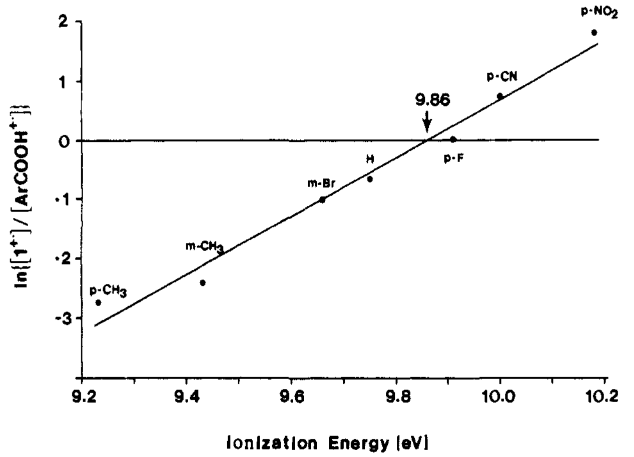

Figure 1. Plot of ln {[**1**$^{\bullet+}$]/[ArCOOH$^{\bullet+}$)} from ionized glycidol benzoates vs IE(ArCOOH).

while isomerization to **2**$^{\bullet+}$ or **3**$^{\bullet+}$ is inconsistent with the predominant loss of CH_2 (84%; CHD, 3%; CD_2, 13%) from methylene-d_2-oxirane$^{\bullet+}$ (**1**-$d_2^{\bullet+}$).[17]

Neutralization of the mass-analyzed beam of $C_3H_4O^{\bullet+}$ yields a beam of fast neutrals; their reionization $\sim 10^{-6}$ s later produces the $^+NR^+$ mass spectra[11,18] of Table I. For **1**$^{\bullet+}$, 16% of the products are undissociated, reflecting relatively high stabilities (especially versus **7**) for both the neutral and the reionized species. It is conceivable that this results from rearrangement of the newly formed **1** neutrals to a more stable isomer; however, no low-energy isomer[19] appears to be logical. The $^+NR^+$ spectrum of **8**$^{\bullet+}$ shows H loss 30× that of **1**$^{\bullet+}$. For **6**$^{\bullet+}$, CAD (He, 30% transmittance) of its neutrals $\sim 10^{-6}$ s after formation, followed by reionization,[11,18e] doubles the abundance of m/z 28 with little effect on m/z 53, while the same CAD of neutrals from **1**$^{\bullet+}$ doubles m/z 53 without affecting m/z 28. Further, the $^+NR^+$ spectrum of **1**$^{\bullet+}$ is similar to that from CAD (favored m/z 42, 30, 14), with **1**-d_2 losses of 79% CH_2, 1% CHD, and 20% CD_2 inconsistent with isomerization to **2** or **3**. Thus these products appear to arise mainly from dissociation, after reionization, of the long-lived methyleneoxirane (**1**).

An independent effort to generate **1** utilized flash-vacuum pyrolysis mass spectrometry.[20] Pyrolysis of 1-(phenylsulfinyl)-2,3-epoxypropane (500–650 °C) and of glycidol acetate and trifluoroacetate (750–850 °C) afforded no C_3H_4O. However, pyrolysis of **4** (800 °C) gave C_3H_4O ($\sim$1% yield) of ionization energy (IE, inverse convolution method)[21] 9.81 ± 0.05 eV. Using an independent method,[2c] we find that the log plot of the relative intensities of ArCOOH$^{\bullet+}$ and **1**$^{\bullet+}$ from esters **5** against IE(ArCOOH)[22] (Figure 1) is linear (correlation coefficient, 0.990) with the intercept at 9.86 eV. These values are further supported by $-\epsilon_{HOMO}$ from MNDO[23] (9.85 eV) and ab initio[16] (9.70 eV) calculations and differ substantially from those reported for isomers.[24] The high ionization energy of **1** versus linear enol ethers[24] is likely due to Coulombic factors imposed by the hybridization of the ring σ-bond framework.[25]

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Ab Initio Bond Strengths in Ethylene and Acetylene

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Accurate determinations of bond dissociation energies (BDEs) are essential for quantifying the thermodynamics of chemical reactions. The sequential C–H and C–C bond strengths in simple unsaturated hydrocarbons are very poorly known.[1] For instance, even measurements of the first C–H BDEs in ethylene and acetylene are still controversial: reports of $D_0(H_2CCH-H)$ range in value from 100 to 116.7 ± 1.2 kcal/mol,[1-7] while D_0(HCC–H) ranges from <126.647 ± 0.002 to 132 ± 5 kcal/mol.[8-12] Further, dramatic differences in estimated[3] strengths of the four C–H bonds in C_2H_4 require a theoretical explanation.

Recently, Ervin et al. measured the gas-phase acidities of HCCH, C_2H_4, and C_2H_3 radical and electron affinities of C_2H, C_2H_3, and H_2CC in order to derive D_0^{exp}(HCC–H) = 131.3 ± 0.7 kcal/mol, $D_0^{exp}(H_2CCH-H)$ = 109.7 ± 0.8 kcal/mol, and $D_0^{exp}(H_2CC-H)$ = 81.0 ± 3.5 kcal/mol.[3] Other C–H and C–C BDEs in C_2H_4 and C_2H_2 have not been measured directly. Ervin et al. derived the other C–H and C–C BDEs in C_2H_4 and C_2H_2 using current literature values for the heats of formation of C, C_2, CH, and CH_2. It is difficult to assess error bars for such derived BDEs, since the data are from a variety of sources.

A number of ab initio calculations of D_0(HCC–H) and $D_0(H_2CCH-H)$ have been performed,[14-17] but few included high

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Table I. Sequential Adiabatic Bond Energies for Ethylene and Acetylene

species[a]	D_0,[b,c] kcal/mol	D_0 (expt),[d] kcal/mol	D_0 (theory),[e] kcal/mol
$H_2CCH{-}H$	109.5	108.5 ± 2,[1] 116.7 ± 1.2,[2] 109.7 ± 0.8,[3] 107–110,[4] 105.0 ± 0.3,[5] 100,[6] 105.8 ± 0.4[7]	110.2[14]
$H_2CC{-}H$	74.6	(81.0 ± 3.5),[3] (80.0 ± 5.0)[22]	
$HCCH{-}H$	37.1	(33.6 ± 0.8)[3]	32.8[14]
$H{-}HCC$	79.9	(83.9 ± 4.2)[3]	
$H{-}CCH$	129.7	132 ± 2,[8] 132.6 ± 1.2,[2] 131.3 ± 0.7,[3] 127 ± 1.5,[9] ∠132.9 ± 1.2,[10] ∠126.647 ± 0.002,[11] ∠132.8 ± 0.004,[12] 132 ± 5[13]	133.5,[14] 131.54,[15a] 130.1,[15b], 119.0,[16] 120[17]
$H{-}CC$	97.8	(116.3 ± 2.6)[3]	
$H_2C{=}CH_2$	165.0[19]	(171.0 ± 1.2)[3]	
$H_2C{=}CH$	162.5	(161.8 ± 1.1)[3]	
$H_2C{=}C$	150.6	(160.7 ± 4.2)[3]	162[23]
$HC{\equiv}CH$	206.3[19]	(228.8 ± 0.7)[3]	
$HC{\equiv}C$	165.3	(177.4 ± 0.8)[3]	
$C{\equiv}C$	147.2	143.2,[24] (141.0 ± 2.5)[3]	

[a] Breaking bond indicated by line(s) between incipient fragments. [b] This work. CCCI total energies for all species to be published elsewhere (available on request).[21d] [c] Experimental zero-point energies were used to calculate D_0.[3,24,25] [d] Values in parentheses are derived (not measured directly). D_{298} are converted to D_0 using C_p listed in ref 3. [e] Previous theoretical calculations.

levels of electron correlation. UHF/MP4 calculations predicted $D_0(H_2CCH{-}H)$ = 110.2 kcal/mol, $D_0(HCCH{-}H)$ = 32.8 kcal/mol, and $D_0(HCC{-}H)$ = 133.5 kcal/mol,[14] while recent CI calculations find $D_0(HCC{-}H)$ = 131.54 ± 0.45 kcal/mol[15a] and 130.1 ± 1.0 kcal/mol.[15b]

Up to this point, no high-level ab initio calculations for other BDEs in C_2H_4 and C_2H_2 have been performed. Herein we report the first systematic study of all of the BDEs in C_2H_4 and C_2H_2 (Table I), using ab initio generalized valence bond (GVB)[18] and correlation-consistent configuration interaction (CCCI)[19] theory within a DZP basis set,[20] a method developed for calculating accurate (within 1–5 kcal/mol) dissociation energies for single and double bonds.[19] The geometries of all species were optimized at the GVB(6/12)-PP level by analytic gradient techniques.[21]

Breaking the first C—H bond of $H_2C{=}CH_2$ and $HC{\equiv}CH$ involves cleaving sp^2 and sp bonds, respectively, with little fragment geometric relaxation. We expect the BDE to increase in going from sp^2 to sp orbitals, since the latter are focused more directly along the bond. Indeed, we find that the first C–H BDE in HCCH is much larger than in C_2H_4: $D_0(H_2CCH{-}H)$ = 109.5 kcal/mol and $D_0(HCC{-}H)$ = 129.7 kcal/mol, in superb agreement with experimental results for C_2H_4 (109.7 ± 0.8 kcal/mol)[3] and for HCCH (132 ± 2[8] and 131.3 ± 0.7[3] kcal/mol), as well as with theory.[14,15]

Cleaving the α-CH bond of $H{-}CCH_2$ forms $H_2C{=}C(^1A_1)$ + H. Diabatically, we can break the α-CH bond to produce $H_2C{=}C(^3B_2)$, which then relaxes to its $^1A_1$ ground state. We calculate this adiabatic singlet–triplet splitting to be 45.6 kcal/mol, in excellent agreement with experiment (47.6 ± 0.14 kcal/mol)[22] and previous theory.[23] This relaxation causes the vinyl α-CH BDE to be smaller than the energy of the first C-H bond in C_2H_4: $D_0(H{-}CCH_2)$ = 74.6 kcal/mol, somewhat smaller than 81.0 ± 3.5 kcal/mol, as bracketed by Ervin et al.[3]

Dissociating the β-CH bond of $HC{=}CH_2$ yields $HC{\equiv}CH$ $(^1\Sigma_g^+)$ + H. Diabatic dissociation to $^3B_2$ *cis*-$HC{=}CH$ yields a bond strength of 120.9 kcal/mol, characteristic of an sp^2 C—H bond. However, since a new π bond is formed in the final state (HCCH), the large electronic and geometric relaxation of the final state (83.8 kcal/mol) leads to the smallest predicted D_0(C–H) in C_2H_4: only 37.1 kcal/mol, slightly larger than a derived upper limit (34.4 kcal/mol)[3] and previous theory (32.8 kcal/mol).[14]

Breaking the C–H bond of vinylidene yields a predicted $D_0(H{-}HCC)$ of 79.9 kcal/mol, which agrees well with the derived lower limit (79.7 kcal/mol).[3] While a new C–C π bond is formed in HCC, the C 2s lone pair in vinylidene must be uncoupled to form this new bond. Thus, the relaxation energy is much smaller (20.5 kcal/mol) than for breaking the β-CH vinyl bond, and hence the vinylidene C–H BDE will be much larger than for vinyl (79.9 vs 37.1 kcal/mol).

If we now break the C–H bond in HCC, we expect a diabatic BDE (to produce $^3\Sigma_u^+$ C_2) near that of HCCH (~130 kcal/mol). Electronic relaxation of $^3\Sigma_u^+$ C_2 to the $^1\Sigma_g^+$ ground state weakens the bond by 38.06 kcal/mol;[24] thus we expect a BDE of ~90 kcal/mol. We predict that D_0 = 97.8 kcal/mol, substantially lower than a suggested value of 116.3 ± 2.6 kcal/mol.[3] Since we overestimate the known electronic relaxation energy of C_2 by 4 kcal/mol ($\Delta E_{ST}^{\mathrm{theory}}$ = 42.3 kcal/mol), the true $D_0(H{-}CC)$ may be 98 + 4 = 102 kcal/mol.

The C=C double BDEs calculated by the GVB–CCCI method for $H_2C{=}CH_2$, $H_2C{=}CH$, and $H_2C{=}C$ are 165.0,[19] 162.5, and 150.6 kcal/mol, respectively, in reasonable agreement with experimentally derived values (171.0 ± 1.2, 161.8 ± 1.1, and 160.7 ± 4.2 kcal/mol).[3] By contrast, the triple BDE in $HC{\equiv}CH$ calculated by the CCCI method is ~10% too low, indicating that simultaneous excitations involving more than two electrons are very important for obtaining an accurate triple BDE.[19] Our GVB-CCCI calculation for HCC yields $D_e(HC{\equiv}C)$ = 170.0 kcal/mol. Correcting for a 10% correlation error for CCCI triple bond strengths, we estimate $D_e(HC{\equiv}C)$ ~ 188.5 kcal/mol and thus $D_0(HC{\equiv}C)$ ~ 180.5 kcal/mol, in good agreement with the derived experimental value of 177.4 ± 0.8 kcal/mol.[3] Finally, the predicted isomerization energy for the conversion of H_2CC $(^1A_1)$ to $HC{\equiv}CH(^1\Sigma_g^+)$ is 44.3 kcal/mol, again in excellent agreement with experiment (46.4 ± 5.5[22] and ≤44.1–44.7[12] kcal/mol).

In summary, our calculations agree very well with recent direct experimental measurements for three C–H bond strengths in C_2H_4, while they agree less well with indirectly derived values. Our work provides the first accurate and comprehensive theoretical study of sequential bond dissociation in ethylene and acetylene. In particular, for the bond strengths that have not been measured directly (i.e., the majority), our results suggest new values for these thermochemical processes.

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New Aspects of Chiral Heteroorganocuprates and an X-ray Crystal Structure with Unprecedented Magnesium–Sulfur Bonds

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Heterocuprates with both transferable groups (e.g., alkyl and aryl anions) and nontransferable groups (e.g., cyanide and thiolate anions) are excellent reagents for the formation of new C–C bonds in organic synthesis.[2,3] Although some information concerning the structural features of homocuprates in the solid state[4a] and in solution is available,[4] little is known about the nature of heterocuprates. In the course of our study directed to the rational synthesis of chiral heterocuprates having well-defined stoichiometries, we recently reacted both $LiC{\equiv}C\text{-}^tBu$ and $CuC{\equiv}C\text{-}^tBu$ with the novel, trimeric copper(I) thiophenolate, $[CuSC_6H_4(CH(Me)NMe_2)\text{-}2]_3$ (**1**; $[CuSAr]_3$), which has intramolecular Cu—N coordination as a special feature.[5] Surprisingly, in both reactions a mixed organo–thiophenolato copper compound, $[Cu_3(SAr)_2(C{\equiv}C\text{-}^tBu)]_2$, was formed quantitatively.[6] In the reaction of **1** with $LiC{\equiv}C\text{-}^tBu$ an alkynyl–thiophenolate anion exchange has occurred to generate this heteroorganocopper compound and a lithium thiophenolate rather than the expected heterocuprate.

We now report that whereas the reaction of **1** with dimesitylmagnesium affords a unique heterocuprate, **2**, its reaction with mesitylcopper as organometallic reagent affords a heteroorganocopper compound **3** (see Scheme I).

A mixture of $[CuSAr]_3$ (**1**) (3.68 mmol) and $[Mg(Mes)_2(THF)_2]$ (5.54 mmol; 0.5 equiv/Cu) was dissolved in 75 mL of boiling toluene. Distillation was used to remove the THF and to concentrate the reaction solution to 65 mL. On cooling of the solution to room temperature, the new heterocuprate $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (**2**) crystallized out as pale yellow crystals (73%).

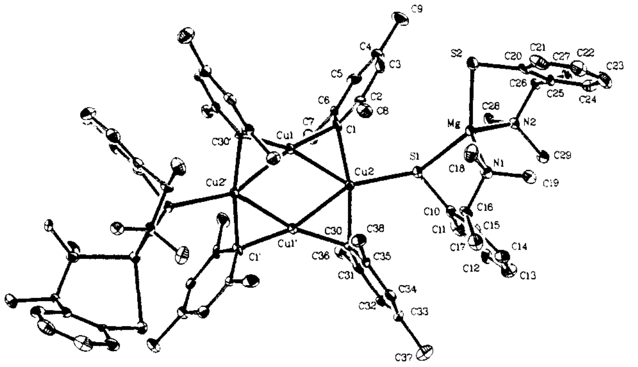

Figure 1. ORTEP drawing (50% probability level) of $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (**2**). Selected bond lengths (Å) and angles (deg): Cu1–C1, 1.981 (8); Cu1–C30′, 2.025 (8); Cu2–C1, 2.064 (8); Cu2–C30, 2.044 (8); Cu2–S1, 2.389 (2); Mg–N1, 2.186 (8); Mg–N2, 2.180 (7); Cu1⋯Cu1′, 2.700 (1); Cu1⋯Cu2, 2.464 (1); Cu1⋯Cu2′, 2.431 (1); Cu2⋯Cu2′, 4.079 (1); Cu1–C1–Cu2, 75.0 (3), Cu1′–C30–Cu2, 73.4 (3); Cu2–S1–Mg, 136.4 (1); S1–Mg–S2, 132.5 (2); N1–Mg–N2, 116.4 (3); S1–Mg–N1, 95.8 (2); S2–Mg–N2, 95.9 (2).

The heteroorganocopper compound $[Cu_2(SAr)(Mes)]_2$ (**3**) was formed from the reaction of **1** (2.21 g; 9.09 mmol of Cu) with $[CuMes]_5$[7] (1.66 g; 9.09 mmol of Cu) in 25 mL of benzene at room temperature and was obtained as a yellow solid after the solvent was distilled off. On the basis of ^1H NMR spectroscopic results, molecular weight determination (cryoscopy in benzene), and microwave titration of mesitylcopper with **1** (equivalence point at a 1:1 molar (Cu) ratio), we conclude that **3** exists in solution as a tetranuclear copper compound $[Cu_2(Mes)(SAr)]_2$.[8] Moreover, ^1H NMR studies of **3** in solution showed it to be a stable, discrete compound which does not undergo exchange with excess of either $[CuSAr]_3$ or mesitylcopper.

Recrystallization of $[(CuMes)_4(\mu\text{-}SAr)_2(MgSAr)_2]$ (**2**) from toluene gave crystals of a toluene solvate that were suitable for an X-ray structure determination.[9] The molecular structure found, shown in Figure 1, reveals **2** to be a heterocuprate with a structure consisting of a tetranuclear mesitylcopper unit bound to two bis(thiophenolato)magnesium units. The most noteworthy aspect is the presence of Mg–S bonds; one thiophenolate unit is S,N chelated to the magnesium center, and the other (N bound to Mg) uses its sulfur atom to bridge between copper and magnesium. Furthermore, this structure shows that during the synthesis complete exchange of thiophenolate and mesityl groups between copper and magnesium has occurred.

The overall structure of the central tetranuclear arylcopper unit in **2** is comparable to those of $[Cu_4(Mes)_4(THT)_2]$ (THT = tetrahydrothiophene)[10] and the *o*-tolylcopper compound $[Cu_4(C_6H_4Me\text{-}2)_4(SMe_2)_2]$.[11] The four copper atoms in **2** are almost coplanar with Cu⋯Cu distances (2.431 (1) and 2.464 (1) Å) that

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(8) Molecular weight (cryoscopy in the concentration range of 105–25.6 g kg^{-1} benzene): 813 g mol^{-1} (calcd for $[Cu_2(SAr)(Mes)]_2$ (**3**): 850 g mol^{-1}). ^1H NMR (toluene-d_8, 233 K): δ 1.12 (s, 3 H, NCH_3), 1.54 (d, 3 H, $ArCCH_3$), 1.71 (s, 3 H, NCH_3), 2.11 (s, 3 H, *p*-Mes-CH_3), 2.33 (s, 3 H, *o*-Mes-CH_3), 2.63 (q, 1 H, HCMe), 2.82 (s, 3 H, *o*-Mes-CH_3), 6.53 (s, 1 H, H-Mes), 6.61 (d, 1 H, 3-H-ArS), 6.82 (s, 1 H, H-Mes), 6.91 (dt, 1 H, 4-H-ArS), 7.06 (dt, 1 H, 5-H-ArS), 7.93 (d, 1 H, 6-H-ArS).

(9) Crystal data for **2**: $C_{76}H_{100}Cu_4Mg_2N_4S_4\cdot 2C_7H_8$, rod-shaped crystal (0.08 × 0.13 × 0.90 mm), orthorhombic, space group $P2_12_12$, with $a = 25.140$ (3) Å, $b = 19.026$ (2) Å, $c = 8.554$ (1) Å, $V = 4091.5$ (8) Å^3, $Z = 2$, $d_{calcd} = 1.368$ g cm^{-3}, $F(000) = 1776$, μ(Mo Kα) = 11.9 cm^{-1}; 6236 independent reflections ($0.81 < \theta < 29.4°$; $\omega/2\theta$-scan; $T = 100$ K) were measured on an Enraf-Nonius CAD-4F diffractometer using Zr-filtered Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentz polarization effects and for a small linear decay (0.4%). The structure was solved by Patterson (SHELXS 86) and difference Fourier techniques and refined by full-matrix least squares (SHELX 76) to an R value of 0.056, $wR = 0.061$, $w^{-1} = (\sigma^2(F) + 0.00106F^2)$ for 3674 reflections with $I > 2.5\sigma(I)$. Hydrogen atoms were introduced on calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. A final difference Fourier map showed no residual density outside 0.90 and −0.58 e/Å^3 (near the Cu atoms). Geometrical details of the structure are provided as supplementary material.

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