J. Am. Chem. Soc. 1993, 115, 1507-1514

are 38.4, 103.7, 53.3, and 116.5 kcal/mol, respectively. The two carbon reactions (2 and 8) are much more exothermic than their silicon counterparts, and the barriers for reactions 2 and 8 appear to be zero. The barrier height for the insertion of SiH_2 into H_2 (4) is predicted to be small (1-2 kcal/mol[11]) but nonzero, probably reflecting the greater difficulty in inserting a silicon, rather than a carbon, into the H-H bond. Because reaction 1 is 15 kcal/mol less exothermic than reaction 4, Hammond's postulate would predict a larger barrier for reaction 1. At the same level of theory, the exothermicity of reaction 3, the insertion of SiH into an Si-H bond of silane, is found to be 39.3 kcal/mol. This is essentially the same as the exothermicity predicted for reaction 1. So on purely thermodynamic grounds, one would predict similar barriers to reactions 1 and 3. The fact that reaction 1 appears to have a larger barrier very likely reflects the greater ease of insertion into an Si-H bond rather than an H-H bond. This "steric factor" has been found to play a role in the insertions of SiH_2 into a variety of X-H and X-Y bonds.[39]

The relative barrier heights for reactions 1 and 2, CH versus SiH insertion, may be viewed from an electronic point of view as well. The unpaired electron in both CH and SiH is a p orbital. Because CH_3 is essentially flat, the unpaired electron remains in a p orbital throughout the reaction. In contrast, SiH_3 is pyramidal, suggesting that the orbital containing the unpaired electron must undergo a (energy-demanding) hybridization as the reaction proceeds. The rather distorted nature of the geometry of the saddle point (Figures 1 and 2) suggests that most of this rehybridization occurs by the time the reaction reaches the transition-state region.

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Thermochemistry and Ion-Molecule Reactions of Isomeric $C_3H_2^{\cdot+}$ Cations

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Abstract: Ab initio molecular orbital calculations at the Gaussian-2 (G2) level of theory have been used to examine the heats of formation and ion-molecule reactions of isomeric forms of the $C_3H_2^{\bullet+}$ cation. The linear structure l-$C_3H_2^{\bullet+}$ is predicted to lie higher in energy than the cyclic form c-$C_3H_2^{\bullet+}$ by 28 kJ mol^{-1} at 0 K (or 31 kJ mol^{-1} at 298 K), energy differences significantly smaller than previous theoretical estimates (~50 kJ mol^{-1}). The calculated kinetic and thermodynamic stabilities (at 298 K) of cyclic and linear $C_3H_2^{\bullet+}$ with respect to hydrogen-atom-abstraction reactions with H_2CO, CH_3OH, CH_4, c-C_3H_6, and H_2O are consistent with experimental observations. Interestingly, the reaction of c-$C_3H_2^{\bullet+}$ with H_2O is found to be inhibited by a kinetic barrier of 23 kJ mol^{-1}. This provides a counterexample to the assumption that ion-molecule hydrogen-atom-abstraction reactions will occur (i.e., are barrier free) whenever they are exothermic except for reactions involving molecular hydrogen. Consistent with experimental observations, the reaction l-C_3H^+ + H_2 → c-$C_3H_2^{\bullet+}$ + $H^\bullet$ is calculated to be slightly endothermic (by 4 kJ mol^{-1}). The hydrogen-atom-abstraction reaction c-$C_3H_2^{\bullet+}$ + H_2 → c-$C_3H_3^+$ + $H^\bullet$ is predicted to have a small barrier (4 kJ mol^{-1}) despite a large exothermicity (91 kJ mol^{-1}). This result is consistent with kinetic studies of the reaction. Our best theoretical estimate of the heat of formation ($\Delta H_f{}^\circ{}_{298}$) of c-$C_3H_2^{\bullet+}$ is 1387 kJ mol^{-1}, agreeing well with an experimental value (1389 kJ mol^{-1}) derived from the enthalpy change for the reaction between C_3H^+ and H_2 but differing significantly from a value (1347 kJ mol^{-1}) deduced from ion-molecule bracketing reactions. For l-$C_3H_2^{\bullet+}$, our predicted $\Delta H_f{}^\circ{}_{298}$ is 1418 kJ mol^{-1}. Both the linear and cyclic isomers of $C_3H_2^{\bullet+}$ are predicted to react with CO to form strongly bound ionized ketenes; the calculated binding energies are 225 and 168 kJ mol^{-1}, respectively. The calculated structures and ionization energies of the $C_3H_2^{\bullet+}$ isomers are in good accord with recent experimental data.

Introduction

There has been considerable recent interest in the thermochemistry and ion-molecule reactions of isomeric forms of the $C_3H_2^{\bullet+}$ cation. The cyclic structure of $C_3H_2^{\bullet+}$ (c-$C_3H_2^{\bullet+}$) has been proposed[1] as a possible precursor in ion-molecule reactions which lead to the cyclic neutral molecules c-C_3H_2 and c-$C_3H^\bullet$, both of which have been observed in interstellar clouds.[2] The heats of formation and hydrogen-abstraction reactions of the $C_3H_2^{\bullet+}$ cations have been studied extensively by selected-ion flow-tube (SIFT) and flowing afterglow-SIFT (FA-SIFT) experiments.[3,4] Recent photoelectron experiments[5] have provided information on the structures and ionization energies of the $C_3H_2^{\bullet+}$ isomers.

The existence of two isomeric forms of $C_3H_2^{\bullet+}$, cyclic (**1**) and linear (**2**), was first demonstrated by Smith and Adams[3b] in 1987. They had earlier[3a] obtained two estimates of the heat of formation of one form of $C_3H_2^{\bullet+}$, 1389 and 1377 kJ mol^{-1}. This form of

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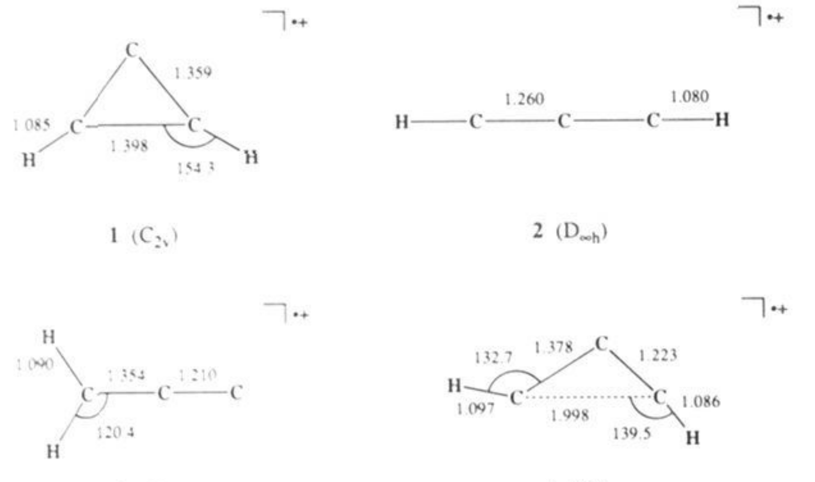


1 (C_{2v}) **2** ($D_{\infty h}$) **3** (C_{2v}) **4** (C_s)

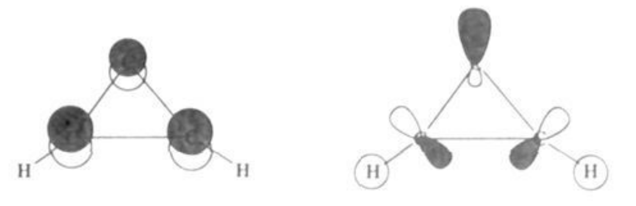
Figure 1. Optimized geometries (MP2/6-31G*) for equilibrium and transition structures of $C_3H_2^{\bullet+}$.

$C_3H_2^{\bullet+}$ was initially assigned as the linear structure **2**, but subsequent experiments[3b] suggested a reassignment to the cyclic structure **1**; a heat of formation of 1377 kJ mol^{-1} was then recommended for **1**. The experimental conclusions were supported by ab initio calculations,[6] which also indicated that the cyclic structure is the lowest-energy isomer of $C_3H_2^{\bullet+}$, in agreement with previous theoretical work.[7] Recently, Prodnuk, DePuy, and Bierbaum (PDB)[4] obtained new information concerning the cyclic and linear forms of $C_3H_2^{\bullet+}$ by studying their hydrogen-atom-abstraction reactions with a variety of neutral reagents. They concluded from bracketing experiments that the heat of formation of cyclic $C_3H_2^{\bullet+}$ is 1347 kJ mol^{-1}, some 30 kJ mol^{-1} less than the value reported by Smith and Adams.[3b]

In the present paper, we attempt to resolve the discrepancy concerning the thermochemistry of the $C_3H_2^{\bullet+}$ isomers and to understand the kinetics of their hydrogen-atom-abstraction reactions by carrying out high-level ab initio calculations at the Gaussian-2 (G2) level of theory.[8] Systematic studies[8,9] have shown that the G2 method is capable, in general, of reproducing molecular energies (atomization energies, ionization energies, proton affinities, electron affinities, and acidities) to an accuracy of ±10 kJ mol^{-1}. We have calculated the structures, ionization energies, and heats of formation of various $C_3H_2^{\bullet+}$ isomers and examined their ion molecule reactions, and we compare our theoretical results with recent experimental data.

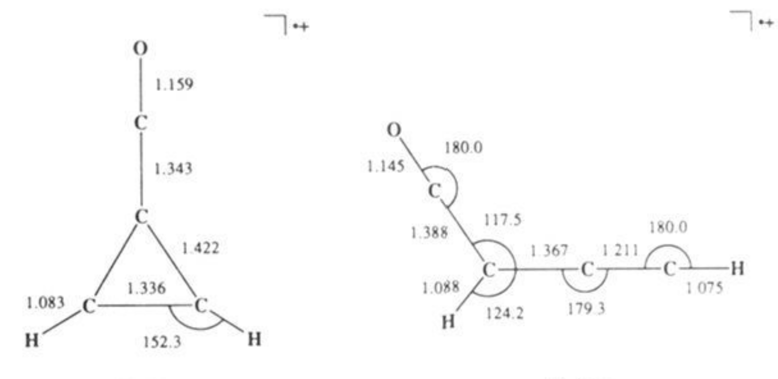
Method and Results

Standard ab initio molecular orbital calculations[10] were carried out with the GAUSSIAN 90,[11] GAUSSIAN 92,[12] and CADPAC 5[13] series of programs.



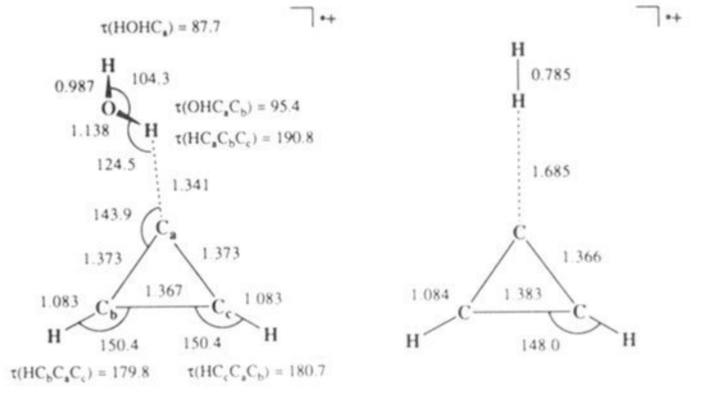
(a) NHOMO (b) HOMO

Figure 2. Highest occupied molecular orbital (HOMO) and next highest occupied molecular orbital (NHOMO) of $c\text{-}C_3H_2$.



7 (C_{2v}) **8** (C_s)

Figure 3. Optimized geometries (MP2/6-31G*) for cyclic (**7**) and acyclic (**8**) $C_3H_2CO^{\bullet+}$ (ionized ketene) cations.



9 (C_1) **10** (C_{2v})

Figure 4. Optimized transition structures (MP2/6-31G*) for hydrogen-abstraction reactions: (a) $c\text{-}C_3H_2^{\bullet+} + H_2O$ and (b) $c\text{-}C_3H_2^{\bullet+} + H_2$.

Energies of the cyclic (**1**) and linear (**2**) structures of $C_3H_2^{\bullet+}$ were calculated with a variety of theoretical methods: unrestricted (UHF), restricted open-shell (ROHF), and projected unrestricted (PUHF) Hartree–Fock theories; unrestricted (UMP), restricted (RMP),[14] and projected unrestricted (PMP)[15] Møller–Plesset perturbation theories terminated at second, third, and fourth orders (MP2, MP3, and MP4);[16] quadratic configuration interaction with single and double excitations (QCISD) and with a perturbative estimation of the triples (QCISD(T));[17] and G1 and G2 theories.[8,18]

All systems except where noted have been examined at the Gaussian-2 (G2) level of theory. This corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G(d) energies together with zero-point vibrational and isogyric corrections. Spin-restricted theory (RHF) was used for closed-shell species and spin-unrestricted theory (UHF) for open-shell systems. Within the G2 procedure, harmonic vibrational frequencies are calculated at the HF/6-31G* level and scaled by 0.8929 to account for their average overestimation at this level of theory.[8] For the C_3H_2 and $C_3H_2^{\bullet+}$ isomers, we have found significant differences between (scaled) HF/6-31G* and (scaled) UMP2/6-31G* frequencies and we have uniformly used MP2/6-31G* values, scaling in this case by 0.93.[19] Temperature corrections were obtained from scaled HF/6-31G* (MP2/6-31G* for C_3H_2 and $C_3H_2^{\bullet+}$ isomers) vibrational frequencies in

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Table I. Calculated G2 Total Energies (hartrees) and Temperature Corrections ($H_{298} - H_0$, kJ mol^{-1})

			total energy		
species	state	symmetry	E_e	E_0	$H_{298} - H_0$
c-$C_3H_2^{\bullet+}$ (**1**)	$^2A_1$	C_{2v}	−114.832 63	−114.801 55^a	10.66^a
$HCCCH^{\bullet+}$ (**2**)	$^2\Pi$	$D_{\infty h}$	−114.818 57	−114.790 82^a	13.95^a
$CH_2CC^{\bullet+}$ (**3**)	$^2A_1$	C_{2v}	−114.758 44	−114.727 64^a	12.24^a
TS **2** → **1** (**4**)	$^2A'$	C_s	−114.746 53	−114.721 46^a	12.39^a
c-C_3H_2	$^1A_1$	C_{2v}	−115.170 83	−115.140 28^a	10.77^a
HCCCH	$^3A''$	C_s	−115.141 05	−115.115 42^a	14.03^a
CH_2CC	$^1A_1$	C_{2v}	−115.148 96	−115.119 58^a	12.80^a
c-$C_3H_2^{\bullet+\,b}$	$^2A_1$	C_{2v}	−114.821 09	−114.790 02	
$HCCCH^{\bullet+\,b}$	$^2A'$	C_s	−114.816 00	−114.788 25	
$CH_2CC^{\bullet+\,b}$	$^2A_1$	C_{2v}	−114.754 50	−114.723 70	
c-$C_3H_3^+$ (**5**)	$^1A_1'$	D_{3h}	−115.542 72	−115.499 29	10.79
$CH_2CCH_2^+$ (**6**)	$^1A_1$	C_{2v}	−115.497 60	−115.456 56	12.93
TS **1** + H_2O → **5** + $OH^\bullet$ (**9**)	$^2A'$	C_s	−191.173 92	−191.123 89	16.85
TS **1** + H_2 → **5** + $H^\bullet$ (**10**)	$^2A_1$	C_{2v}	−116.005 77	−115.964 56	14.29
C_3H^+	$^1\Sigma^+$	$C_{\infty v}$	−114.159 95	−114.140 58	12.11
c-C_3H_6	$^1A_1'$	D_{3h}	−117.709 07	−117.631 15	11.45
c-$C_3H_5^\bullet$	^2A	C_1	−117.022 61	−116.958 07	11.52
CH_3OH	$^1A'$	C_s	−115.584 29	−115.534 89	11.28
$CH_3O^\bullet$	$^2A'$	C_s	−114.903 50	−114.867 54	10.40
H_2CO	$^1A_1$	C_{2v}	−114.364 95	−114.338 88	10.02
$HCO^\bullet$	$^2A'$	C_s	−113.711 66	−113.698 83	9.98
CH_4	$^1A_1$	T_d	−40.453 54	−40.410 88	10.02
$CH_3^\bullet$	$^2A_2'$	D_{3h}	−39.772 74	−39.745 09	11.15
H_2O	$^1A_1$	C_{2v}	−76.352 57	−76.332 05	9.23
$OH^\bullet$	$^2\Pi$	$C_{\infty v}$	−75.652 04	−75.643 91	8.68
H_2	$^1\Sigma_g^+$	$D_{\infty h}$	−1.175 81	1.166 36	8.68
$H^\bullet$	^2S	K_h	−0.500 00	−0.500 00	6.20

^{a}Calculated using MP2/6-31G* vibrational frequencies, scaled by 0.93. See text. ^{b}Based on the geometry of the corresponding neutral. Zero-point vibrational energy assumed to be the same as for the equilibrium structure of the monocation.

Table II. Calculated Total Energies^{a,b} (hartrees) and Relative Energies^c (kJ mol^{-1}) of the Cyclic (**1**) and Linear (**2**) Structures of $C_3H_2^{\bullet+}$

	total energy		
level	cyclic	linear	relative energy
UHF	−114.355 75	−114.336 82	49.7
UMP2	−114.697 23	−114.670 90	69.1
UMP3	−114.715 50	−114.689 65	67.9
UMP4	−114.737 51	−114.719 57	47.1
PUHF	−114.358 58	−114.353 39	13.6
PMP2	−114.699 32	−114.684 28	39.5
PMP3	−114.716 92	−114.698 68	47.9
PMP4	−114.738 93	−114.728 60	27.1
ROHF	−114.352 29	−114.314 37	99.6
RMP2	−114.702 22	−114.693 25	23.6
RMP3	−114.719 62	−114.696 96	59.5
RMP4	−114.742 84	−114.735 30	19.8
UQCISD	−114.721 59	−114.706 16	40.5
UQCISD(T)	−114.739 50	−114.726 08	35.2
G1	−114.831 61^d	−114.819 56^d	31.6 (22.9)^e
G2	−114.832 63^d	−114.818 57^d	36.9 (28.2)^e

^{a}6-311G** basis set (except G1 and G2 calculations). ^{b}Based on MP2/6-31G* optimized geometries. $^c E_{\text{cyclic}} - E_{\text{linear}}$. $^d E_e$ values. ^{e}Values in parentheses include zero-point vibrational corrections at 0 K (MP2/6-31G*).

Table III. Calculated Dipole Moments (μ, D) and Harmonic Vibrational Frequencies (cm^{-1}) of $C_3H_2^{\bullet+}$ Isomers^a

$C_3H_2^{\bullet+}$ isomer	μ	frequencies
c-$C_3H_2^{\bullet+}$ (**1**)	1.38	770 (b_1), 854 (a_1), 923 (a_2), 938 (b_2), 1141 (a_1), 1263 (b_2), 1560 (a_1), 3084 (b_2), 3107 (a_1)
$HCCCH^{\bullet+}$ (**2**)	0.00	119 (π_u), 274 (π_g), 313 (π_u), 418 (π_u), 813 (π_u), 827 (π_g), 1275 (σ_g), 1816 (σ_u), 3158 (σ_u), 3167 (σ_g)
$CH_2CC^{\bullet+}$ (**3**)	1.34	286 (b_1), 357 (b_2), 1003 (b_2), 1083 (a_1), 1114 (b_1), 1405 (a_1), 2228 (a_1), 2968 (a_1), 3076 (b_2)

^{a}MP2/6-31G* values. ^{b}Scaled by 0.93.

order to obtain reaction enthalpies and heats of formation at 298 K, where desired.

To examine the effect of electron correlation and basis set on the structures of three-membered ring systems, we have systematically optimized the cyclic structures of C_3H_4, C_3H_2, and $C_3H_2^{\bullet+}$ with a hierarchy of standard basis sets and a sequence of correlated levels, MP2, QCISD, and QCISD(T).

For the $C_3H_2CO^{\bullet+}$ complexes, the binding energies were computed at the MP4/6-311+G(2df,2p)//MP2/6-31G* level, evaluated with the use of the additivity approximation

$$\Delta E(\text{MP4/6-311+G(2df,2p)}) \approx \Delta E(\text{MP4/6-311G**}) - \Delta E(\text{MP2/6-311G**}) + \Delta E(\text{MP2/6-311+G(2df,2p)}) \quad (1)$$

together with zero-point energy contributions (HF/6-31G*).

The full set of optimized (MP2/6-31G*) $C_3H_2^{\bullet+}$ equilibrium and transition structures is displayed in Figure 1. G2 total energies and temperature corrections for all species are collected in Table I. Calculated energy differences between the linear and cyclic structures are given in Table II. Calculated dipole moments and harmonic vibrational frequencies of $C_3H_2^{\bullet+}$ isomers are given in Table III. Optimized structural parameters for c-C_3H_4, c-C_3H_2, and c-$C_3H_2^{\bullet+}$ are summarized in Tables IV and V. The highest occupied molecular orbital (HOMO) and next highest occupied molecular orbital (NHOMO) of c-$C_3H_2^{\bullet+}$ are displayed in Figure 2. Ionization energies of C_3H_2 isomers are presented in Table VI. Energy information relating to $C_3H_2CO^{\bullet+}$ complexes and associated fragments is given in Table VII. Optimized structures of $C_3H_2CO^{\bullet+}$ complexes and transition structures for hydrogen-abstraction reactions are shown in Figures 3 and 4, respectively. Schematic potential energy profiles for the reactions (a) c-$C_3H_2^{\bullet+}$ + H_2O → c-$C_3H_3^+$ + $OH^\bullet$ and (b) c-$C_3H_2^{\bullet+}$ + H_2 → c-$C_3H_3^+$ + $H^\bullet$ are shown in Figure 5. Enthalpies for hydrogen-atom-abstraction reactions of **1** and **2** are summarized in Table VIII. Finally, calculated heats of formation of C_3H^+ and $C_3H_2^{\bullet+}$ isomers are given in Table IX. Throughout this paper, bond lengths are given in angstroms and bond angles in degrees.

Discussion

Relative Energies. We have previously[6] studied aspects of the $C_3H_2^{\bullet+}$ potential energy surface at the CISD(Q)/6-311G**//CISD/6-31G* + ZPVE level. Four stable equilibrium structures were identified, including the cations of cyclopropenylidene, c-$C_3H_2^{\bullet+}$ (**1**, $^2A_1$), propargylidene, $HCCCH^{\bullet+}$ (**2**, $^2\Pi$), propadienylidene, $CH_2CC^{\bullet+}$ (**3**, $^2A_1$), and propanediylidyne $CCH_2C^{\bullet+}$ ($^2A_1$). The cyclic structure **1** was found to be the lowest-energy structure, lying 53 kJ mol^{-1} below the linear structure **2**. No stable structures corresponding to nonlinear or symmetrical linear forms of **2** were found. The $CH_2CC^{\bullet+}$ and $CCH_2C^{\bullet+}$ isomers lie rela-

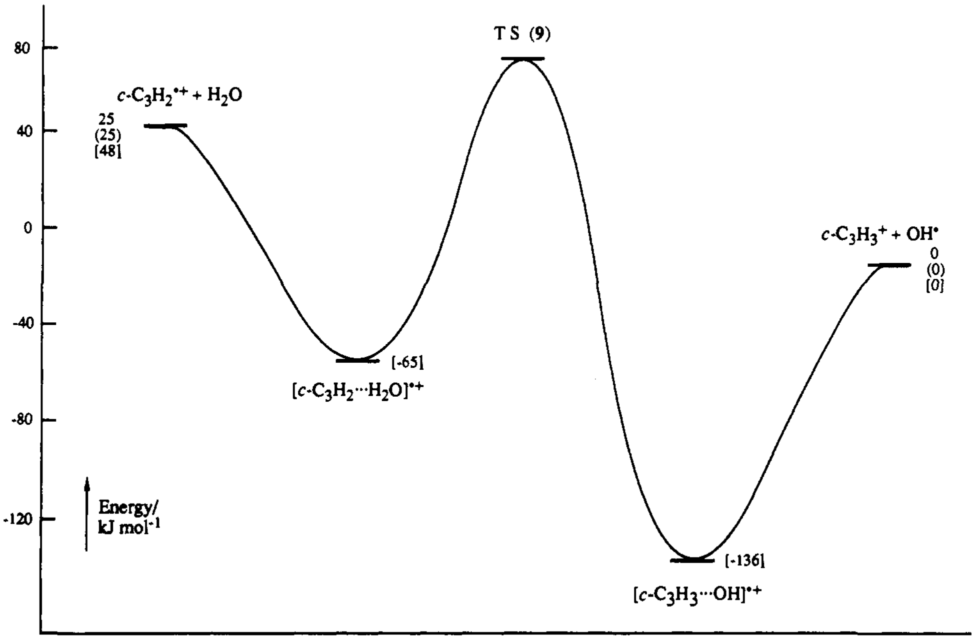

Figure 5. Schematic energy profile showing hydrogen transfer in the [c-C_3H_2···H_2O]$^{•+}$ system (G2 results at 298 K, with G2 results at 0 K in parentheses and MP2 results at 0 K in brackets).

Table IV. Optimized Geometries for c-C_3H_4, c-C_3H_2, and c-$C_3H_2^{•+}$

	level					
parameter[a]	MP2/6-31G*	QCISD/6-31G*	QCISD(T)/6-31G*	QCISD/6-311G**	MP2/6-311+G(2df,p)	expt[b]
			c-C_3H_4			
r(C′—C)	1.505	1.510	1.513	1.515	1.506	1.509
r(C═C)	1.301	1.301	1.308	1.302	1.297	1.296
r(C—H)	1.091	1.094	1.095	1.092	1.088	1.088
r(C′—H)	1.078	1.081	1.082	1.078	1.076	1.072
∠HC′H	113.5	113.4	113.4	114.0	114.2	114.6
∠HCC	150.0	150.0	150.0	149.9	149.9	149.9
			c-C_3H_2			
r(C′—C)	1.428	1.431	1.438	1.433	1.418	1.417
r(C═C)	1.329	1.326	1.331	1.330	1.328	1.320
r(C′—H)	1.081	1.083	1.085	1.081	1.078	1.075
∠HCC	148.2	148.1	148.2	147.9	147.7	149.8
			c-$C_3H_2^{•+}$			
r(C′—C)	1.359	1.361	1.366	1.363	1.353	1.340
r(C═C)	1.398	1.396	1.403	1.401	1.396	1.394
r(C′—H)	1.085	1.087	1.089	1.086	1.084	1.084
∠HCC	154.3	154.0	154.2	154.1	154.3	151.4

[a] C′ is the unique carbon. [b] Taken from ref 23 (c-C_3H_4), ref 24 (c-C_3H_2), and ref 5c (c-$C_3H_2^{•+}$).

Table V. Optimized Structural Parameters of c-C_3H_2 at the MP2 Level[a]

basis set	r(C′–C)	r(C–C)	r(C–H)	∠HCC
6-31G*	1.428	1.329	1.081	148.2
6-31G**	1.430	1.331	1.076	148.3
6-311G*	1.432	1.335	1.080	147.3
6-31+G*	1.425	1.334	1.081	147.7
6-31G(2d)	1.435	1.334	1.085	148.3
6-31G(df)	1.425	1.327	1.076	148.0
6-311+G(2df,p)	1.418	1.328	1.078	147.7
expt[b]	1.417	1.320	1.075	149.8

[a] C′ is the unique carbon. [b] Taken from ref 24.

Table VI. Calculated and Experimental Ionization Energies (IE_a, IE_v, eV) of $C_3H_2^{•+}$ Isomers

process	IE_v[a]	IE_a[a]	expt[b]
c-C_3H_2 → c-$C_3H_2^{•+}$	9.53	9.22	9.15
CH_2CC → $CH_2CC^{•+}$	10.77	10.67	10.43
HCCCH → $HCCCH^{•+}$	8.90	8.83	

[a] Based on the calculated G2 total energies from Table I. [b] From ref 5c.

tively high in energy, 185 and 484 kJ mol^{-1}, respectively, above **1**. In the present study, we have considered the three lowest energy isomers of $C_3H_2^{•+}$ (**1**, **2**, and **3**) and the transition structure **4** for rearrangement of **2** to **1**.

The energy difference between the linear (**2**) and cyclic (**1**) structures of $C_3H_2^{•+}$ has also been investigated by PDB,[4a] using MP4 theory based on unrestricted Hartree–Fock (UHF) wave functions. It is well established that spin contamination in UHF wave functions for open-shell systems is often associated with slow convergence of the UMP series. This can occur not only for stretched molecules but also for equilibrium structures.[20] For the two equilibrium structures considered here, the cyclic form **1** has an $\langle S^2 \rangle$ value (0.77) close to that required for a pure doublet (0.75). However, the linear structure **2** has a significant degree of spin contamination ($\langle S^2 \rangle$ = 0.90). As a consequence, there may be problems with UMP convergence which would adversely

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[20] (a) Nobes, R. H.; Pople, J. A.; Radom, L.; Handy, N. C.; Knowles, P. J. *Chem. Phys. Lett.* **1987**, *138*, 481. (b) Gill, P. M. W.; Pople, J. A.; Radom, L.; Nobes, R. H. *J. Chem. Phys.* **1988**, *89*, 7307. (c) Nobes, R. H.; Moncrieff, D.; Wong, M. W.; Radom, L.; Gill, P. M. W.; Pople, J. A. *Chem. Phys. Lett.* **1991**, *182*, 216.

Table VII. Calculated Total Energies[a] (hartrees), Zero-Point Vibrational Energies[b] (ZPVE, kJ mol^{-1}), and Entropies[b] (S, J mol^{-1} K^{-1}) of $C_3H_2CO^{\bullet+}$ Cations and Related Species

species	total energy MP2/6-311G**	total energy MP2/6-311+G(2df,2p)	total energy MP4/6-311G**	ZPVE	S
c-$C_3H_2CO^{\bullet+}$ (**7**)	−227.837 97	−227.956 53	−227.896 58	121.0	290.0
l-$C_3H_2CO^{\bullet+}$ (**8**)	−227.841 47	−227.958 55	−227.905 56	115.8	299.6
c-$C_3H_2^{\bullet+}$ (**1**)	−114.697 23	−114.752 94	−114.737 51	93.7	240.3
l-$C_3H_2^{\bullet+}$ (**2**)	−114.670 90	−114.727 42	−114.719 57	80.7	242.3
CO	−113.074 48	−113.129 65	−113.098 62	14.6	197.3

[a] MP2/6-31G* optimized geometries. All total energies refer to frozen calculations. [b] (Unscaled) HF/6-31G* values.

Table VIII. Enthalpies (kJ mol^{-1}) of Ion–Molecule Reactions of Cyclic (**1**) and Linear (**2**) $C_3H_2^{\bullet+}$ and C_3H^+ at 298 K

reaction	cyclic theory[a]	cyclic PDB[b]	cyclic rn[c]	linear theory[a]	linear PDB[b]	linear rn[c]
$C_3H_2^{\bullet+} + H_2CO \rightarrow C_3H_3^+ + HCO^\bullet$	−151.4	−121.3	R	−68.5	−62.8	R
$C_3H_2^{\bullet+} + CH_3OH \rightarrow C_3H_3^+ + CH_3O^\bullet$	−80.5	−104.6	R	2.3	−46.8	R
$C_3H_2^{\bullet+} + CH_4 \rightarrow C_3H_3^+ + CH_3^\bullet$	−82.6	−58.6	R	0.2	0.0	R
$C_3H_2^{\bullet+}$ + c-$C_3H_6 \rightarrow C_3H_3^+$ + c-$C_3H_5^\bullet$	−64.5	−54.4	R	18.3	4.2	N
$C_3H_2^{\bullet+} + H_2O \rightarrow C_3H_3^+ + OH^\bullet$	−25.6	0.0	N	57.2	58.6	N
$C_3H_2^{\bullet+} + H_2 \rightarrow C_3H_3^+ + H^\bullet$	−90.9			−8.1		
l-$C_3H^+ + H_2 \rightarrow C_3H_2^{\bullet+} + H^\bullet$	4.0			35.5		

[a] Theoretical values calculated from G2 total energies and temperature corrections in Table I. [b] Prodnuk, Depuy, and Bierbaum (PDB) estimates (from ref 4a). 4n = reaction. [c] R denotes that the reaction occurs and N denotes that the reaction does not occur (from ref 4a).

Table IX. Calculated and Experimental Heats of Formation ($\Delta H_f{}^\circ{}_0$, $\Delta H_f{}^\circ{}_{298}$, kJ mol^{-1}) of C_3H^+ and $C_3H_2^{\bullet+}$ Isomers

species	$\Delta H_f{}^\circ{}_0{}^a$	$\Delta H_f{}^\circ{}_{298}{}^{a,b}$	expt
c-$C_3H_2^+$ (**1**)	1387.8	1386.9	1347,[c] 1377,[d] 1389[d]
$HCCCH^+$ (**2**)	1416.0	1418.3	1398[c]
CH_2CC^+ (**3**)	1581.9	1582.5	
C_3H^+	1594.4	1599.2	1602,[e] 1593[f]

[a] Calculated from the theoretical (G2) energy changes for the reactions $C_3H_n{}^{\bullet+} + e^- \rightarrow 3C + nH^\bullet$ (see text). [b] Calculated using theoretical $H_{298} - H_0$ values of $C_3H_n{}^{\bullet+}$. [c] From ref 4a. [d] From ref 3. [e] From ref 29. [f] From ref 30.

affect the previous UMP4 estimate of the energy difference between **2** and **1**.

Several theoretical procedures have been proposed to circumvent the spin contamination problem. For systems with a moderate amount of spin contamination, quadratic configuration interaction calculations with single and double excitations (QCISD) and with a perturbative correction for triple excitations (QCISD(T)) have been found to provide satisfactory energies.[17] Alternatively, one can employ the projected MP (PMP)[15] method or the more recent restricted open-shell MP (RMP)[14] procedure to attempt to overcome the problem. Here, we have calculated energy difference between **2** and **1** with the UMP, PMP, RMP, QCISD, and QCISD(T) methods using the 6-311G** basis set (Table II). The most advanced method considered in this study is QCISD(T). The calculated relative energy at this level of theory is 35 kJ mol^{-1}, significantly smaller than the UMP estimates. Although PMP2 and RMP2 provide better relative energies than UMP2, the convergence of the perturbation series is rather poor for both RMP and PMP. For example, in the RMP series, the calculated ROHF, RMP2, RMP3, and RMP4 relative energies are 100, 24, 60, and 20 kJ mol^{-1}, respectively. It should be noted that our earlier theoretical study involving CISD(Q)/6-311G** calculations, based on restricted open-shell wave functions, also led to a relatively large energy difference between **1** and **2** (47 kJ mol^{-1}).[6] Inclusion of the triples correction at the QCISD(T) level is found to have a significant effect on the calculated relative energy (−5 kJ mol^{-1}).

At our best level of theory (G2), the cyclic structure is lower in energy than the linear form by 37 kJ mol^{-1} before zero-point vibrational corrections or 28 kJ mol^{-1} after zero-point corrections, a significantly smaller energy difference than the previous theoretical estimates (~50 kJ mol^{-1}).[4a,6] Note that the (scaled) zero-point vibrational energy (ZPVE) difference between **1** and **2** calculated at the MP2/6-31G* level (8.8 kJ mol^{-1}) differs significantly from the (scaled) Hartree–Fock value (11.6 kJ mol^{-1}). At 298 K, **1** is predicted to be more stable than **2** by 31 kJ mol^{-1}.

At the G2 level of theory, the propadienylidene cation $CH_2CC^{\bullet+}$ (**3**) is predicted to lie 194 kJ mol^{-1} above the global minimum **1**, a result similar to that which we obtained previously (185 kJ mol^{-1}).[6]

Rearrangement of the linear structure **2** to the cyclic form **1** via transition structure **4** requires a substantial barrier of 182 kJ mol^{-1}; a recent lower-level theoretical treatment gave 209 kJ mol^{-1}.[21] It would seem, therefore, that interconversion of the linear and cyclic isomers at low temperature will not be straightforward. It is worthwhile to note that rearrangement of linear to cyclic $C_3H_3^+$ is impeded by a considerably greater barrier of 408 kJ mol^{-1}.[22]

To facilitate future experimental characterization of the three stable $C_3H_2^{\bullet+}$ isomers examined in this study, we report in Table III the dipole moments and the complete set of harmonic vibrational frequencies for **1**–**3**, calculated at the MP2/6-31G* level.

Structural Comparisons. The structure of c-$C_3H_2^{\bullet+}$ (**1**) has been investigated very recently, both experimentally and theoretically.[5c] Clauberg and Chen[5c] have determined the geometry of c-$C_3H_2^{\bullet+}$ from the vibrationally resolved photoelectron spectrum of cyclopropylidene. In addition, they have calculated the molecular structure of c-$C_3H_2^{\bullet+}$ at the MP2/6-31G* level. The calculated geometrical parameters are in good accord with their experimental values. To explore further the effect of electron correlation on this cyclic species and other three-membered ring systems, the molecular structures of c-C_3H_4, c-C_3H_2, and c-$C_3H_2^{\bullet+}$ were optimized with three different levels of theory, MP2, QCISD, and QCISD(T) with the 6-31G* basis set. Reliable geometrical parameters for c-C_3H_4 and c-C_3H_2 have been determined previously by microwave spectroscopy.[23,24] From Table IV, it can be seen that MP2/6-31G* geometries are generally in reasonable agreement with experimental data, although the calculated carbon–carbon and carbon–hydrogen bond lengths tend to be somewhat longer than the corresponding experimental values by up to about 0.01 Å. Only small structural changes are observed in going from MP2 to the higher level QCISD procedure. However, inclusion of triple substitutions, as in QCISD(T), leads to bond lengthening and somewhat poorer agreement with experiment. The calculated C–C bond lengths are significantly overestimated at the QCISD(T)/6-31G* level. This result is rather surprising in view of the fact that inclusion of triple excitations is known to be important for multiple bonds.[25] Similar

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(21) Unpublished results quoted in ref 4b.

(22) Wong, M. W.; Radom, L. *J. Am. Chem. Soc.* **1989**, *111*, 6976.

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findings have been reported for the calculated $C{\equiv}N$ bond length in HCN.[26] The QCISD(T)/6-31G* result may, however, reflect at least partly deficiencies in the 6-31G* basis set.

To explore the effect of basis set, we have optimized cyclopropenylidene systematically with a hierarchy of basis sets, including 6-31G*, 6-311G*, 6-31+G*, 6-31G(2d), 6-311G(df), and 6-311+G(2df,p), at the MP2 level of theory. From Table V, it can be seen that the effect of increasing the basis set size from 6-31G* is small but not insignificant. Expanding the basis set from double-ζ valence to triple-ζ valence (6-31G* → 6-311G*) or from one set of d-polarization functions to two (6-31G* → 6-31G(2d)) leads in each case to longer carbon–carbon bond lengths and hence poorer agreement with experiment. On the other hand, inclusion of f functions on carbon (6-31G* → 6-31G(df)) yields shorter carbon–carbon equilibrium distances. Inclusion of diffuse sp functions on carbon (6-31G* → 6-31+G*) leads to longer C–C but shorter C'–C bond lengths (where C' is the unique carbon atom). Inclusion of p-polarization functions on hydrogen and inclusion of extra d (6-31G(2d)) or f (6-31G(df)) functions on carbon result in shorter C–H equilibrium distances. Interestingly, additivity of basis set enhancements is not observed. For instance, using a simple additivity scheme, one would predict a C'–C bond length of 1.435 Å at the MP2/6-311+G(2df,p) level, but the directly calculated value is 1.418 Å. We conclude from this comparison of basis sets that the use of the larger 6-311+G(2df,p) basis certainly leads to a significant improvement over the standard 6-31G* basis set. The importance of the use of a large basis set for accurate geometry predictions at the MP2 level has been pointed out previously.[27]

It is interesting to compare the optimized geometries of the three cyclic molecules at the QCISD(T)/6-31G*, QCISD/6-311G**, and MP2/6-311+G(2df,p) levels (Table IV), these requiring comparable computing resources. Among these three levels of optimizations, MP2/6-311+G(2df,p) shows the best agreement with experiment. This level of theory provides almost perfect agreement with available experimental data for cyclopropene but less good agreement for the cyclopropylidene cation. The calculated C'–C bond length and HCC angle in c-$C_3H_2^{\bullet+}$ are 0.013 Å and 2.9°, respectively, larger than the experimental values. Our results suggest that for cyclic systems, geometry optimization using a large basis set at the MP2 level might generally be preferable to geometry optimization using a smaller basis at a higher level of electron correlation treatment, such as QCISD(T).

Comparison of the carbon–carbon bond lengths of the three cyclic structures shows a gradual progression in going from c-C_3H_4 to c-C_3H_2 to c-$C_3H_2^{\bullet+}$. In c-C_3H_4, the C—C bonds can clearly be distinguished as single ($C—C'$) or double ($C{=}C$). In c-C_3H_2, electron donation can take place from the π orbital of the $C{=}C$ double bond to the formally vacant p orbital at C', as reflected in the NHOMO of c-C_3H_2 (Figure 2a). This leads to a lengthening of the $C{=}C$ bond and a shortening of the $C—C'$ bonds. Finally, removal of an electron from the HOMO of c-C_3H_2 (Figure 2b), leading to c-$C_3H_2^{\bullet+}$, would be expected to lead to a further lengthening of the C—C bond. In addition, the electron removal results in an increased contribution of the 2p(π) orbital at C' to the NHOMO, leading to a shortening of the $C—C'$ bonds. In fact, these effects are sufficiently large that the ordering of bond lengths has actually reversed in c-$C_3H_2^{\bullet+}$ with C—C now slightly longer than $C—C'$.

Ionization Energies. The adiabatic ionization energies of cyclopropenylidene (c-C_3H_2) and propadienylidene (CH_2CC) have been obtained recently by Chen and co-workers[5] using photoelectron spectroscopy. We have calculated both adiabatic (IE_a) and vertical (IE_v) ionization energies at the G2 level of theory for the three forms of C_3H_2 that are the precursors for the $C_3H_2^{\bullet+}$ isomers **1**, **2**, and **3** (Table VI). Systematic calculations on a wide selection of molecules have indicated that G2 theory is able, in general, to reproduce ionization energies to within 0.1 eV.[8,9] The calculated IE_a (9.22 eV) for c-C_3H_2 is in close agreement with the experimental value (9.15 eV), whereas the IE_a of CH_2CC (10.67 eV) is slightly higher than the experimental value (10.43 eV). Clauberg et al.[5b] have pointed out that their measured value for propadienylidene should strictly be considered a lower bound. Our calculations suggest indeed that the experimental ionization energy of propadienylidene is probably too low by 0.1–0.2 eV. The ionization energy of the linear isomer of $C_3H_2^{\bullet+}$ (**2**) is predicted to be 8.83 eV, consistent with a rough experimental estimate (8.7–8.8 eV).[5b]

Clustering Reactions with CO. Both the cyclic and linear isomers of $C_3H_2^{\bullet+}$ are found to cluster with a number of neutral reagents, e.g., CO, CH_3CN, C_6H_6, N_2, and NH_3.[3b,4] In particular, Smith and Adams[3b] have shown that the linear isomer associates with CO much more rapidly than does the cyclic isomer. The different association rates were used as "fingerprints" for the cyclic and linear structures of $C_3H_2^{\bullet+}$.[3b,4] We have examined the structures (Figure 3) and energies (Table VII) of the cyclic and "linear" $C_3H_2CO^{\bullet+}$ complexes (**7** and **8**). The linear $C_3H_2^{\bullet+}$ isomer is found to bind more strongly to CO than the cyclic form; the calculated binding energies (MP4/6-311+G(2df,2p) + ZPVE) are 225 and 168 kJ mol^{-1} for **8** and **7**, respectively. Our optimized C–C "intermolecular" distances for both complexes are very short (1.343 and 1.388 Å for **7** and **8**, respectively), comparable to normal $C{=}C$ double bonds. Indeed, our calculated structures indicate that **7** and **8** should really be considered as ionized ketenes. The difference in association rates of cyclic and linear $C_3H_2^{\bullet+}$ with CO may be rationalized partly in terms of the structures of **7** and **8** and partly in terms of the entropy changes of the clustering reactions. The acyclic ketene **8** can be formed by attack of CO on either terminal carbon of l-$C_3H_2^{\bullet+}$, whereas the formation of the cyclic ketene **7** requires attack of CO on the unique carbon atom of c-$C_3H_2^{\bullet+}$ with a specific orientation. In addition, the overall entropy change is calculated to be more favorable for the association of CO with linear $C_3H_2^{\bullet+}$ than that with cyclic $C_3H_2^{\bullet+}$ (Table VII).

Ion–Molecule Reactions and Heats of Formation. Prodnuk, Depuy, and Bierbaum (PDB)[4a] have studied extensively the hydrogen-atom-abstraction reactions of $C_3H_2^{\bullet+}$ with several neutral reagents, H_2CO, CH_3OH, CH_4, c-C_3H_6, and H_2O. Based on the observed reactivities (or lack of reactivity), they concluded that the heat of formation of c-$C_3H_2^{\bullet+}$ should be 1347 kJ mol^{-1}, some 30 kJ mol^{-1} less than a value (1377 kJ mol^{-1}) deduced by Smith and Adams.[3] There are two key assumptions in the PDB bracketing analysis: (1) the energy difference between the cyclic and linear isomers of $C_3H_2^{\bullet+}$ is about 50 kJ mol^{-1} and (2) hydrogen-atom-abstraction will occur, i.e., it is barrier free, whenever it is exothermic except for reactions involving molecular hydrogen.

In the present work, we have investigated both the kinetic and thermodynamic stabilities of the two isomeric forms of $C_3H_2^{\bullet+}$ with respect to the ion–molecule reactions used to bracket their heats of formation. Our calculated reaction enthalpies at 298 K together with the PDB estimated values are summarized in Table VIII. The PDB estimates[4a] were obtained from a ΔH_f° value for c-$C_3H_2^{\bullet+}$ of 1347 kJ mol^{-1} that they believed was necessary to explain their reactivity data, a ΔH_f° value for l-$C_3H_2^{\bullet+}$ of 1397 kJ mol^{-1} based on the calculated energy difference between linear and cyclic forms of ~50 kJ mol^{-1}, and literature values of the heats of formation for the other species in the reactions.[28]

For the cyclic isomer, PDB observed hydrogen abstraction (yielding c-$C_3H_3^+$) in reactions with H_2CO, CH_3OH, CH_4, and c-C_3H_6 but no reaction with H_2O.[4a] PDB explained the failure of c-$C_3H_2^{\bullet+}$ to react with H_2O in terms of an endothermicity for the reaction, and it was on this basis that they concluded that the heat of formation of c-$C_3H_2^{\bullet+}$ should not exceed 1347 kJ mol^{-1}. Our calculations indicate, however, that hydrogen abstraction by c-$C_3H_2^{\bullet+}$ from H_2O is exothermic by 26 kJ mol^{-1} (Table VIII)

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(28) The ΔH_f° value for $CH_3O^\bullet$ (−34 kJ mol^{-1}) that appears to have been used by PDB is quite different from the currently accepted value (25 kJ mol^{-1}, see ref 9a).

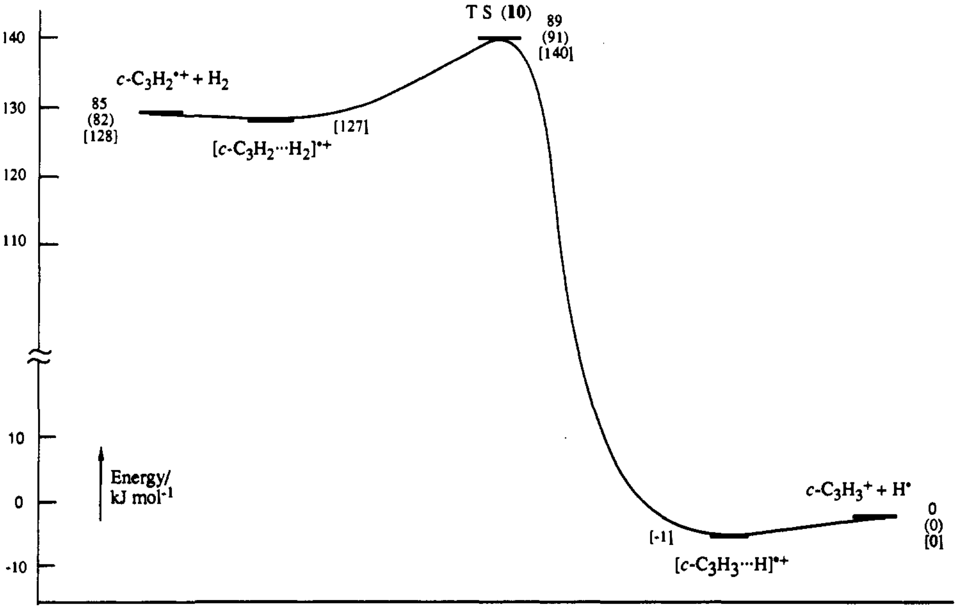

Figure 6. Schematic energy profile showing hydrogen transfer in the $[c\text{-}C_3H_2\cdots H_2]^{\bullet+}$ system (G2 results at 298 K, with G2 results at 0 K in parentheses and MP2 results at 0 K in brackets).

and that the failure to observe any reaction is, in fact, due to the presence of a kinetic barrier of 23 kJ mol^{-1}. This result provides a counter example to the assumption[4a] that ion–molecule hydrogen-abstraction reactions are barrier free, except for reactions involving molecular hydrogen. We note that for reactions of c-$C_3H_2^{\bullet+}$ with CH_3OH and CH_4 we find no evidence for a kinetic barrier. Our calculations for the hydrogen-abstraction reactions of c-$C_3H_2^{\bullet+}$ are thus consistent with all the experimental observations: reaction takes place with H_2CO, CH_3OH, CH_4, and c-C_3H_6 for which the reactions are both exothermic and barrier free but not with H_2O where the reaction, while exothermic, is impeded by a significant barrier.

The minimum energy path for the hydrogen transfer reaction of c-$C_3H_2^{\bullet+}$ with H_2O, shown in Figure 5, proceeds via two complexes, the first resembling a complex of c-$C_3H_2^{\bullet+}$ with H_2O and the second resembling a complex of c-$C_3H_3^+$ with $OH^\bullet$. At the MP2/6-31G* level, the $[c\text{-}C_3H_2^{\bullet+}\cdots H_2O]$ complex lies in a well of depth of 113 kJ mol^{-1} while the $[c\text{-}C_3H_3^{+}\cdots OH^\bullet]$ complex lies in a well of depth of 136 kJ mol^{-1}. The hydrogen-abstraction reaction occurs via transition structure **9** (Figure 4), with a barrier (at the G2 level at 298 K) of 23 kJ mol^{-1} (26 kJ mol^{-1} at 0 K).

In the previous section, we pointed out that our best theoretical estimate (31 kJ mol^{-1} at 298 K) of the energy difference between the linear and cyclic isomers of $C_3H_2^{\bullet+}$ is 19 kJ mol^{-1} less than the PDB calculated value (50 kJ mol^{-1}). This smaller relative energy changes the reaction enthalpies of the hydrogen-abstraction reactions of linear $C_3H_2^{\bullet+}$ (Table VIII). At the G2 level of theory, reactions of l-$C_3H_2^{\bullet+}$ involving H_2CO, CH_3OH, and CH_4 are predicted either to be close to thermoneutral or exothermic whereas reactions involving c-C_3H_6 and H_2O are predicted to be endothermic. This result is consistent with the observed hydrogen-abstraction reactivities of l-$C_3H_2^{\bullet+}$. The PDB estimates for the reaction enthalpies are also consistent for the most part with the observed reactivities, although the failure to observe reaction with cyclopropane is more difficult to explain.

Next, we consider the ion–molecule reaction

$$\text{l-}C_3H^+ + H_2 \rightarrow \text{c-}C_3H_2^{\bullet+} + H^\bullet \qquad (2)$$

The enthalpy change in this hydrogen-transfer reaction remains controversial. From a variable temperature selected-ion flow drift tube experiment, Smith and Adams[3b] showed that the reaction product is exclusively cyclic **1**, and they suggested that the slowness of the reaction is due to a reaction endothermicity of 4 kJ mol^{-1}. On the other hand, on the basis of ion–molecule bracketing reactions, PDB[4a] deduced that this hydrogen-abstraction reaction is exothermic, with a barrier of 4 kJ mol^{-1}. Our best calculations indicate a slight endothermicity of 4 kJ mol^{-1} at 298 K (Table VIII). We have calculated an energy profile for reaction 2 using the H···H distance as the reaction coordinate and optimizing all remaining geometrical parameters at each point. The resulting profile indicates that the reverse reaction can take place without a barrier. Hence, although the endothermicity is small and within the limits of uncertainty of G2 theory, our calculations would tend to support the Smith and Adams proposition. Note that the hydrogen-abstraction reaction of linear C_3H^+ with H_2 to form linear $C_3H_2^{\bullet+}$ (**2**) is predicted to be endothermic by 36 kJ mol^{-1}.

Using an experimental heat of formation for C_3H^+ from the literature[29] and their calculated endothermicity for reaction 2 of 4 kJ mol^{-1}, Smith and Adams[3a] deduced a heat of formation for c-$C_3H_2^{\bullet+}$ of 1389 kJ mol^{-1}. However, because the literature ΔH_f° value[29] for C_3H^+ has a large uncertainty (21 kJ mol^{-1}), Smith and Adams recommended an alternative $\Delta H_f^\circ(C_3H_2^{\bullet+})$ value of 1377 kJ mol^{-1} on the basis of an analysis which we examine and question below.

The hydrogen-abstraction reaction between c-$C_3H_2^{\bullet+}$ and molecular hydrogen may provide an important source of cyclopropenyl cations, c-$C_3H_3^+$. However, experimental studies have shown that this reaction occurs very slowly.[1c,3a] Smith and Adams[3a] have measured the reaction rate and deduced an endothermicity of 17 kJ mol^{-1}. On the other hand, PDB[4a] have suggested that the slowness of the reaction is due to the presence of a kinetic barrier. We have investigated both the kinetic and thermodynamic stabilities of this ion-molecule reaction using G2 theory. The hydrogen-abstraction reactions for the cyclic and linear isomers

$$\text{c-}C_3H_2^{\bullet+}\ (\mathbf{1}) + H_2 \rightarrow \text{c-}C_3H_3^+\ (\mathbf{5}) + H^\bullet \qquad (3a)$$

$$\text{l-}C_3H_2^{\bullet+}\ (\mathbf{2}) + H_2 \rightarrow \text{l-}C_3H_3^+\ (\mathbf{6}) + H^\bullet \qquad (3b)$$

are both calculated to be exothermic (by 91 and 8 kJ mol^{-1}, respectively). For the cyclic isomer, the abstraction reaction is inhibited by a barrier of 4 kJ mol^{-1} at 298 K (9 kJ mol^{-1} at 0 K), occurring via transition structure **10** (Figure 4). As for the c-$C_3H_2^{\bullet+}$ + H_2O reaction, the minimum energy pathway proceeds via two stable complexes, $[c\text{-}C_3H_2^{\bullet+}\cdots H_2]$ and $[c\text{-}C_3H_3^{+}\cdots H^\bullet]$ (see Figure 6), but in this case the well depths are just 1 kJ mol^{-1}. Although the calculated barrier height is within the limits of uncertainty of G2 theory, our calculated energy profile for this reaction is consistent with the observed slow rate, the lack of

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[29] Raksit, A. B.; Bohme, D. K. *Int. J. Mass Spectrom. Ion Phys.* **1983**, *49*, 275.

reactivity being attributed to the existence of a kinetic barrier, as proposed by PDB.[4a] The reaction of the linear isomer with H_2 is found to be barrier free.

We believe that the analysis that produced the heat of formation for c-$C_3H_2^{\bullet+}$ of 1377 kJ mol^{-1}, recommended by Smith and Adams,[3] is not soundly based. This $\Delta H_f°$ was assigned initially[3a] to the l-$C_3H_2^{\bullet+}$ isomer on the basis of the endothermicity (determined from the measured rate) of a reaction assumed to be 3b, together with the $\Delta H_f°$ for l-$C_3H_3^+$. Subsequently, the $C_3H_2^{\bullet+}$ isomer involved in the reaction was reassigned as c-$C_3H_2^{\bullet+}$ and the $\Delta H_f°$ of 1377 kJ mol^{-1} similarly reassigned to c-$C_3H_2^{\bullet+}$ *without any reanalysis*. This would be valid only if the reaction being observed involved c-$C_3H_2^{\bullet+}$ reacting with H_2 to produce l-$C_3H_3^+$, an unlikely state of affairs. We suggest that the appropriate experimental value for $\Delta H_f°(C_3H_2^{\bullet+})$ should be that derived directly from reaction 2, i.e., 1389 kJ mol^{-1}.[3a]

Theoretical estimates of the heats of formation at 0 K ($\Delta H_f°_0$) of the $C_3H_2^{\bullet+}$ isomers may be obtained from calculated G2 heats of the atomization reaction

$$C_3H_2^{\bullet+}{}_{(g)} + e^- \rightarrow 3C_{(g)} + 2H^{\bullet}{}_{(g)} \qquad (4)$$

in conjunction with accurate literature $\Delta H_f°_0$ values for atomic $C_{(g)}$ and $H^{\bullet}{}_{(g)}$ (216.0 and 711.2 kJ mol^{-1}, respectively).[30] The heats of formation at 298 K may then be determined from the $\Delta H_f°_0$ values together with theoretical $H_{298} - H_0$ values for the $C_3H_2^{\bullet+}$ isomers and experimental $H_{298} - H_0$ values for $C_{(s)}$ and $H_{2(g)}$ (6.54 and 8.47 kJ mol^{-1}, respectively).[31] In a recent systematic study of heats of formation of C_1–C_3 hydrocarbons and carbocations using the same approach,[8d] we have found that the calculated G2 values are predicted within 10 kJ mol^{-1} of the experimental $\Delta H_f°$ values in cases where the latter are accurately known. Our best theoretical estimate for the heat of formation ($\Delta H_f°_{298}$) of c-$C_3H_2^{\bullet+}$ (**1**) is 1387 kJ mol^{-1}, agreeing well with the revised experimental value (1389 kJ mol^{-1}) that we have suggested above. The predicted $\Delta H_f°_{298}$ values for $HCCCH^{\bullet+}$ (**2**) and $CH_2CC^{\bullet+}$ (**3**) are 1418 and 1583 kJ mol^{-1}, respectively. We have also calculated the heat of formation of C_3H^+ using the above scheme. Our computed value of $\Delta H_f°_{298}(C_3H^+)$, 1599 kJ mol^{-1}, is in good agreement with the experimental vlaue of 1602 kJ mol^{-1}.[29] This lends confidence to the experimental $\Delta H_f°_{298}$ value of 1389 kJ mol^{-1} for c-$C_3H_2^{\bullet+}$, which required the experimental $\Delta H_f°_{298}$ for C_3H^+ in its derivation.

In summary, our calculated kinetic and thermodynamic stabilities of cyclic and linear isomers of $C_3H_2^{\bullet+}$ with respect to the various hydrogen-atom-abstraction reactions are all consistent with experimental observations. The discrepancies between the previous heats of formation for the $C_3H_2^{\bullet+}$ isomers can be readily explained by our calculated G2 results. We suggest that the most reliable experimental estimate of $\Delta H_f°(c\text{-}C_3H_2^{\bullet+})$ corresponds to the Smith and Adams estimate (1389 kJ mol^{-1}),[3a] derived directly from the enthalpy of the reaction l-C_3H^+ + H_2 → c-$C_3H_2^{\bullet+}$ + $H^{\bullet}$.

Concluding Remarks

Several important points are revealed in this study.

(1) High-level ab initio calculations at the G2 level of theory predict that the energy difference between the linear (**2**, $^2\Pi$) and cyclic (**1**, $^2A_1$) structures of $C_3H_2^{\bullet+}$ is 28 kJ mol^{-1} at 0 K or 31 kJ mol^{-1} at 298 K, significantly smaller than previous theoretical estimates (~50 kJ mol^{-1} at 0 K).

(2) The calculated kinetic and thermodynamic stabilities of the cyclic and linear $C_3H_2^{\bullet+}$ cations with respect to hydrogen-abstraction reactions with various neutral reagents are consistent with extensive experimental observations. In contrast to previous assumptions, hydrogen abstraction from H_2O by c-$C_3H_2^{\bullet+}$ is found to be inhibited by a kinetic barrier of 23 kJ mol^{-1}.

(3) The heat of formation ($\Delta H_f°_{298}$) of c-$C_3H_2^{\bullet+}$ is predicted to be 1387 kJ mol^{-1}, differing significantly from a recent experimental value (1347 kJ mol^{-1}) derived from ion–molecule bracketing reactions.

(4) Consistent with the experimental observations of Smith and Adams, the ion–molecule reaction l-C_3H^+ + H_2 → c-$C_3H_2^{\bullet+}$ + $H^{\bullet}$ is calculated to be slightly endothermic (by 4 kJ mol^{-1}).

(5) The highly exothermic hydrogen-abstraction reaction c-$C_3H_2^{\bullet+}$ + H_2 → c-$C_3H_3^+$ + $H^{\bullet}$ is predicted to be inhibited by a small barrier (of 4 kJ mol^{-1}). This result is consistent with the observed slow reaction rate.

(6) The calculated ionization energies of the C_3H_2 isomers are in good agreement with recent values from photoelectron spectroscopy experiments.

(7) Both cyclic and linear isomers of $C_3H_2^{\bullet+}$ are predicted to react with CO to form ionized ketenes, the calculated binding energies being 168 and 225 kJ mol^{-1}, respectively.

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