Molecular Orbital Theory of the Electronic Structure of Organic Molecules. 40. Structures and Energies of C_1–C_3 Carbocations, Including Effects of Electron Correlation

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Abstract: Ab initio molecular orbital theory with the inclusion of electron correlation using Møller–Plesset perturbation theory has been applied to study the structures and energetics of C_1–C_3 carbocations. All the geometries have been optimized with basis sets including polarization functions (6-31G*). The effect of electron correlation on molecular geometries has been studied for the smaller systems (up to $C_2H_7^+$). These geometries have been used in Møller–Plesset perturbation calculations up to fourth order. Zero-point vibrational corrections have been applied in some cases by using analytical force constant calculations. The agreement with known experimental data suggests that this level of theory is reliable to within 5 kcal/mol.

There is a continuing refinement in the study of the structures and energies of carbocations by both gas-phase experimental[1] and theoretical[2] methods. These approaches are complementary. Heats of formation can be readily obtained experimentally, but only general information about the structure of the observed ions is available. Theory at the ab initio level provides much more detailed data on geometries and potential surfaces, but the absolute energies only permit relative stabilities to be evaluated. Agreement between gas-phase and theoretical relative energies is thus a potentially important means of assigning structures, provided the errors or uncertainties in both approaches can be reduced to the point where the reliability of such comparisons can be established. We now report the detailed examination of carbocations with one, two, and three carbon atoms at uniform levels of theory at degrees of sophistication higher than any previously reported investigation.

Most of the early ab initio calculations were performed with the Hartree–Fock (HF) single-determinant form of the wave function by using simple basis sets containing only s and p functions (s functions only on hydrogen).[3-6] In a series of papers, we presented a number of structures for singlet carbocations with up to three carbon atoms using the minimal STO-3G basis (HF/STO-3G structures).[3-7] These studies suggested that the vinyl and ethyl cations were most stable in their classical forms. However, later work[8,9] indicated that nonclassical or bridged forms were stabilized preferentially if polarization functions (particularly d functions for carbon) were added to the basis set. Zurawski, Ahlrichs, and Kutzelnigg[10] then found that inclusion of electron correlation (neglected in Hartree–Fock theory) also favored bridged structures and that if both polarization function and correlation effects are taken into account, bridged structures are favored for vinyl and ethyl. Further studies[11-14] of small carbocations support these conclusions.

We have now investigated the principal carbocations (up to $C_3H_7^+$) by employing large basis sets and perturbative correlation methods. Many of the previous higher level calculations employed geometries determined only at the minimal basis (HF/STO-3G) level. Since polarization functions are known to modify relative energies substantially, a full set of reoptimized geometries (HF/6-31G*) has been obtained for all the carbocations considered. These geometries were used for higher level single-point calculations, including electron correlation at various levels of Møller–Plesset perturbation theory.[15] In addition, some of the geometries have been optimized at the second-order perturbation level (MP2/6-31G*) to study any further significant changes with the inclusion of electron correlation. The energies predicted in this manner provide relative stabilities (by simple formal reactions) which can be compared with the available experimental data. Furthermore, to determine the nature of the stationary points on the potential-energy surface, analytical second derivatives of the energy with respect to all nuclear coordinates (force constants) have been evaluated for some of the structures.

Computational Methods

The Hartree–Fock (HF) procedure was used as the starting point throughout. For triplet states, the spin-restricted Hartree–Fock (UHF) method was used. Three basis sets were employed. The first[16] is 6-31G*, which has polarization (d-type) basis functions on nonhydrogen atoms. The second[16] is 6-31G**, which also has p-type functions on hydrogen. Finally, 6-311G** is a larger basis[17] with additional s, p functions designed for studies beyond the Hartree–Fock level. The total energies with the three basis sets are listed in Tables I–III. Electron correlation effects

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(1) For reviews, see (a) D. H. Aue and M. T. Bowers, *Gas Phase Ion Chem.*, **2**, 91 (1979); (b) H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, (1977), and references therein.

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Table I. Total Energies Using the 6-31G* Basis and HF/6-31G* Geometries

molecule	structure	HF	MP2	MP3	MP4(SDQ)
CH^+		−37.89554	−37.96160	−37.97967	−37.98574
CH_3^+ (singlet)	1, D_{3h}	−39.23064	−39.32514	−39.34158	−39.34467
(triplet)	3 ($^3B_1$), C_{2v}	−39.09016	−39.17507	−39.19029	−39.19355
	4 ($^3A_2$), C_{2v}	−39.09095	−39.17850	−39.19414	−39.19722
CH_5^+	5, C_s	−40.38850	−40.53018	−40.54805	−40.55149
	6, C_s	−40.38844	−40.53006	−40.54795	−40.55140
	7, C_{2v}	−40.38241	−40.52995	−40.54712	−40.55001
	8, C_{4v}	−40.37782	−40.52847	−40.54580	−40.54851
	9, D_{3h}	−40.36763	−40.51945	−40.53705	−40.53999
C_2H^+	$^3\Pi$, $C_{\infty v}$	−75.78555	−75.94091	−75.96010	−75.96598
	$^1\Delta$, $C_{\infty v}$	−75.72678			
	$^1\Sigma^+$, $C_{\infty v}$	−75.61775	−75.83839	−75.85042	−75.85865
	$^3\Sigma^-$, $C_{\infty v}$	−75.77350	−75.93024	−75.95604	−75.96154
$C_2H_3^+$	10, C_{2v}, classical	−77.08673	−77.30658	−77.32746	−77.33374
	11, C_{2v}, bridged	−77.07556	−77.31276	−77.32848	−77.33289
$C_2H_5^+$	12, C_{2v}, bridged	−78.30994	−78.55184	−78.57579	−78.58060
	13, C_s, classical	−78.31123	−78.54289	−78.56852	−78.57406
	14, C_s, classical	−78.31021	−78.54102	−78.56686	−78.57243
$C_2H_7^+$	15, C_2, C–C bridged form	−79.45524	−79.71486	−79.74401	−79.75045
	16, C_s, C–H bridged form	−79.43918	−79.68864	−79.71939	−79.72645
C_3H^+	17, $C_{\infty v}$, linear form	−113.65480	−113.98788	−113.99683	−114.00839
	18, C_{2v}, bent form	−113.58872	−113.88446	−113.91389	−113.92409
$C_3H_3^+$	19, D_{3h}, cyclopropenyl	−115.00702	−115.34801	−115.36777	−115.37076
	20, C_{2v}, propargyl	−114.95110	−115.29569	−115.31383	−115.32141
$C_3H_5^+$	21, C_{2v}, allyl	−116.19321	−116.54302	−116.57008	−116.57635
	22, C_s, perpendicular allyl	−116.13899	−116.48291	−116.51371	−116.52078
	23, C_s, 2-propenyl	−116.16664	−116.52084	−116.55029	−116.55818
	24, C_s, 1-propenyl	−116.14123	−116.49062	−116.52031	−116.52860
	25, C_s, cyclopropyl	−116.13219	−116.48421	−116.51362	−116.51975
	26, C_s, corner-protonated cyclopropene	−116.12484	−116.49480	−116.51852	−116.52385
$C_3H_7^+$	27, C_{2v}, 2-propyl	−117.38076	−117.74505	−117.78034	−117.78778
	29, C_s, 1-propyl	−117.35111	−117.71290	−117.74828	−117.75583
	30, C_s, corner-protonated cyclopropane	−117.35916	−117.73745	−117.76877	−117.77462
	31, C_{2v}, edge-protonated cyclopropane	−117.35073	−117.73415	−117.76498	−117.77100

Table II. Total Energies Using the 6-31G** Basis and HF/6-31G* Geometries

molecule	structure	HF	MP2	MP3	MP4(SDQ)
CH^+		−37.89753	−37.96892	−37.98749	−37.99354
CH_3^+ (singlet)	1, D_{3h}	−39.23629	−39.34653	−39.36450	−39.36737
(triplet)	3 ($^3B_1$), C_{2v}	−39.09848	−39.19447	−39.21049	−39.21348
	4 ($^3A_2$), C_{2v}	−39.10138	−39.20107	−39.21741	−39.22009
CH_5^+	5, C_s	−40.40610	−40.57316	−40.59267	−40.59518
	6, C_s	−40.40603	−40.57302	−40.59254	−40.59506
	7, C_{2v}	−40.40063	−40.57394	−40.59246	−40.59432
	8, C_{4v}	−40.39317	−40.56913	−40.58735	−40.58895
	9, D_{3h}	−40.38024	−40.55646	−40.57479	−40.57658
C_2H^+	$^3\Pi$, $C_{\infty v}$	−75.78766	−75.94735	−75.96691	−75.97267
	$^1\Delta$, $C_{\infty v}$	−75.72895			
	$^1\Sigma^+$, $C_{\infty v}$	−75.61982	−75.84475	−75.85709	−75.86513
	$^3\Sigma^-$, $C_{\infty v}$	−75.77554	−75.93672	−75.96288	−75.96825
$C_2H_3^+$	10, C_{2v}, classical	−77.09309	−77.32758	−77.34951	−77.35506
	11, C_{2v}, bridged	−77.08443	−77.33593	−77.35246	−77.35594
$C_2H_5^+$	12, C_{2v}, bridged	−78.32094	−78.59098	−78.61710	−78.62065
	13, C_s, classical	−78.32051	−78.58025	−78.60808	−78.61244
	14, C_s, classical	−78.31931	−78.57819	−78.60623	−78.61064
$C_2H_7^+$	15, C_2, C–C bridged form	−79.46973	−79.77144	−79.80417	−79.80888
	16, C_s, C–H bridged form	−79.45341	−79.74025	−79.77356	−79.77925
C_3H^+	17, $C_{\infty v}$, linear form	−113.65686	−113.99439		
	18, C_{2v}, bent form	−113.59088	−113.89133		
$C_3H_3^+$	19, D_{3h}, cyclopropenyl	−115.01329	−115.36937		
	20, C_{3v}, propargyl	−114.95689	−115.31679		
$C_3H_5^+$	21, C_{2v}, allyl	−116.20207	−116.58063		
	22, C_s, perpendicular allyl	−116.14832	−116.52052		
	23, C_s, 2-propenyl	−116.17638	−116.55806		
	24, C_s, 1-propenyl	−116.15060	−116.52785		
	25, C_{2v}, cyclopropyl	−116.14190	−116.52164		
	26, C_s, corner-protonated cyclopropene	−116.13418	−116.53134		
$C_3H_7^+$	27, C_{2v}, 2-propyl	−117.39328	−117.81406		
	29, C_s, 1-propyl	−117.36332	−117.78240		
	30, C_s, corner-protonated cyclopropane	−117.37152	−117.80654		
	31, C_{2v}, edge-protonated cyclopropane	−117.36551	−117.80609		

Table III. Total Energies Using the 6-311G** Basis and MP2/6-31G* Geometries

molecule	structure	HF	MP2	MP3	MP4(SDQ)
CH^+		−37.90456	−37.97781	−37.99707	−38.00329
CH_3^+ (singlet)	1, D_{3h}	−39.24357	−39.35618	−39.37491	−39.37810
(triplet)	3 ($^3B_1$), C_{2v}	−39.10736	−39.20844	−39.22548	−39.22868
	4 ($^3A_2$), C_{2v}	−39.11061	−39.21465	−39.23196	−39.23487
CH_5^+	5, C_s	−40.41500	−40.59006	−40.60991	−40.61234
	6, C_s	−40.41490	−40.58985	−40.60972	−40.61217
	7, C_{2v}	−40.41026	−40.58918	−40.60853	−40.61057
	8, C_{4v}	−40.40305	−40.58564	−40.60479	−40.60647
	9, D_{3h}	−40.38882	−40.57289	−40.59200	−40.59372
C_2H^+	$^3\Pi$, $C_{\infty v}$	−75.80009	−75.96579	−75.98555	−75.99112
	$^1\Delta$, $C_{\infty v}$	−75.74127			
	$^1\Sigma^+$, $C_{\infty v}$	−75.62774	−75.86854	−75.87784	−75.88784
	$^3\Sigma^-$, $C_{\infty v}$	−75.78740	−75.95533	−75.98236	−75.98786
$C_2H_3^+$	10, C_{2v}, classical	−77.10588	−77.34858	−77.37065	−77.37638
	11, C_{2v}, bridged	−77.09857	−77.36117	−77.37713	−77.38108
$C_2H_5^+$	12, C_{2v}, bridged	−78.33443	−78.61336	−78.64039	−78.64426
	14, C_s, classical	−78.33145	−78.60067	−78.62922	−78.63397
$C_2H_7^{+a}$	15, C_2, C–C protonated form	−79.46798	−79.77399	−79.80576	−79.81001
	16, C_s, C–H protonated form	−79.45347	−79.76425	−79.79432	−79.79801

[a] With the 6-31G** basis.

were included by the Møller–Plesset (MP) perturbation treatment,[15] starting with the HF wave function. We have used full second- and third-order theories (MP2 and MP3)[18,19] as well as a partial fourth-order theory[20] [MP4(SDQ)] which is correct to fourth order in the space of single, double, and quadruple substitutions. At this fourth-order level, the unlinked cluster contributions to the correlation energy have been included through the quadruple substitutions, but triple substitutions are neglected.

Some of the previous work was carried out with other correlation procedures, e.g., the independent electron pair approximation (IEPA), configuration interaction with single and double substitutions (CISD), and the coupled electron pair approximation (CEPA). For comparative purposes, it may be noted that IEPA is correct to second order in a Møller–Plesset expansion while CID and CEPA are correct to third order. CEPA results should be more reliable than CID since the latter method handles unlinked clusters incorrectly. However, both are incorrect in fourth order in the SDQ space.

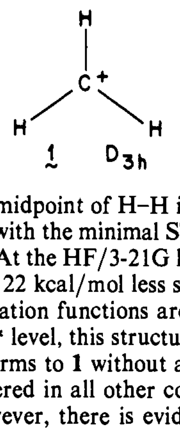
Two general types of computation have been carried out. In the first, which has been applied to all systems, the geometries have been optimized (by general minimization) by using the Hartree–Fock procedure and the 6-31G* basis (HF/6-31G* model). Full details of these structures are given elsewhere.[21] These geometries are then used for single-point calculations with the 6-31G** basis and including correlation corrections. At the fourth-order level, such a model may be described by the compound description MP4(SDQ)/6-31G**//HF/6-31G*. In this notation, the model used for the single-point calculation precedes the // sign and is followed by the level used for geometry optimization. For the larger carbocations (with three carbon atoms), MP4(SDQ)/6-31G** calculations were not technically feasible. Consequently, the 6-31G* basis (no p functions on hydrogen) was used for computation of the third- and fourth-order energy perturbation terms. Experience with the smaller systems suggests that errors in relative energies (Tables IV–XVI) introduced by this approximation should be less than 1 kcal/mol. Such results will be described as "projected SDQ".

In the second general computational procedure, applied only to the systems with one or two carbon atoms, the geometries were reoptimized with correlation included at the second-order level (MP2/6-31G*).[22] Single-point computations to fourth order were then carried out with the larger 6-311G** basis [MP4(SDQ)/6-311G**//MP2/6-31G*]. For the larger $C_2H_7^+$ systems the final correlation calculations were performed with the 6-31G** basis. Only the valence shell correlation contribution is used in all cases.

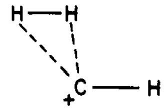
Discussion

CH^+. CH^+, a molecule found in interstellar clouds,[23] has a $^1\Sigma^+$ ground state. The bond length at HF/6-31G* level is 1.105 Å. At MP2/6-31G* level, the bond length increases to 1.120 Å in better agreement with experiment[24] (1.131 Å).

CH_3^+. The methyl cation **1** is found to have a D_{3h} equilibrium structure at the HF/6-31G* level corresponding to a minimum on the potential surface. Another structure, **2**, corresponding to a long-range interaction of CH^+ with H_2[25] (the distance from C to the midpoint of H–H is ~1.8 Å), is found to be a local minimum with the minimal STO-3G basis and the extended 3-21G[26] basis. At the HF/3-21G level, it is considerably higher in energy, being 122 kcal/mol less stable than the methyl cation **1**. When polarization functions are included in the basis set at the HF/6-31G* level, this structure is no longer a local minimum and it transforms to **1** without activation. Only the D_{3h} structure **1** is considered in all other computations of singlet CH_3^+.



1 D_{3h}



2 C_s

However, there is evidence for "high kinetic-energy" CH_3^+ cations which conceivably could be excited electronic states.[1b] Consequently, we examined triplet CH_3^+; two Jahn-Teller forms, both possessing C_{2v} symmetry (T-shaped $^3B_1$ **3** and Y-shaped $^3A_2$ **4**) are possible. Cation **3** has a bond angle H_1CH_2 of 160.6° at MP2/6-31G* level while **4** has a much smaller bond angle H_1CH_2 of 77.2°. The $^3A_2$ form **4** is somewhat more stable at all theoretical levels. At MP4(SDQ)/6-31G**//MP2/6-31G* level it is 3.9 kcal/mol more stable than **3**. At this level, **4** is 89.9 kcal/mol less stable than the singlet methyl cation **1**. Considering the

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(19) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem., Symp.*, **10**, 1 (1976).

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(21) R. A. Whiteside, J. S. Binkley, R. Krishnan, D. J. DeFrees, H. B. Schlegel, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Archive, 1980; available from the authors.

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(23) A. E. Douglas and G. Herzberg, *Astrophys. J.*, **94**, 381 (1941).

(24) "Doñees Spectroscopiques Relatives and Molecules Diatomiques", B. Rosen, Ed., Pergamon, Oxford, 1971.

(25) The H_2·CH^+ complex was discovered (by accident) by Professor M. Saunders during an examination of the CH_3^+ potential-energy surface by MINDO/3. H_2·CH^+ is indicated to be a local minimum at that level.

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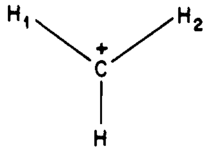
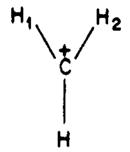
Table IV. Relative Energies (kcal/mol) of CH_5^+ Structures Using the 6-311G** Basis and MP2/6-31G* Optimized Geometries

structure	HF	MP2	MP3	MP4(SDQ)
5, C_s	0.0	0.0	0.0	0.0
6, C_s	0.1	0.1	0.1	0.1
7, C_{2v}	3.0	0.6	0.9	1.1
8, C_{4v}	7.5	2.8	3.2	3.7
9, D_{3h}	16.4	10.8	11.2	11.7



3 ($^3B_1$) C_{2v}



4 ($^3A_2$) C_{2v}

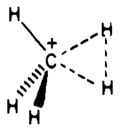
energies of the reactions (experimental values of the heats of formation[1b] in kcal/mol in parentheses

$$\underset{(334)}{CH_2^+} + \underset{(52)}{H} \xrightarrow{-124} \underset{(262)}{CH_3^+}$$

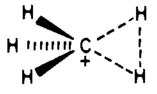
$$\underset{(94)}{CH_2} + \underset{(365)}{H^+} \xrightarrow{-197} \underset{(262)}{CH_3^+}$$

triplet CH_3^+ is bound; it might be possible to observe this species experimentally.

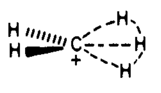
CH_5^+. Protonated methane has been investigated previously at Hartree–Fock and correlated levels.[3,8,11] As with these earlier studies, we have considered a number of symmetry-constrained structures, including the C_s forms **5** and **6**, the C_{2v} form **7**, the square-pyramid **8**, and the trigonal-bipyramid **9**. The relative energies at various theoretical levels are summarized in Table IV.



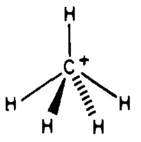
5 C_s



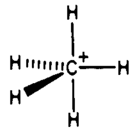
6 C_s



7 C_{2v}



8 C_{4v}



9 D_{3h}

Consistent with the previous work, **5** (corresponding to a three-center bond complex between CH_3^+ and H_2) is most stable at all levels examined. Structure **6** is always very close in energy, indicating nearly free "turnstile" rotation (barrier 0.1 kcal/mol) for the CH_3^+ and H_2 groups.

When correlation corrections are included, the energies of **5**–**9** are compressed into a smaller range. The relative energy of **7** (corresponding to protonation of methane along an HCH bisector) is lowered, and at the MP4(SDQ)/6-311G**//MP2/6-31G* level, **7** is only 1.1 kcal/mol above **5**. This close proximity of the correlated energies of **5**–**7** noted previously by Dyczmons and Kutzelnigg,[11] implies a low activation barrier for interchange or "scrambling" of the hydrogen nuclei in CH_5^+. The C_{4v} form **8**, which can be used to model a number of carbocation systems for which there is experimental evidence,[42] is also relatively stable; the **5**–**8** energy difference is only 3.7 kcal/mol. The energy difference between **5** and the less stable trigonal-bipyramid **9** is lowered from 16.4 to 11.7 kcal/mol [MP4(SDQ)/6-311G**//MP2/6-31G*] with the inclusion of electron correlation.

Table V. Dissociation Energy of CH_5^+ into CH_3^+ and H_2 Using the 6-311G** Basis and MP2/6-31G* Optimized Geometries

procedure	dissociation energy, kcal/mol
HF	24.1
MP2	46.2
MP3	43.2
MP4(SDQ)	41.7
MP4(SDQ) + zero-point vibrational correction[a]	34.7
exptl	40.0[b]

[a] See text for details. [b] Reference 28.

Table VI. Relative Energies (kcal/mol) of C_2H^+ Structures Using the 6-311G** Basis and MP2/6-31G* Optimized Geometries

structure	HF	MP2	MP3	MP4(SDQ)
$^3\Pi$	0.0	0.0	0.0	0.0
$^1\Delta$	36.9			
$^1\Sigma^+$	108.2	61.0	67.6	64.8
$^3\Sigma^-$	8.0	6.6	2.0	2.1

As noted before, geometries for the various forms of CH_5^+ have been optimized both at the Hartree–Fock level (HF/6-31G*) and with the inclusion of electron correlation (MP2/6-31G*). This permits the study of changes in geometry due to the inclusion of electron correlation. Correlation strengthens the three-center bond complex between CH_3^+ and H_2 in **5** and **6**; the bond length C–H_1 in **5** which is 1.228 Å at HF/6-31G* reduces to 1.185 Å at MP2/6-31G* level. A similar but more dramatic effect is seen later in the case of $C_2H_7^+$.

For a determination of the nature of the stationary points on the potential-energy surface, analytical second derivatives of the energy with respect to all nuclear coordinates[27] were evaluated for structures **5**–**9** at HF/6-31G* level. The number of negative frequencies of the resulting force constant matrix characterizes the stationary point. Only **5** is found to be a local minimum on the potential surface (no negative frequencies), and **6**–**9** are found to be saddle points (one or more negative frequencies).

The energy of dissociation

$$CH_5^+ \rightarrow CH_3^+ + H_2$$

is known experimentally[28] to be 40 kcal/mol. Using the 6-311** basis and MP2/6-31G* optimized geometries, values calculated at various correlation levels are shown in Table V. Electron correlation makes a large contribution to the binding of H_2 with CH_3^+. The dissociation energy at MP4(SDQ)/6-311G** is 41.7 kcal/mol. Zero-point vibrational effects, important for such a dissociation process, have been calculated by an analytical evaluation of the force constants and harmonic vibrational frequencies[27] at the HF/6-31G* level. When these corrections are included, the dissociation energy reduces to 34.7 kcal/mol. It should be noted, however, that the calculations give the reaction energies at absolute zero ($\Delta H°_0$) whereas the experimental values are at the measured temperature ($\Delta H°_T$).

C_2H^+. The ethynyl cation has been investigated previously at the HF level.[3a,b] Four states have been examined (all linear).

$$1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 1\pi^4 \qquad {}^1\Sigma^+$$

$$1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 5\sigma^2\, 1\pi^2 \qquad {}^1\Delta$$

$$1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 5\sigma^2\, 1\pi^2 \qquad {}^3\Sigma^-$$

$$1\sigma^2\, 2\sigma^2\, 3\sigma^2\, 4\sigma^2\, 5\sigma\, 1\pi^3 \qquad {}^3\Pi$$

The lowest energy state with the 6-311G** basis is $^3\Pi$ with three

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(27) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem., Symp.*, **13**, 225 (1979).

(28) K. Hiraoka and P. Kebarle, *J. Am. Chem. Soc.*, **98**, 6119 (1976), and references cited therein.

Table VII. Relative Energies *E*(Classical) - *E*(Bridged) for $C_2H_3^+$ (kcal/mol)

basis//geometry model	HF	MP2	MP3	MP4-(SDQ)
6-31G**//HF/6-31G*	−5.4	5.2	1.9	0.6
6-311G**//MP2/6-31G*	−4.6	7.9	4.1	3.0

π electrons and a C–C bond length of 1.24 Å (MP2/6-31G*). The other triplet $^3\Sigma^-$ with two π electrons (MP2/6-31G* bond length C–C = 1.37 Å) is 8.0 kcal/mol higher at the HF/6-311G** level. Inclusion of electron correlation reduces this energy difference to 2.1 kcal/mol at the MP4(SDQ)/6-311G**//MP2/6-31G* level. The lowest singlet state is $^1\Delta$ with two π electrons. Complex molecular orbitals are used to describe this state which is studied only at the HF/6-311G**//HF/6-31G* level (C–C = 1.36 Å). At this level it is 36.9 kcal/mol less stable than the $^3\Pi$ form. $^1\Delta$, although not studied with electron correlation (since the orbitals are complex), is expected to remain above $^3\Sigma^-$ since the same orbitals are populated in both. The $^1\Sigma^+$ state, characterized by an MP2/6-31G* bond length of 1.22 Å, is considerably higher in energy. It is 108.2 kcal/mol higher than the $^3\Pi$ state at HF/6-311G**//MP2/6-31G* level. Inclusion of electron correlation reduces the singlet triplet difference, but even at MP4(SDQ)/6-311G**, it is 64.8 kcal/mol less stable than the $^3\Pi$ state. Unfortunately, the $^1\Sigma^+$ state was the only one considered by Montgomery and Dykstra[29] in their prediction of rotational constants which might be of use in detecting HCC^+ in interstellar space. They obtain similar bond lengths for this state (1.18–1.22 Å) by using various basis sets and correlation methods, but do not consider the other states which are lower in energy.

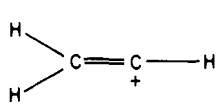
The heat of formation of C_2H^+ can be calculated from the energy of the isodermic reaction

$$HC{\equiv}CH + CH_3^+ \rightarrow HC{\equiv}C^+\ (^1\Sigma^+) + CH_4$$

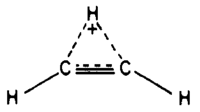
[134.7 kcal/mol at MP4(SDQ)/6-311G**//MP2/6-31G*].

Combining this with the experimental heats of formation[1b] of CH_4, CH_3^+, and C_2H_2 gives a heat of formation for the $^1\Sigma^+$ species as 468.8 kcal/mol. Since the $^1\Sigma^+$ is 64.8 kcal/mol less stable than the $^3\Pi$ state, the heat of formation of the $^3\Pi$ state of C_2H^+ is calculated to be 404.0 kcal/mol. This is in good agreement with the experimental values[1b] which range from 399 to 414 kcal/mol.

$C_2H_3^+$. The vinyl cation is the simplest carbocation for which classical and nonclassical (bridged) structures are easily compared. Following earlier work[8] we have examined the C_{2v} structures **10** and **11**. Calculated energy differences (Table VII) are quite dependent on the theoretical level employed.



10 C_{2v}



11 C_{2v}

After full geometry optimization at the HF/6-31G* level, the classical form **10** is more stable by 7.0 kcal/mol; this is reduced to 5.4 kcal/mol at HF/6-31G**//HF/6-31G*. When correlation is included at second order (MP2/6-31G**//HF/6-31G*), the order of stability is changed and **11** becomes more stable than **10** by 5.2 kcal/mol. This effect was first discovered by Zurawski et al.[10] using IEPA. However, this preferential stabilization of the bridged form is moderated at higher orders of perturbation theory; the difference is only 0.6 kcal/mol at MP4(SDQ)/6-31G**//HF/6-31G*. This overestimation of correlation energy effects at the MP2 level, a general effect in most of the systems we have studied, is consistent with the decreases in the energy differences found by Lischka and Kohler[14] in going from IEPA to CEPA. Weber et al.[12] find **10** and **11** to be equally stable using CISD on a double-zeta plus polarization basis. These authors found a small energy barrier separating these structures.

Table VIII. Relative Energies (kcal/mol) of $C_2H_5^+$ Structures Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

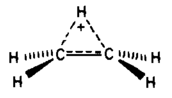
structure	HF	MP2	MP3	MP4(SDQ)
12, bridged	0.0	0.0	0.0	0.0
13, classical	0.3	6.7	5.7	5.2
14, classical	1.0	8.0	6.8	6.3

Table IX. Relative Energies (kcal/mol) of $C_2H_5^+$ Structures Using the 6-311G** Basis and MP2/6-31G* Geometries

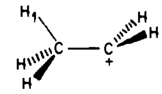
structure	HF	MP2	MP3	MP4(SDQ)
12, bridged	0.0	0.0	0.0	0.0
14, classical	1.9	8.0	7.0	6.5

Since inclusion of electron correlation has a major impact on **10** and **11**, the optimized MP2/6-31G* geometries were determined. The C–C bond length in **11** increases from 1.21 at HF/6-31G* to 1.23 Å at MP2/6-31G*. The distance of the bridging hydrogen to the middle of the C–C bond stays the same (1.18 Å). There is no significant change in the geometry for the classical structure **10**. Use of these geometries results in a slight additional stabilization to the bridged form, the MP4(SDQ)/6-31G**//MP2/6-31G* energy difference being 1.3 kcal/mol. With the larger 6-311G** basis, the bridged structure is stabilized further, and our final result at MP4(SDQ)/6-311G**//MP2/6-31G* indicates **11** to be more stable than **10** by 3.0 kcal/mol. Lischka and Kohler[14] have used CEPA method on a comparable basis set (and geometries which are very similar to our HF/6-31G* geometries) and obtain the bridged form to be 4.0 kcal/mol lower in energy than the classical form.

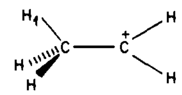
$C_2H_5^+$. The ethyl cation has already been the subject of numerous ab initio studies.[2,8,10,14] We have considered the nonclassical bridged structure **12** and the two C_s classical structures **13** and **14**. The relative energies at the various 6-31G**//HF/6-31G* correlation levels are shown in Table VIII.



12 C_{2v}



13 C_s



14 C_s

At all levels of theory, the classical form **13** is more stable than its classical alternative **14**. The energy difference between **13** and **14** is the sixfold rotational barrier and is 1.1 kcal/mol at MP4-(SDQ)/6-31G**//HF/6-31G*. The angle H_1CC in **13** is only 98.2°, (in **14** H_1CC = 114.9°) and this suggests that the proton H_1 has moved partly toward a bridging position. At the HF/6-31G**//HF/6-31G* level, the bridged form **12** is only marginally more stable (by 0.3 kcal/mol) than the classical form **13**. As with $C_2H_3^+$, if correlation corrections are included, the bridged structure **12** is favored preferentially. It is 5.2 kcal/mol more stable than **13** at the MP4(SDQ)/6-31G**//HF/6-31G* level.

Optimization of the geometries at the MP2/6-31G* level shows interesting features. At this level, the classical form **13** is not a local minimum and is transformed without activation to the bridged structure **12**. However, the energy of classical $C_2H_5^+$ can be estimated from **14** which cannot collapse to **12** due to the imposed C_s symmetry constraint. The bridged form **12** is 6.5 kcal/mol lower than the classical form **14** at MP4(SDQ)/6-311G**//MP2/6-31G* (Table IX). Analysis of the analytical force constants and vibrational frequencies of **14** at HF/6-31G* level shows, however, that it is a rotational transition structure,

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(29) J. A. Montgomery, Jr. and C. E. Dykstra, *J. Chem. Phys.*, 71, 1380 (1979).

Table X. Relative Energies E(C–H Protonated Form) – E(C–C Protonated Form) for $C_2H_7^+$ (kcal/mol)

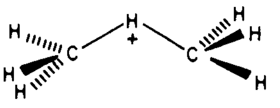
basis//geometry model	HF	MP2	MP3	MP4-(SDQ)
6-31G**//HF/6-31G*	10.1	19.3	19.0	18.4
6-31G**//MP2/6-31G*	9.1	4.8	6.1	6.8

the second derivative matrix having one negative eigenvalue. Hence the bridged structure **12** is the only minimum on the $C_2H_5^+$ potential surface. The energy difference of 6.5 kcal/mol between **12** and **14** may be considered as the activation energy for the scrambling of hydrogens in $C_2H_5^+$.

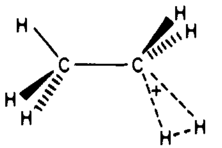
These results may be compared with the best of the previous calculations. Using IEPA, Zurawski et al.[10] find the bridged structure to be 9.0 kcal/mol lower in energy. Lischka and Kohler[14] have used the CEPA method with a double-zeta plus polarization basis and report the bridged structure to be favored by 7.3 kcal/mol.

Recently, Houle and Beauchamp[30] have obtained the photoelectron spectrum of the ethyl radical. The vertical and adiabatic ionization potentials are separated by ~3 kcal/mol. The adiabatic peak could be interpreted as a transition to the bridged ethyl cation and the vertical peak as corresponding to the classical form which is closer to the structure of the radical. According to this interpretation, the ~3 kcal/mol energy difference between the adiabatic and vertical IP's would correspond approximately to the classical, bridged energy difference. Our calculations are in reasonable agreement with this value. In another determination of $\Delta H°_f$ (gas) of $C_2H_5^+$, Baer[31] calls attention to the discrepancies in the experimental values, well beyond the uncertainties of the methods employed, when this ion is generated by different methods. He suggests that the structures of C_2H_5 and the most stable form of $C_2H_5^+$ may be different.

$C_2H_7^+$. Protonated ethane has been studied both experimentally and theoretically. The kinetics and equilibrium of ethyl cation hydrogenation (Hiraoka and Kebarle[28]) indicate the existence of two isomeric forms of $C_2H_7^+$ with an energy difference of 7–8 kcal/mol. These forms interpreted as C–C and C–H protonated ethane species, **15** and **16**, have been studied theoretically at the HF[3a,b] and CEPA[32] levels.



15 C_1



16 C_s

At all levels of theory, the C–C protonated C_2 form **15** is lower in energy than the C–H protonated C_s form **16**. The relative energies are summarized in Table X. At the optimized HF/6-31G* level, **15** is strongly distorted from a D_{3d} structure with an angle CH_1C of 121.7°. It is also twisted by about 30° from a staggered C_s configuration. At this level, **16** is a very loose complex between $C_2H_5^+$ and H_2 (at a distance of 2.7 Å). Using these geometries at the HF/6-31G** level, **15** is lower in energy by 10.1 kcal/mol. Inclusion of correlation favors **15** further, and at MP4(SDQ)/6-31G**//HF/6-31G*, **15** is 18.4 kcal/mol more stable than **16**.

Optimization of the geometries with the inclusion of correlation at the MP2/6-31G* level changes the picture dramatically. Correlation strongly favors the interaction between $C_2H_5^+$ and H_2 in **16**, and in the optimized structure, the distance between $C_2H_5^+$ and H_2 is shortened to 1.3 Å. This structure is now very similar to the structure **5** of CH_5^+. This change in the strength of interaction with the inclusion of electron correlation has been noted by Kohler and Lischka.[32] The CH_1C angle in **15** decreases to 105.8°. Using these geometries at the MP4(SDQ)/6-31G** level, **15** is now lower in energy by 6.8 kcal/mol, in good agreement with experiment (Table X).

Table XI. Dissociation Energy of $C_2H_7^+$ into $C_2H_5^+$ and H_2 Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

procedure	dissociation energy kcal/mol
HF	11.0
MP2	14.3
MP3	15.0
MP4(SDQ)	14.9
MP4(SDQ) + zero-point vibrational correction[a]	7.4
exptl	11.8[b]

[a] See text for details. [b] Reference 28.

Table XII. Dissociation Energy of $C_2H_7^+$ into CH_3^+ and CH_4 Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

procedure	dissociation energy, kcal/mol
HF	19.9
MP2	37.8
MP3	35.7
MP4(SDQ)	35.2
MP4(SDQ) + zero-point vibrational correction[a]	31.4
exptl	36[b]

[a] See text for details. [b] Reference 28.

Table XIII. Relative Energies[a] (kcal/mol) of C_3H^+ Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

structure	HF	MP2	MP3	MP4(SDQ)
7, linear form	0.0	0.0	0.0	0.0
8, bent form	41.4	64.7	(51.8)	(52.7)

[a] Values in parentheses are projected estimates based on the third- and fourth-order effects on the 6-31G* basis.

Hiraoka and Kebarle[28] have measured the energy of dissociation of $C_2H_7^+$

$$C_2H_7^+\ (\mathbf{15}) \rightarrow C_2H_5^+ + H_2$$

to be 11.8 kcal/mol. Table XI shows the values calculated at various perturbation levels with the 6-31G** basis. At the MP4(SDQ) level the dissociation energy is 14.7 kcal/mol. Zero-point vibrational effects, calculated by an analytical evaluation of the force constants[27] at the HF/6-31G* level, reduce the dissociation energy to 7.4 kcal/mol.

Another dissociation process for which experimental data is available[28] is

$$C_2H_7^+\ (\mathbf{15}) \rightarrow CH_3^+ + CH_4$$

The calculated values with the 6-31G** basis are summarized in Table XII. The final MP4(SDQ)/6-31G** values after the zero-point correction is 31.4 kcal/mol, in good agreement with the experiment (36 kcal/mol).

C_3H^+. The structures for C_3H^+ have been investigated previously at the HF level.[7b,43] These correspond to protonation of neutral C_3 at a terminal carbon (**17**) and on the central carbon (**18**), respectively. However, a large apparent discrepancy in our earlier estimated heat of formation and the experimental range[1b] led us to search for more stable structures. None were found.

The linear form **17** is the lower energy form at all levels of theory (Table XIII). At HF/6-31G** level it is 41.4 kcal/mol lower in energy than the C_{2v} form **18**. Inclusion of correlation favors the linear form further, the energy difference rising to 64.7

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(30) F. A. Houle and J. L. Beauchamp, *J. Am. Chem. Soc.*, **101**, 4067 (1979).

(31) T. Baer, *J. Am. Chem. Soc.*, **102**, 2482 (1980).

(32) H.-J. Kohler and H. Lischka, *Chem. Phys. Lett.*, **58**, 175 (1978).

Table XIV. Relative Energies[a] (kcal/mol) of $C_3H_3^+$ Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

structure	HF	MP2	MP3	MP4(SDQ)
19, cyclopropenyl	0.0	0.0	0.0	0.0
20, propargyl	35.4	33.0	(34.0)	(31.1)

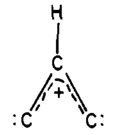
[a] Values in parentheses are projected estimates based on the third- and fourth-order effects on the 6-31G* basis.

Table XV. Relative Energies[a] (kcal/mol) of $C_3H_5^+$ Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

structure	HF	MP2	MP3	MP4(SDQ)
21, allyl	0.0	0.0	0.0	0.0
22, perpendicular allyl	33.7	37.7	(35.4)	(34.9)
23, 2-propenyl	16.1	14.2	(12.7)	(11.6)
24, 1-propenyl	32.3	33.1	(31.5)	(30.2)
25, cyclopropyl	37.8	37.0	(35.6)	(35.6)
26, corner-protonated cyclopropene	42.6	30.9	(33.0)	(33.6)

[a] Values in parentheses are projected estimates based on the third- and fourth-order effects on the 6-31G* basis.

17 $C_{\infty v}$



18 C_{2v}

Table XVI. Relative Energies[a] (kcal/mol) of $C_3H_7^+$ Using the 6-31G** Basis and HF/6-31G* Optimized Geometries

structure	HF	MP2	MP3	MP4(SDQ)
27, 2-propyl	0.0	0.0	0.0	0.0
29, 1-propyl	18.8	19.9	(19.8)	(19.7)
30, corner-protonated cyclopropane	13.7	4.7	(7.2)	(8.2)
31, edge-protonated cyclopropane	17.4	5.0	(7.8)	(8.7)

[a] Values in parentheses are projected estimates based on the third- and fourth-order effects on the 6-31G* basis.

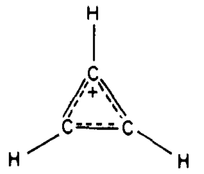
kcal/mol at MP2/6-31G** level. However, the overshoot of correlation effects at the MP2 level, previously observed for the vinyl and ethyl cations, is seen here also, and at the final projected MP4(SDQ)/6-31G** level, the linear form is lower in energy by 52.7 kcal/mol.

Experimentally, the C_3H^+ ion has been detected in mass spectroscopy; a wide range of estimates of the heat of formation between 280 and 425 kcal/mol is given in a recent compilation.[1b] Theoretically, we can use the calculated energy of the isodesmic reaction

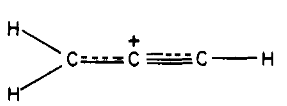
$$^{+}{:}C{-}C{\equiv}CH + CH_4 \rightarrow {:}^{+}CH + CH_3{-}C{\equiv}CH$$

[66.2 kcal/mol at MP4(SDQ)/6-31G* level] and the experimental heats of formation of CH_4, CH^+, and $CH_3C{\equiv}CH$[1b] to calculate a heat of formation of 383 kcal/mol. This is in almost perfect agreement with experimental values, 384 and 387 kcal/mol, reported in the latest investigations.[33] It appears that lower values are incorrect.

$C_3H_3^+$. Various $C_3H_3^+$ structures have been investigated previously with HF theory;[7] we consider here those of lowest energy, the cyclopropenyl (**19**) and the propargyl (**20**) cations (Table XIV). At the HF/6-31G** level, **19** is indicated to be more stable by 35.4 kcal/mol. This is considerably higher than the experimental energy difference[1b] of 24 kcal/mol. Inclusion of electronic correlation lowers the energy difference, and at the projected MP4(SDQ)/6-31G** level, the cyclopropenyl cation **19** is lower in energy by 31.1 kcal/mol.

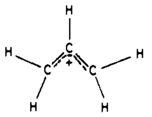


19 D_{3h}

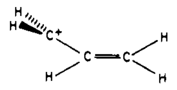


20 C_{2v}

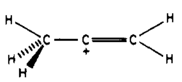
$C_3H_5^+$. Various isomers of $C_3H_5^+$ have been studied extensively at the HF level.[7] The structures considered include the planar allyl cation **21**, the perpendicular allyl cation **22**, the 2-propenyl ion **23**, the 1-propenyl ion **24**, the cyclopropyl cation **25**, and the corner-protonated cyclopropene **26**. The relative energies at the MP/6-31G**//HF/6-31G* levels are summarized in Table XV.



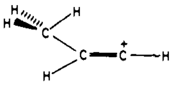
21 C_{2v}



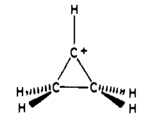
22 C_s



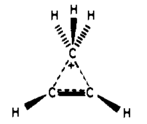
23 C_s



24 C_s



25 C_{2v}



26 C_s

At all levels of theory, the allyl cation **21** is the most stable form in agreement with experiment.[35] Its C–C bond, 1.373 Å at the optimized HF/6-31G* level, is intermediate in length between a normal single and double bond. The perpendicular allyl cation **22**, which models the rotational transition state, is 34.9 kcal/mol higher in energy at the projected MP4(SDQ)/6-31G** level; this value is rather independent of the ab initio theoretical model employed.[34] The C–C bond lengths, 1.318 and 1.444 Å, are clearly distinguishable as double and single bonds. Experimentally, there is no direct determination of the rotational barrier of the allyl cation,[34] but an indirect one based on extrapolated results[34] is 34 kcal/mol.

The 2-propenyl cation **23** is the second lowest energy form (next to the allyl cation) at all levels of theory. At HF/6-31G**, **23** is 16 kcal/mol less stable than **21**. The inclusion of correlation reduces this difference to 11.6 kcal/mol at the projected MP4(SDQ)/6-31G** level, in good agreement with experimental values of 11 kcal/mol.[36] Analytical calculations of the force constants and vibrational frequencies with the smaller 3-21G basis shows that it is a local minimum at this level, in agreement with experimental evidence for the existence of long-lived 2-propenyl cations in the gas phase.[37,38] The 1-propenyl cation **24** is 30.2 kcal/mol higher in energy than the allyl cation **21**. The 1-propenyl cation is also found to be a local minimum with the 3-21G basis.

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Table XVII. Stabilization Energies of Some Carbonium Ions Relative to CH_3^{+}[a]

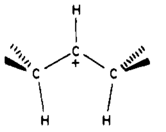
molecule	structure	HF/ 6-31G**	MP4(SDQ)/ 6-31G**	MP4(SDQ)/ 6-311G**	exptl
$C_2H_3^+$	10, C_{2v}, classical	12.3	18.2	17.2	23[b]
	11, C_{2v}, bridged	6.9	18.8	20.4	
$C_2H_5^+$	12, C_{2v}, bridged	29.9	33.8		36.4[d]
	14, C_s, classical	30.2	39.0		40.3[c]
$C_3H_3^+$	19, D_{3h}, cyclopropenyl	93.0	(92.8)		88[b]
	20, C_{2v}, propargyl	32.0	(39.7)		43[b]
$C_3H_5^+$	21, C_{2v}, allyl	53.9	(54.5)		58[b]
	23, C_s, 2-propenyl	37.8	(42.9)		47[b]
$C_3H_7^+$	27, C_{2v}, 2-propyl	51.8	(58.5)		64,[b] 67.3,[c] 63.8[d]
	29, C_s, 1-propyl	33.0	(38.3)		

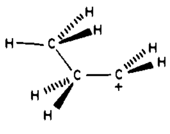
[a] Values in parentheses are projected estimates. [b] Reference 1b. [c] Reference 30. [d] Reference 31.

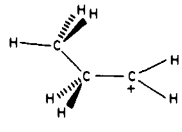
A direct analytical calculation of the force constants and vibrational frequencies of **24** with the larger 6-31G* basis was not technically feasible. However, previous investigations at the HF/6-31G* level[7] suggests that the barrier to the conversion of 1-propenyl cation to the 2-propenyl cation by means of a 1,2-hydride shift is likely to be very small. The cyclopropyl ion **25** (a local minimum at HF/3-21G) and corner-protonated cyclopropene **26** are also comparable in energy (35.6 and 33.6 kcal/mol higher than the allyl cation **21**, respectively).

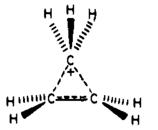
The 1-propenyl cation **24** and the corner-protonated cyclopropene **26** can be interpreted as the classical and nonclassical forms of the methyl substituted vinyl cation. At the HF/6-31G**//HF/6-31G* level, the classical form **24** is 10.3 kcal/mol more stable than the bridged form **26**. Here again, inclusion of correlation favors the bridged form relative to the classical form (by 6.9 kcal/mol), and at the projected MP4(SDQ)//HF/6-31G* level, the classical form is more stable by 3.4 kcal/mol.

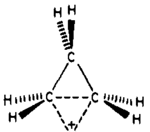
$C_3H_7^+$. The $C_3H_7^+$ cations have been investigated previously at the HF[5,9] and CEPA[14] levels. The structures are 2-propyl cation **27**, 1-propyl cations **28** and **29**, corner-protonated cyclopropane **30**, and edge-protonated cyclopropane **31**. The relative energies of the various forms are summarized in Table XVI. 2-Propyl cation **27** is the most stable form at all levels of theory. Analysis of the force-constant matrix with the smaller 3-21G basis reveals that the C_{2v} structure **27** has a negative frequency corresponding to a distortion to C_2 symmetry. This has been observed before by Hout and Hehre.[39] However, the energy lowering from such a distortion is very small, and hence the C_{2v} structure itself is used in all calculations with the 6-31G* basis. The 1-propyl cation **28** is not a local minimum at HF/6-31G* level and is converted without activation to the corner-protonated cyclopropane **30** on optimization. An energy for the 1-propyl cation can be obtained by artificially imposing a symmetry constraint, e.g., a C_s plane as in **29**. At the projected MP4(SDQ)/6-31G** level, **29** is 19.7 kcal/mol less stable than the 2-propyl cation **27**. An earlier experimental value[1b] for this difference is 16 kcal/mol, but Houle and Beauchamp[40] recently obtained a higher value of 23.5 kcal/mol from the photoelectron spectrum of the 1-propyl radical.


27 C_{2v}


28 C_s


29 C_s


30 C_s


31 C_{2v}

The other structures considered are the corner- and edge-protonated cyclopropanes (**30** and **31**). A $C_3H_7^+$ species considered to be a protonated cyclopropane has been found experimentally[41] to be about 8 kcal/mol less stable than the 2-propyl ion. At the HF/6-31G** level, the corner-protonated form **30** is lower in energy than the edge-protonated form **31** by 3.7 kcal/mol. Inclusion of electron correlation favors the edge-protonated form; at the projected MP4(SDQ)/6-31G** level, the corner-protonated form is only 0.5 kcal/mol more stable than the edge-protonated form. Analysis of the force constants for the edge-protonated form with the smaller 3-21G basis reveals that it is not a local minimum. The negative frequency corresponds to conversion to the corner-protonated form. With the larger 6-31G* basis set, it is difficult to say with certainty which form is more stable. The energy difference between 2-propyl ion **27** and the corner-protonated form is 8.2 kcal/mol, in good agreement with the experimental value of 8 kcal/mol.

These results are different from those of Lischka and Kohler,[14] who used an approximate CEPA method in which they evaluated the pair interactions between nonneighboring bonds by IEPA. A double-zeta + polarization basis comparable to our 6-31G** basis was employed. However, our basis has more primitive Gaussians, and our total energies are lower. They reported the edge protonated to be lower in energy than the corner-protonated form by 5 kcal/mol. This discrepancy may be in part due to their use of STO-3G geometries, whereas we optimized the geometries at the HF/6-31G* level. The approximate nature of the CEPA energy evaluation probably may also contribute to the difference in results. We conclude that the energy difference between corner- and edge-protonated $C_3H_7^+$ is too small to make a definite prediction concerning the lower energy form.

Relative Stabilities of Carbonium Ions

Sets of total energies at the same level permit the relative stabilities of different cations to be evaluated.[2] Any cation R^+ can be compared with the methyl cation CH_3^+ by means of the energy of the isodermic reaction.

$$R^+ + CH_4 \rightarrow RH + CH_3^+$$

The positive energies found (Table XVII) mean that R^+ is more stable than CH_3^+ in the sense that H^- is more easily removed from RH than it is from CH_4.

The calculated methyl stabilization energies at various levels are compared with the corresponding experimental information[1b] in Table XVII. For the vinyl cation, there is a discrepancy of about

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10 kcal/mol at the HF level. At the MP4(SDQ)/6-311G**//MP2/6-31G* level, this reduces to 2.6 kcal/mol. Similarly, the HF/6-31G** value of 29.9 kcal/mol for the ethyl cation is 10 kcal/mol less than the experimental value. Correlation improves the value to 39.0 kcal/mol, in very good agreement with experiment. There is a similar 8 kcal/mol improvement for the propargyl cation **20**; the improvements for **23**, **27**, and **29** are all 5–7 kcal/mol. The overall level of agreement with experiment thus improves considerably from HF theory. This agreement should help in assigning structures to ions for which only the energies are known. For example, the ion with heat of formation 235 kcal/mol, assigned to cyclopropyl cation in ref 1a, cannot be this species because it does not fit in with relative energies listed in Table XV.

Conclusion

Electron correlation methods at the MP4(SDQ) level with reasonably large basis sets have been used to study C_1–C_3 carbocations. Since much experimental data is available in this area, fruitful comparisons between theory and experiment can be made. Such a comparison suggests that this level of theory gives results reliable to within 5 kcal/mol, a considerable improvement over HF theory. The effect of electron correlation on carbocation geometries has been investigated for the smaller systems. Dramatic changes in geometry and energetics of the $C_2H_7^+$ carbocations reveal the importance of electron correlation in such systems. It must be remembered that this level of theory neglects the effect of triple substitutions. A systematic investigation of this and other effects will help in the understanding of these small systems. This understanding could be usefully applied in the case of larger systems on which such large-scale calculations are not feasible.

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Supplementary Material Available: MP2/6-31G* geometries for C_1–C_2 carbocations (6 pages). Ordering information is given on any current masthead page.

First Determination of the Structure of an Ion-Paired Species in Nonpolar Media: ^{1}H, ^{13}C, and ^{7}Li NMR Spectra of Peralkylcyclohexadienyllithium Compounds

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Received January 28, 1981

Abstract: Peralkylcyclohexadienyllithium compounds (**2a**,**b**), formed by addition of alkyllithiums to triene **1**, are shown to exist as ion-paired aggregates containing conjugated anions bent out of the plane at the saturated ring carbon. Both ^{13}C and ^{7}Li NMR spectra show **2a**,**b** to form two distinctly different ion-paired species—tight peripherally solvated ion-pair aggregates in the presence of mainly tertiary amines and loose separated ion-pair dimers favored with THF, glymes, and HMPT. The latter exhibit two $^{7}Li^+$ peaks, one due to Li sandwiched between two anions in a *triple ion* and the other situated external to it. In the case of **2b** with THF both ion-pair species are dimers, and the equilibrium $(A^-Li^+)_2 \cdot (THF)_2 + THF \rightleftarrows (A_2Li)^- + Li\,(THF)_3^+$ is characterized with $\Delta H = -4$ kcal and $\Delta S = -16$ eu. The exchange of ions between ion pairs of **2b** with THF is generally slow on the NMR time scale. However, above 0 °C the lithium exchange rate between the solvated site in the loose ion-pair dimer and the lithium in the tighter ion-pair dimer lies on the NMR time scale. The mean lifetime of lithium in the triple ion is always >10 s. The slow ion-exchange rates are ascribed to the crowded substitution around **2a**,**b**.

Ion pairing in solution has been the object of extensive investigation;[1-8] still several significant questions remain unanswered. They concern the structures of ion pairs, their mode of solvation, and dynamic behavior—how fast and by what mechanisms ions exchange from one ion pair to another.

Most carbanion salts are only soluble in a few ethers and amines. This severely limits what may be learned about solvation and ion pairing from solution spectroscopic investigations. Also, in general, exchange of ions among ion pairs in solution is fast relative to the NMR time scale. Thus NMR spectra of solutions containing different kinds of ion pairs of the same salt show only single averaged spectra.

We have already described how alkyllithium compounds cleanly add, both unsolvated in hydrocarbon solvents and in the presence of ligands, to 1,1,2,3,5,6-hexamethyl-4-methylene-2,5-cyclohexadiene (**1**) to give stable, soluble, substituted cyclohexadienyllithium compounds (**2**).[9] The latter aromatize on heating to give, in >95% yield, peralkylbenzenes (**3**), with extrusion of methyllithium.

The compounds **2a–c** have unusual properties which render them particularly useful for studies of ion pairing and electronic structure in carbanion salts; **2a–c** are among the few conjugated organolithium compounds which are soluble in many media in-

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