-C_2-C_3-C_4-C_5-H$
bond length H-C_1 1.0648 C_1-C_2 1.2497 C_2-C_3 1.3111	bond length H_7-C_1 1.0808 C_1-C_2 1.2850 C_2-C_3 1.2901 C_2-C_3 1.3251 C_2-C_3 1.2389 H_6-C_5 1.0648 angle H_7-C_1-C_2 135.0 C_1-C_2-C_3 169.4 C_2-C_3-C_4 164.2 C_3-C_4-C_5 177.5 C_4-C_5-H_6 172.8	bond length H-C_1 1.0741 C_1-C_2 1.2466 C_2-C_3 1.3028
5 (C_{2v}) $^1A_1$	**5** (C_S) $^3A''$	$\mathbf{5}^{\bullet+}$ (C_S) $^2A'$
		
bond length C_1-C_2 1.2981 C_2-C_3 1.3037 C_3-C_4 1.2726 C_4-C_5 1.3242 C_5-H 1.0891 angle C_1-C_2-C_3 180.0 C_2-C_3-C_4 180.0 C_3-C_4-C_5 180.0 H-C_5-C_4 122.0	bond length C_1-C_2 1.3156 C_2-C_3 1.3075 C_3-C_4 1.2764 C_4-C_5 1.3372 C_5-H_6 1.0862 C_5-H_7 1.0862 angle C_1-C_2-C_3 169.4 C_2-C_3-C_4 180.0 C_3-C_4-C_5 180.0 H_6-C_5-C_4 121.4 H_7-C_5-C_4 121.4	bond length C_1-C_2 1.3401 C_2-C_3 1.2821 C_3-C_4 1.2895 C_4-C_5 1.3178 C_5-H_6 1.0928 C_5-H_7 1.0928 angle C_1-C_2-C_3 170.4 C_2-C_3-C_4 180.0 C_3-C_4-C_5 180.0 H_6-C_5-C_4 121.6 H_7-C_5-C_4 121.6
7 (C_S) $^1A'$	**7** (C_S) $^3A''$	$\mathbf{7}^{\bullet+}$ (C_S) $^2A'$
		
bond length C_1-C_2 1.2955 C_2-C_3 1.3449 C_3-C_4 1.4119 C_4-C_5 1.2181 C_5-H_6 1.0656 C_3-H_7 1.0941 angle C_1-C_2-C_3 179.5 C_2-C_3-C_4 125.0 C_3-C_4-C_5 179.8 H_6-C_5-C_4 179.1 H_7-C_3-C_2 119.3	bond length C_1-C_2 1.2367 C_2-C_3 1.3869 C_3-C_4 1.3964 C_4-C_5 1.2244 C_5-H_6 1.0645 C_3-H_7 1.0887 angle C_1-C_2-C_3 179.2 C_2-C_3-C_4 124.0 C_3-C_4-C_5 179.0 H_6-C_5-C_4 179.7 H_7-C_3-C_2 117.8	bond length C_1-C_2 1.2323 C_2-C_3 1.3817 C_3-C_4 1.3757 C_4-C_5 1.2287 C_5-H_6 1.0733 C_3-H_7 1.0944 angle C_1-C_2-C_3 178.6 C_2-C_3-C_4 124.3 C_3-C_4-C_5 178.2 H_6-C_5-C_4 179.8 H_7-C_3-C_2 118.1

[a] Optimizations performed using the B3LYP/6-31G level of theory. All bond lengths are in angstroms and all angles in degrees.

SCHEME 5



Conclusions

Gas-phase negative ion chemistry has been shown to be an efficient and structurally sensitive method of generating isomers of C_5H_2 radical anions. The technique of neutralization reionization mass spectrometry allows the formation of their neutral counterparts. This is the first reported observation of C_2CHC_2H. The stability of the radical anions and neutrals has been supported by ab initio calculations indicating these connectivities to be bound on both surfaces. The observation of C_5H_2 transient neutrals lends support to their candidacy as possible interstellar species.

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Supporting Information Available: The geomtries of the two transition states, **TS5$^{\bullet-}$/7$^{\bullet-}$** and **TS4$^{\bullet-}$/6$^{\bullet-}$**; a table of comparative geometries for the ground-state neutrals **4**, **5**, and **7** calculated at B3LYP/6-31G, MP2/cc-pVDZ and CCSD(T)/cc-pVTZ levels of theory (2 pages). Ordering and access information is given on any current masthead page.

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(37) (a) We have used the HO substituent instead of MeO, because the latter, although forming $C_5H_2^{\bullet-}$, also undergoes some hydride transfer to form $C_5H_3^-$ (*m*/*z* 63) and CH_2O. (b) Competing initial deprotonation also occurs at OH, but the resulting alkoxide species does not fragment to yield $C_5H_2^{\bullet-}$. (c) The MeO substituted precursor also gave $C_2CHC_2D^{\bullet-}$ (*m*/*z* 63) and is the precursor of choice here because its higher isotopic purity precludes a contribution from $HC_5D^{\bullet-}$ in the spectrum.

(38) It should be noted that the spectrum of $DC_5D^{\bullet-}$ also shows a number of very small peaks at *m*/*z* 63 and 61; it is suggested that these are fragmentations from the ^{13}C isotopomer of $C_2CDC_2H^{\bullet-}$, which may make a small contribution to the *m*/*z* 64 parent ion.

(39) A reviewer has suggested that isotopic scrambling may occur during the chemical ionization process itself. While this possibility cannot be excluded, the spectral data presented indicates that, if occurring at all, scrambling is incomplete and probably a minor process.

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(42) A reviewer has suggested possible problems arising from the B3LYP method with systems of this type. We have therefore repeated the

geometrical optimizations of the three ground-state neutrals at the MP2/cc-pVDZ level (see Supporting Information) but find that the B3LYP structures reported here show better agreement with the CCSD(T) structures of Seburg and co-workers.[11]

(43) Two of these values are greater than the EA of the hydroxide radical (1.827 67 ± 0.000 021 eV[44]), while in the third case, the value is only slightly lower than that of $HO^{\bullet}$. This may explain why the hydroxyl function in these systems undergoes such facile carbon−oxygen bond homolysis (see Schemes 1 and 2).

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