Theoretical Thermochemistry of the 1-Buten-3-yn-1-yl Radical and Its Chloro Derivatives

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High-level electronic structure calculations combined with empirical adjustments predict the standard enthalpy of the C−H bond dissociation in $HC \equiv C - CH = CH_2$ to be equal to 115.1 ± 1.4 kcal/mol, i.e., ca. 4.0 kcal/mol higher than that of the analogous bond cleavage in ethene. This difference in bond strengths stems from resonance stabilization of the parent molecule. The standard enthalpy of formation of the 1-buten-3-yn-1-yl radical is estimated at 133.8 ± 1.5 kcal/mol, which is significantly higher than all of the previously published values. As in the case of polychlorinated alkanes, the BLYP approximation is found to seriously underestimate the strengths of the C−H and C−Cl bonds in chloro derivatives of $HC \equiv C - CH = CH_2$. On the other hand, the BLYP/6-311G**, MP2/6-311G**, QCISD/6-311G**, and CCSD(T)/6-311G** predictions for the standard enthalpy of ethyne dimerization all closely match their experimental counterpart.

Introduction

The 1-buten-3-yn-1-yl radical ($HC \equiv C - CH = CH^\bullet$, n-$C_4H_3^\bullet$) is believed to play a pivotal role in combustion of small hydrocarbons such as CH_4 and C_2H_2. For many years, the reaction

$$2C_2H_2 \rightarrow n\text{-}C_4H_3^\bullet + H^\bullet \qquad (1)$$

has been regarded as the initiation step of the thermally induced radical-chain polymerization of ethyne.[1] However, the rate of formation of n-$C_4H_3^\bullet$ offered by this bimolecular process has been shown to be much too low to account for the observed polymerization kinetics.[2−4] Invoking reaction mechanisms that involve autocatalytic processes[5] does not eliminate this discrepancy.[6]

In fuel-rich C_2H_2/O_2 and CH_4/O_2 flames, benzene is produced primarily via recombination of propargyl radicals.[7,8] However, in fuel-lean C_2H_2/O_2 flames the addition of C_2H_2 to n-$C_4H_3^\bullet$ constitutes an important reaction pathway to benzene.[7,9] Analogous reactions take place during pyrolysis and combustion of polychlorinated hydrocarbons, such as C_2HCl_3 and C_2Cl_4.[10−12] Thus, the formation of hexachlorobenzene during pyrolysis of those compounds most probably involves the n-$C_4Cl_3^\bullet$ radical pathway,[11] which begins with dichloroethyne.[10]

Despite its importance to modeling of combustion reaction kinetics, the standard enthalpy of formation $\Delta H_f^o(HC \equiv C - CH = CH^\bullet)$ of the 1-buten-3-yn-1-yl radical has not been accurately established. The few estimates of $\Delta H_f^o(HC \equiv C - CH = CH^\bullet)$ that have been published so far vary widely: 124,[1] 125,[8] 127,[13] and 130 kcal/mol.[6] Even worse, the thermochemistry of chloro derivatives of n-$C_4H_3^\bullet$ has not been investigated either experimentally or theoretically. This lack of data has prompted the research described in this paper.

Details of Calculations

All the calculations were carried out with the Gaussian 94 suite of programs.[14] Full geometry optimizations were performed

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TABLE 1: Computed Standard Enthalpies of the C−H Bond Dissociation in the $CX_1X_2 = CX_3H$ Molecules[a]

X_1	X_2	X_3	BLYP	MP2	QCISD	CCSD(T)
H	H	H	106.72	112.21	107.13	107.91
H	H	Cl	104.70	112.04	106.03	106.64
H	Cl	Cl	106.53	115.08	108.10	108.76
Cl	H	Cl	104.35	113.70	106.79	107.36
H	$HC \equiv C$	H	109.50	123.60	112.12	112.90
$HC \equiv C$	H	H	109.52	123.33	112.12	112.87
Cl	$ClC \equiv C$	H	107.75	124.79	112.54	113.22
$ClC \equiv C$	Cl	H	109.40	124.96	113.32	114.06
H	$ClC \equiv C$	Cl	106.59	122.83	110.10	110.76
$ClC \equiv C$	H	Cl	106.35	122.73	109.82	110.49
Cl	$HC \equiv C$	Cl	104.91	124.16	110.57	111.19
$HC \equiv C$	Cl	Cl	106.54	125.10.	111.34	112.06

[a] All values in kcal/mol. The substituents X_1 and X_3 are in the *cis* position, the latter being attached to the carbon atom of the C−H bond undergoing dissociation.

at the BLYP/6-311G**, MP2/6-311G**, and QCISD/6-311G** levels of theory. All structures were confirmed to be local minima on potential energy hypersurfaces by the computed BLYP/6-311G** and MP2/6-311G** vibrational frequencies. CCSD(T)/6-311G** energies at the optimized QCISD/6-311G** geometries were also obtained. Spin-unrestricted wave functions were used as reference states in all calculations on radicals.

The standard enthalpies of all the species under study were calculated from the respective geometries and unscaled harmonic vibrational frequencies. The MP2/6-311G** zero-point energies and thermal corrections were used to convert the QCISD/6-311G** and CCSD(T)/6-311G** energies to the corresponding standard enthalpies.

Results and Discussion

The standard enthalpy $\Delta H_{C-H}^o(H_2C = CH \cdot H)$ of the C−H bond dissociation in ethene equals 111.2 ± 0.8 kcal/mol.[15] Among the four levels of theory employed in the present study, the MP2 approximation used in conjunction with the 6-311G** basis set appears to match this experimental figure most closely (Table 1). However, this agreement undoubtedly arises from a

TABLE 2: Computed Standard Enthalpies of the C−Cl Bond Dissociation in the CX_1X_2=CX_3Cl Molecules[a]

X_1	X_2	X_3	BLYP	MP2	QCISD	CCSD(T)
H	H	H	88.14	98.63	86.40	89.13
H	Cl	H	86.83	99.93	86.52	89.38
Cl	H	H	85.06	98.65	85.49	88.23
H	Cl	Cl	81.51	97.61	82.35	85.34
Cl	H	Cl	79.31	95.82	80.96	83.82
H	ClC≡C	H	89.87	109.65	90.24	93.18
ClC≡C	H	H	89.99	109.41	90.56	93.43
Cl	HC≡C	H	85.63	109.67	89.31	92.19
HC≡C	Cl	H	87.30	110.23	90.48	93.42
H	HC≡C	Cl	82.78	107.17	85.78	88.80
HC≡C	H	Cl	82.65	107.02	85.76	88.75
Cl	ClC≡C	Cl	79.13	106.20	83.72	86.87
ClC≡C	Cl	Cl	80.79	107.58	84.90	88.14

[a] All values in kcal/mol. The substituents X_1 and X_3 are in the *cis* position, the latter being attached to the carbon atom of the C−Cl bond undergoing dissociation.

TABLE 3: Empirically Adjusted Predictions for the Standard Enthalpies of the C−H Bond Dissociation in the CX_1X_2=CX_3H Molecules[a]

X_1	X_2	X_3	BLYP	MP2	QCISD	CCSD(T)
H	H	H	111.2[b]	111.2[b]	111.2[b]	111.2[b]
H	H	Cl	109.2	111.0	110.1	109.9
H	Cl	Cl	111.0	114.1	112.2	112.1
Cl	H	Cl	108.8	112.7	110.9	110.7
H	HCC	H	114.0	122.6	116.2	116.2
HCC	H	H	114.0	122.3	116.2	116.2
Cl	ClCC	H	112.2	123.8	116.6	116.5
ClCC	Cl	H	113.9	124.0	117.4	117.4
H	ClCC	Cl	111.1	121.8	114.2	114.1
ClCC	Cl	Cl	110.8	121.7	113.9	113.8
Cl	HCC	Cl	109.4	123.2	114.6	114.5
HCC	Cl	Cl	111.0	124.1	115.4	115.4

[a] All values in kcal/mol. The substituents X_1 and X_3 are in the *cis* position, the latter being attached to the carbon atom of the C−H bond undergoing dissociation. [b] Assumed (see the text for explanation).

TABLE 4: Empirically Adjusted Predictions for the Standard Enthalpies of the C−Cl Bond Dissociation in the CX_1X_2=CX_3Cl Molecules[a]

X_1	X_2	X_3	BLYP	MP2	QCISD	CCSD(T)
H	H	H	95.1[b]	95.1[b]	95.1[b]	95.1[b]
H	Cl	H	93.8	96.4	95.2	95.3
Cl	H	H	92.0	95.1	94.2	94.2
H	Cl	Cl	88.5	94.1	91.0	91.3
Cl	H	Cl	86.3	92.3	89.7	89.8
H	ClC≡C	H	96.8	106.1	98.9	99.2
ClC≡C	H	H	96.9	105.9	99.3	99.4
Cl	HC≡C	H	92.6	106.1	98.0	98.2
HC≡C	Cl	H	94.3	106.7	99.2	99.4
H	HC≡C	Cl	89.7	103.6	94.5	94.8
HC≡C	H	Cl	89.6	103.5	94.5	94.7
Cl	ClC≡C	Cl	86.1	102.7	92.4	92.8
ClC≡C	Cl	Cl	87.8	104.0	93.6	94.1

[a] All values in kcal/mol. The substituents X_1 and X_3 are in the *cis* position, the latter being attached to the carbon atom of the C−Cl bond undergoing dissociation. [b] Assumed (see the text for explanation).

TABLE 5: QCISD/6-311G Optimized Geometries of the X_1C_a≡C_b−C_cX_2=$C_dX_3X_4$ Molecules[a]**

X_1	X_2	X_3	X_4	C_a−C_b	C_b−C_c	C_c−C_d	C_a−C_b−C_c	C_b−C_c−C_d
H	H	H	H	1.213	1.441	1.344	178.2	123.4
H	H	H	•	1.209	1.449	1.325	178.7	122.5
H	H	•	H	1.208	1.445	1.325	177.6	124.1
H	H	Cl	Cl	1.212	1.431	1.344	177.3	124.0
H	H	Cl	•	1.208	1.442	1.330	178.6	123.6
H	H	•	Cl	1.208	1.441	1.328	177.6	122.6
H	Cl	H	Cl	1.212	1.434	1.344	179.5	120.7
H	Cl	H	•	1.208	1.441	1.320	178.9	122.8
H	Cl	•	Cl	1.207	1.436	1.326	179.8	122.0
H	Cl	Cl	H	1.211	1.430	1.343	179.5	124.9
H	Cl	Cl	•	1.207	1.436	1.328	179.0	123.7
H	Cl	•	H	1.207	1.439	1.318	180.0	124.4
Cl	H	H	Cl	1.211	1.435	1.341	177.8	121.9
Cl	H	H	•	1.207	1.447	1.325	178.3	122.6
Cl	H	•	Cl	1.206	1.438	1.329	177.1	122.7
Cl	H	Cl	H	1.211	1.432	1.343	176.8	125.0
Cl	H	Cl	•	1.207	1.440	1.330	178.1	123.7
Cl	H	•	H	1.207	1.443	1.325	177.1	124.2
Cl	Cl	H	H	1.210	1.434	1.341	179.8	123.9
Cl	Cl	H	•	1.206	1.438	1.320	178.9	123.0
Cl	Cl	•	H	1.205	1.436	1.318	179.8	124.5
Cl	Cl	Cl	Cl	1.210	1.426	1.350	178.9	122.7
Cl	Cl	Cl	•	1.206	1.433	1.328	179.1	123.8
Cl	Cl	•	Cl	1.206	1.433	1.326	179.6	122.1

[a] Bond lengths in angstroms and bond angles in degrees. The substituents X_2 and X_4 are in the *cis* position. The dot denotes the unpaired electron.

fortuitous cancellation of two errors, namely, the underestimation of stability of the radical due to spin contamination and the relative underestimation of stability of the parent molecule due to the low level of electron correlation treatment and the moderate size of the basis set. Indeed, a closer inspection of the data computed for the radical reveals the Hartree−Fock $\langle \hat{S}^2 \rangle$ value of 0.921 and the difference between the MP2 and the spin-projected MP2 (PMP2) energies amounting to 6.0 kcal/mol.

The standard enthalpy of the C−Cl bond dissociation in chloroethene (vinyl chloride) can be readily computed from the published values of ΔH_f^o for H_2C=$CH^•$, $Cl^•$, and H_2C=CHCl, which equal 71.6 ± 0.8, 29.0,[15,20] and 5.5 ± 0.5 kcal/mol,[16] respectively. The resulting $\Delta H_{C-Cl}^o(H_2C$=$CH^•Cl)$ of 95.1 ± 0.9 kcal/mol is again best reproduced at the MP2/6-311G** level of theory (Table 2). Both the C−H and C−Cl bonds are predicted to weaken upon chlorine substitution in the parent molecules. This trend is much more prominent in the BLYP/6-311G** predictions than in those obtained with the conventional treatments of electron correlation. This steep decline in the BLYP/6-311G** standard enthalpies of the C−Cl bond dissociation is reminiscent of a similar artifact present in the analogous data for the $C_2H_{6-n}Cl_n$ series, which has been explained by the inability of DFT-based methods to account for the stabilizing dispersion interactions between proximate chlorine atoms.[17]

The known values of $\Delta H_{C-H}^o(H_2C$=$CH^•H)$ and $\Delta H_{C-Cl}^o(H_2C$=$CH^•Cl)$ can be used to correct the theoretical

predictions by uniformly shifting them to match the experimental data (note that applying such a correction is equivalent to employing the isodesmic reaction H_2C=CH−X + $R^•$ → H_2C=$CH^•$ + R−X, X = H or Cl, in the calculation of ΔH_{C-X}^o). The resulting adjusted standard enthalpies of the C−H and C−Cl bond dissociations are listed in Tables 3 and 4. There is a reasonable agreement among the adjusted data computed for the chloro derivatives of ethene, except for the BLYP/6-311G** predictions pertaining to the polychlorinated compounds. On the other hand, the adjusted MP2/6-311G** standard enthalpies of bond dissociations in n-$C_4H_3^•$ and its chloro analogs deviate strongly from their BLYP, QCISD, and CCSD(T) counterparts. These discrepancies are most probably attributable to the difference in the degree of spin contamination in the unrestricted Hartree−Fock electronic wave functions of the H_2C=$CH^•$ and n-$C_4H_3^•$ radicals. Indeed, the MP2 energy of n-$C_4H_3^•$ exceeds its spin-projected MP2 (PMP2) counterpart by 10.0 kcal/mol, which is 4.0 kcal/mol greater than the corresponding value for

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TABLE 6: Computed Standard Enthalpies of Dimerization[a]

monomer	dimer	BLYP	MP2	QCISD	CCSD(T)
HC≡CH	HC≡C−CH=CH$_2$	−39.54	−38.36	−38.11	−38.69
HC≡CCl	HC≡C−CH=CCl$_2$	−50.50	−52.04	−50.50	−51.60
	(Z)-HC≡C−CCl=CHCl	−50.25	−52.01	−50.77	−51.83
	(E)-HC≡C−CCl=CHCl	−50.20	−51.55	−50.33	−51.39
	(Z)-ClC≡C−CH=CClH	−47.18	−47.31	−46.23	−47.08
	(E)-ClC≡C−CH=CHCl	−47.26	−47.25	−46.48	−47.31
	ClC≡C−CCl=CH$_2$	−45.62	−46.42	−45.37	−46.35
ClC≡CCl	ClC≡C−CCl=CCl$_2$	−54.57	−58.74	−55.71	−57.37

[a] All values in kcal/mol.

$H_2C=CH^{\bullet}$ (see above). This difference in spin contamination, which is very small at the BLYP/6-311G** level of theory, is much less important than that in the case of the QCISD and CCSD(T) approximations.

In light of the above discussion, $\Delta H^{o}_{C-H}(HC\equiv C-CH=CH\cdot H) = 115.1 \pm 1.4$ kcal/mol (which is an average of the corrected CCSD(T)/6-311G** and BLYP/6-311G** predictions with the error bars arrived at by combining the experimental uncertainty in $\Delta H^{o}_{C-H}(H_2C=CH\cdot H)$ employed in the aforedescribed adjustment procedure with the difference between these predictions) constitutes an accurate estimate of the standard enthalpy of the C−H bond dissociation that produces n-C$_4$H$_3{}^{\bullet}$. In order to compute $\Delta H^{o}_{f}(HC\equiv C-CH=CH^{\bullet})$, this estimate has to be combined with $\Delta H^{o}_{f}(H) = 52.1$ kcal/mol (refs 15 and 20) and $\Delta H^{o}_{f}(HC\equiv C-CH=CH_2) = 70.8 \pm 0.5$ kcal/mol, the latter value being readily inferred from the standard enthalpy of hydrogenation of $H_2C=CH-C\equiv CH$ (100.8 $\pm$ 0.5 kcal/mol (ref 18) and $\Delta H^{o}_{f}(n$-C$_4$H$_{10})$ (−30.0 $\pm$ 0.2 kcal/mol (ref 19)). The resulting $\Delta H^{o}_{f}(HC\equiv C-CH=CH^{\bullet}) = 133.8 \pm 1.5$ kcal/mol is significantly higher than all of the known estimates.[1,6,8,13]

The key difference between the present value of $\Delta H^{o}_{f}(HC\equiv C-CH=CH^{\bullet})$ and the previously published data lies in the standard enthalpy of the C−H bond dissociation in the parent molecule, which has been usually assumed to be identical with that in ethene. However, the data compiled in Tables 3 and 4 unequivocally show that the terminal C−H and C−Cl bonds of the ethene moieties in $HC\equiv C-CH=CH_2$ and its chloro derivatives are stronger than those in the corresponding chloroethenes. This bond strengthening is caused by a resonance stabilization of $HC\equiv C-CH=CH_2$ and its congeners, which is conspicuously reflected in their QCISD/6-311G** optimized geometries (Table 5). Thus, the C≡C bond length in $HC\equiv C-CH=CH_2$ equals 1.213 Å, as opposed to 1.209, 1.208, and 1.210 Å in the two geometrical isomers of $HC\equiv C-CH=CH^{\bullet}$ and in HC≡CH. Similarly, the C=C bond in $HC\equiv C-CH=CH_2$ is longer (1.344 Å) than those in the $HC\equiv C-CH=CH^{\bullet}$ radicals (1.325 Å), the $H_2C=CH^{\bullet}$ radical (1.320 Å), and $H_2C=CH_2$ (1.339 Å). As expected, the C−C bond in $HC\equiv C-CH=CH_2$ lengthens from 1.441 Å to 1.445/1.449 Å upon the C−H bond dissociation due to the concomitant diminution of conjugation.

It is of interest to compare the predictions for the standard enthalpy of the ethyne dimerization with the corresponding experimental value. By combining $\Delta H^{o}_{f}(HC\equiv CH) = 54.2 \pm 0.2$ kcal/mol[20] with the previously mentioned $\Delta H^{o}_{f}(HC\equiv C-CH=CH_2) = 70.8 \pm 0.5$ kcal/mol, one arrives at $\Delta H^{o}_{dim}(HC\equiv CH) = 37.6 \pm 0.6$ kcal/mol, which is in an excellent agreement with the data computed at all four levels of theory (Table 6). The computed reaction enthalpies also imply the dimerization of ClC≡CCl to be much more exothermic than that of HC≡CH. Among the products of the HC≡CCl,

$HC\equiv C-CH=CCl_2$ and the two geometrical isomers of $HC\equiv C-CCl=CHCl$ are found to be equally stable and preferred by 4−5 kcal/mol over the other three species.

Conclusions

High-level electronic structure calculations combined with empirical adjustments predict the standard enthalpy of the C−H bond dissociation in $HC\equiv C-CH=CH_2$ to be equal to 115.1 $\pm$ 1.4 kcal/mol, i.e., ca. 4.0 kcal/mol higher than that of the analogous bond cleavage in ethene. This difference in bond strengths stems from resonance stabilization of the parent molecule. The standard enthalpy of formation of the 1-buten-3-yn-1-yl radical is estimated at 133.8 $\pm$ 1.5 kcal/mol, which is significantly higher than all of the previously published values.

As in the case of polychlorinated alkanes, the BLYP approximation is found to seriously underestimate the strengths of the C−H and C−Cl bonds in chloro derivatives of $HC\equiv C-CH=CH_2$. On the other hand, the BLYP/6-311G**, MP2/6-311G**, QCISD/6-311G**, and CCSD(T)/6-311G** predictions for the standard enthalpy of ethyne dimerization all closely match their experimental counterpart.

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