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Electrophilic and Oxidative Activation of the Central C−C Bond in [3.3.*n*]Propellanes: A Theoretical Study

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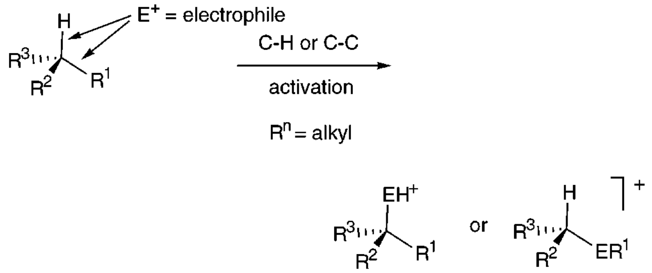
The structures and reaction mechanisms of some tricyclic compounds and propellanes were investigated computationally at the BLYP/6-311+G**//BLYP/6-31G* nonhybrid density functional level, in particular to elucidate the elementary steps of the single-electron transfer (SET) oxidation reactions observed experimentally in the presence of oxidizing electrophiles (e.g., $NO_2^+BF_4^-$). Adiabatic ionization potentials (IP), proton affinities (PA), and strain energies were evaluated, the last from the heats of formation derived from homodesmotic equations. The low IP's and high PA's of highly strained propellanes such as 3,6-dehydrohomoadamantane help rationalize the single electron-transfer reactions that occur with oxidizing electrophiles. Electrophiles need not attack regions of highest electron density (the propellanic bond); the radical cation intermediates are trapped by nucleophiles. SET must be considered as an important potential mechanism for the activation of strained aliphatic hydrocarbons.

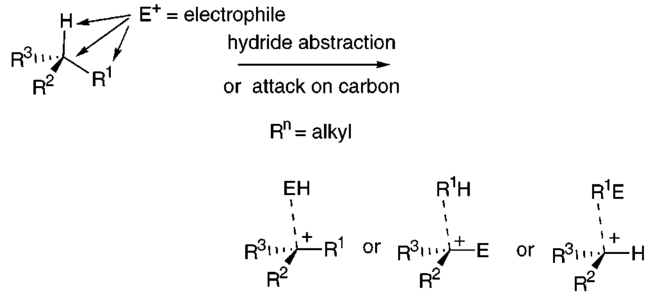
Introduction

Selective electrophilic activation and substitution of aliphatic hydrocarbons are among the major challenges in chemistry; their mechanisms have been studied extensively both experimentally and theoretically.[1−14] Traditional mechanistic concepts[15] involve attack of the electrophile at "regions of highest electronic density," i.e., σ_{CH} or σ_{CC} bonds (Scheme 1) with the formation of three-center two-electron (3c-2e) transition states or intermediates.[15]

Scheme 1. Attack of an Electrophile on the σ-Bonds in Alkanes: The "Traditional" Mechanism



Scheme 2. Attack of an Electrophile on the Atoms Directly, Leading to Hydride Abstraction and Bond Cleavages[a]



[a] Note that the dissociation products normally form weakly bound complexes, as indicated by the dashed lines.

However, recent theoretical studies of the reactions of methane[16] as well as ethane[17] with NO^+ and of methane with the Cl^+, F^+, Li^+, HCO^+, OH^+, and H_2OOH^+ model electrophiles (in their singlet states)[18] as well as with carbenes[13] revealed that electrophiles can attack carbon or hydrogen directly, rather than via 3c-2e intermediates or transition states involving E^+ (Scheme 2).[12−14] Alternatively, electrophiles may oxidize hydrocarbons via single-electron-transfer (SET), followed by subsequent reactions of the intermediate radical cations (Scheme 3). The latter pathway also is indicated in enzymatic hy-

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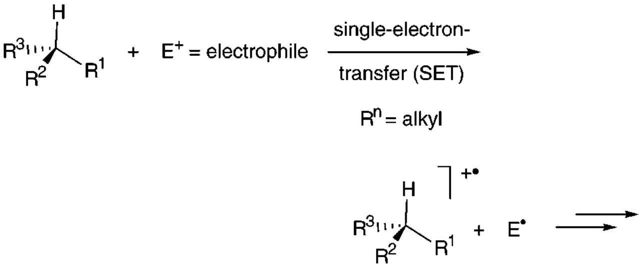
Scheme 3. SET Oxidation of a Hydrocarbon by an Electrophile with a High Oxidation Potential[a]



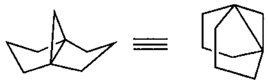
[a] There are many reactions possible for the intermediate radical cation (loss of a proton or an alkyl cation, reaction with a nucleophile, rearrangement and radical recombination, further fragmentation, etc.).

drocarbon oxidations[19−23] and in oxidationsof activated arenes with mixtures of HNO_3/H_2SO_4 in acetic acid.[24−27]

These theoretical findings, however, are quite difficult to corroborate experimentally for the simplest alkanes since the activation barriers can be expected (and are computed) to be quite high. The typically drastic reaction conditions (e.g., superacid) give rise to side reactions. In contrast, the selective oxidation of cage hydrocarbons (bicycloheptanes, bicyclooctanes, adamantanes, and propellanes) under relatively mild conditions (e.g., with enzymes or with N_2O_5) has been achieved by other groups[1,22,28] and in our laboratories.[29,30]

Propellanes[31−33] are very suitable substrates for the study of alkane C−C bond activation because the reactivity of the central C−C bond is quite variable. Moreover, "front-side" attack on this bond is precluded by the cage structure. As has been shown previously,[34,35] propellanes react with various electrophiles with varying selectivities under mild conditions, depending on the ring size, where small-ring propellanes are more reactive and hence less selective.[36] Thus, while small-ring [1.1.*n*]- and [2.2.*n*]-propellanes ($n = 1-3$) are attacked readily by many electrophiles, the reactivity of large-ring propellanes depends on the reagent. Some propellanes (e.g., [4.4.4]-propellane) contain an almost "normal" alkane central C−C bond and exhibit typical paraffinic behavior.[37] Recent synthetic studies on the transformations of some [3.3.*n*]propellanes[29,30] and cage hydrocarbons[1,22,28] with nitronium reagents $NO_2^+Y^-$ ($Y = BF_4$, OAc, ONO_2) as well as other oxidizers[23] revealed two types of addition reactions to the central C−C bond: (a) electrophilic (e.g., nitro derivatives are formed with $NO_2^+Y^-$) and (b) oxidative (two nucleophiles add formally to the central C−C bond). For some [3.3.*n*]propellanes, which are relatively stable toward electrophiles, only the oxidative route b was followed.

The thermodynamics of protonation as well as SET oxidation of cage hydrocarbons has now been studied theoretically by examining reactions of adamantanes and [3.3.*n*]propellanes ($n = 1-3$) **1**−**5** with a proton (the simplest electrophile) and with NO_2^+ (an oxidizing electrophile).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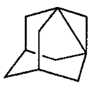
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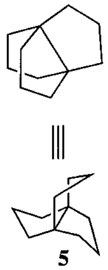
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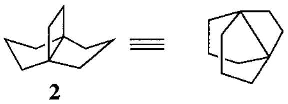
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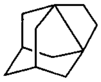
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Methods

Geometries were fully optimized with Gaussian 94[38] by analytical gradient methods[39−41] utilizing Becke's pure (non-Hartree−Fock hybrid) gradient-corrected exchange functional[42] and the Lee−Yang−Parr nonlocal correlation functional[43,44] (BLYP). Although the three-parameter mixed Hartree−Fock gradient corrected[45] Becke-3−Lee−Yang−Parr (B3LYP) functional generally[46−49] (but not always)[50] gives somewhat better results than BLYP, computations with the latter are somewhat faster and require less disk space.[51−53] We also found that the BLYP wavefunctions converge more

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Table 1. Absolute Energies (au) and Zero-Point Energies (ZPE) (kcal mol^{-1}) for the Structures Considered in the Present Study

species	BLYP/6-31G* OPT	BLYP/6-311+G**// BLYP/6-31G*	ZPE
cyclopropane	−117.813 92	−117.853 69	48.7
cyclobutane	−157.103 69	−157.152 74	66.4
cyclopentane	−196.418 23	−196.478 83	84.2
CH_4	−40.479 13	−40.496 49	26.7
C_2H_6	−79.763 22	−79.792 37	45.4
C_3H_8	−119.049 08	−119.090 05	61.8
n-C_4H_{10}	−158.334 91	−158.387 55	78.6
i-C_4H_{10}	−158.335 54	−158.388 30	79.8
n-C_5H_{12}	−197.620 68	−197.684 96	95.9
neo-C_5H_{12}	−197.621 52	−197.686 01	95.3
1	−351.139 33	−351.238 07	126.5
2	−390.429 18	−390.538 45	143.6
3	−389.198 15	−389.299 92	131.0
4	−428.507 63	−428.623 73	148.5
5	−429.741 50	−429.862 20	161.6
1H$_2$-DC	−352.368 37	−352.469 74	141.4
2H$_2$-BC	−391.638 16	−391.751 30	158.9
3H$_2$	−390.469 92	−390.577 80	146.0
4H$_2$	−429.742 51	−429.862 38	162.9
5H$_2$	−430.914 11	−431.038 31	176.5
1$^{\bullet+}$	−350.871 09	−350.962 12	
2$^{\bullet+}$	−390.154 43	−390.255 73	
3$^{\bullet+}$	−388.960 43	−389.056 94	
4$^{\bullet+}$	−428.245 32	−428.353 82	
5$^{\bullet+}$	−429.458 00	−429.570 85	
1^{+}	−351.491 58	−351.584 54	
2^{+}	−390.771 05	−390.874 64	
3^{+}	−389.603 37	−389.702 71	
4^{+}	−428.882 37	−428.992 68	
5^{+}	−430.063 76	−430.179 05	

quickly than B3LYP wavefunctions, especially for the more demanding open-shell radical cations. Two basis sets were employed: 6-31G* for geometry optimizations and 6-311+G** for single-point energies on the BLYP/6-31G* geometries (Table 1). Unless noted otherwise, the energies discussed refer to the BLYP/6-311+G**//BLYP/6-31G* level. Harmonic vibrational frequencies and zero-point energies (scaled by 0.89)[54] were determined for propellanes **1**−**5** and their hydrogenated products **1H$_2$**−**5H$_2$** at the HF/6-31G* level to include thermochemical corrections.

Results and Discussion

Geometries. The computed quaternary C−C bond distances (Figure 1) in **1** (1.537 Å) and **3** (1.589 Å) are typical for propellanes containing three-membered rings.[34,35] The central C−C distances are longer in the corresponding cyclobutane-containing structures **2** (1.601 Å) and **4** (1.603 Å). Note that the central propellanic bond lengthens steadily with increasing ring size. The effect of bridging **1** and **2** in the 4 and 4′ positions (leading to **3** and **4**, respectively) on the geometries is quite significant. In **1** and **2**, the six- and seven-membered rings adopt distorted boat conformations (the boat−chair conformers[55] found to be less stable in 3.2 kcal mol^{-1} and 1.4 kcal mol^{-1} for **1** and **2**, respectively), while **3** and **4** are more rigid systems. Propellane **5** belongs to the C_{3h} point group (the C_s form is 3.4 kcal mol^{-1} less stable).

The geometries around the carbon atoms of the central bonds are strongly deformed in these propellanes. This effect is magnified when the "propellers" are bridged as in **3** and **4** (note the "inverted" geometry of C1 and C2 in **3**). Deviations from tetrahedral geometries can be measured by the angle sum at the bridgehead carbons. While the sum of the six angles in a perfect tetrahedron is 656.8°, rather large deviations are found for **1** (angle sum = 634.9°) and **3** (angle sum = 627.7°). Structures **2** (angle sum = 651.5°), **4** (angle sum = 651.3°), and **5** (angle sum = 655.8°) are much less distorted at the bridgehead carbon. The geometry of **5** compares well with 1,1,2,2-tetraalkylcyclopentanes.[56]

The relative stabilities of **1**−**5** can be estimated using isodesmic eqs 1 and 2 $\Delta_{rxn}H°_{298}$ (Table 2).

$$R + 2CH_4 \rightarrow RH_2 + C_2H_6 \tag{1}$$

$$R + C_nH_{2n+2} \rightarrow RH_2 + \text{cyclo-}C_nH_{2n} \tag{2}$$

The hydrogen-transfer reaction from methane (eq 1, note that R stands for the propellane, while RH_2 refers to its formal hydrogenation product, the nonpropellanic hydrocarbon) reflects the change in relative strain energies of propellanes **1**−**5**, while eq 2 evaluates the strain increase when the appropriate small *n*-membered rings ($n = 3-5$) are taken into account (Table 2). Cyclopropane is employed for **1** and **3**, cyclobutane for **2** and **4**, and cyclopentane for **5**.

Since bicyclo[3.3.1]nonane (**1H$_2$**) can exist[57] in different conformations, e.g., double-chair (**1H$_2$-DC**) and boat−chair (**1H$_2$-BC**), we optimized both to evaluate the relative stability. Conformation **1H$_2$-DC** was found to be 2.8 kcal mol^{-1} more stable than **1H$_2$-BC**; this agrees nicely with experimental[57] data (2.3 kcal mol^{-1}) as well as with previous[58] force-field calculations (2.3 kcal mol^{-1}). The twisted[59] double-boat **1H$_2$-DB** with C_2 symmetry, the third possible minimum of bicyclo[3.3.1]nonane, is 9.6 kcal mol^{-1} less stable than **1H$_2$-DC** and has a C_{2v}-double-boat transition state for enantiomerization (NIMAG = 1; the HF/6-31G* barrier is 2.6 kcal mol^{-1}). For bicyclo[3.3.2]decane **2H$_2$**, the boat-chair conformation **2H$_2$-BC** (C_s symmetry) is 4.1 kcal mol^{-1} lower in energy than the double-boat **2H$_2$-DB** (C_2 symmetry); previous[59] results based on force-field calculations indicated **2H$_2$-DB** to be about 2.5 kcal mol^{-1} less stable than **2H$_2$-BC**. The energies of the bicycloalkanes, **1H$_2$** and **2H$_2$**, in the most stable conformations (Figure 2) were used in eqs 1 and 2.

Equation 1. The energies obtained from experimental $\Delta_fH°_{298}$ data and eq 1 (cyclopropane −22.2 kcal mol^{-1}, cyclobutane −20.8 kcal mol^{-1}, and cyclopentane −1.1 kcal mol^{-1})[60] agree very well with the computed values (Table 2). For propellanes R, relative to their hydrogenated forms RH_2, **5** is the most stable hydrocarbon in this

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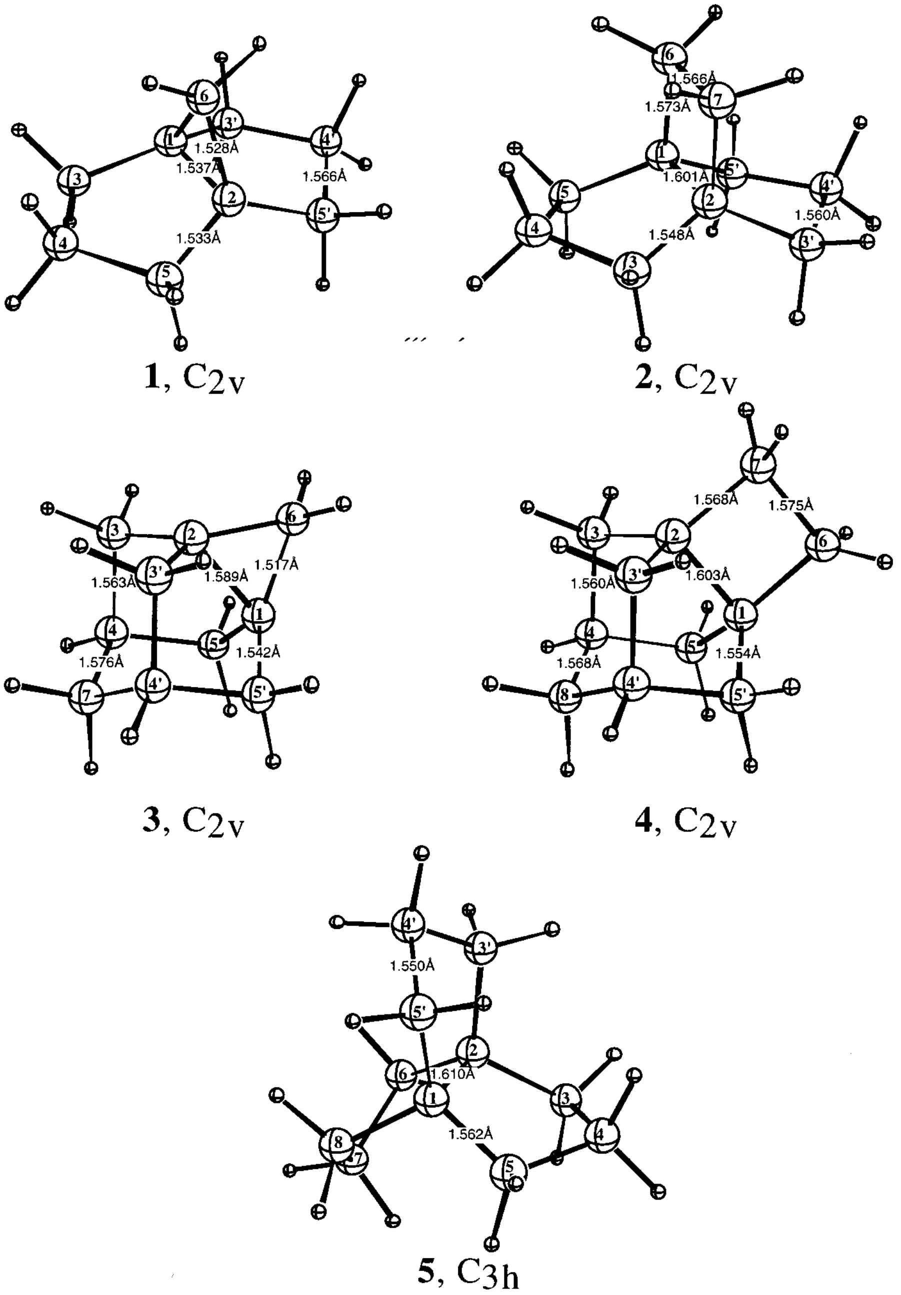

1, C_{2v} **2**, C_{2v}

3, C_{2v} **4**, C_{2v}

5, C_{3h}

Figure 1. Optimized geometries of propellanes **1**−**5**.

series, and the relative stability order from eq 1 is **5** > **2** > **1** > **4** > **3**.

Equation 2. The difference between the reaction enthalpies of **2** and **4** is nearly the same when evaluated with eq 2 ($\Delta\Delta_{rxn}H°_{298}$ = 17.0 kcal mol^{-1}) vs eq 1 ($\Delta\Delta_{rxn}H°_{298}$ = 17.2 kcal mol^{-1}); for cyclopropane-containing[61] propellanes **1** and **3**, this eq 1 − eq 2 difference is larger (3.2 kcal mol^{-1}). The relative stabilities of **1**−**5** given by eq 2 are identical to those of eq 1.

Strain Energies. To evaluate the strain energies of propellanes (Table 3) we computed $\Delta_{rxn}H°_{298}$ of homodesmotic eq 3 (Table 2) where l = 7, m = 0, n = 11 for propellane **1**, l = 8, m = 0, n = 12 for **2**, l = 6, m = 2, n = 13 for **3**, l = 7, m = 2, n = 14 for **4**, l = 9, m = 0, n = 13 for **5**, and k = 2 for all propellanes **1**−**5**. Equation 3, in effect, estimates the strain energies directly, since unstrained reference molecules are employed.

$$kC(CH_3)_4 + lCH_3CH_2CH_3 + mHC(CH_3)_3 \rightarrow R + nCH_3CH_3 \quad (3)$$

We also calculated the heats of formation ($\Delta_fH°_{298}$, Table 3) of propellanes **1**−**5** using BLYP data ($\Delta_{rxn}H°_{298}$, Table 2) and the experimental heats of formation of the acyclic alkanes.[56] The strain energies of cyclopropane, cyclobutane, cyclopentane, and hydrogenated forms **1H$_2$**−**5H$_2$** also were evaluated (Table 3). The extra methylene bridges in **4** and especially in **3** increase the strain in the cage hydrocarbons considerably; hence, the strain energies are 55.5 kcal mol^{-1} in **3** vs 36.1 kcal mol^{-1} in **1** but 41.1 kcal mol^{-1} in **4** vs 34.0 kcal mol^{-1} in **2**. The BLYP strain energy order is **5** > **2** > **1** > **4** > **3**.

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[61] (a) Yanovskaya, L. A.; Dombrowsky, V. A.; Husid, A. H. *Cyclopropanes with Functional Groups*; Nauka: Moscow, 1980. (b) De Meijere, A.; Blechert, S. *Strain and Its Implications in Organic Chemistry*; Kluwer Academic Publ.: Dordrecht, 1989.

Table 2. Propellane 1−5 Reaction Energies and Enthalpies (kcal mol^{-1}) at Two DFT Levels

R	$\Delta_{rxn}E$ BLYP/6-31G*	$\Delta_{rxn}H°_{298}$ BLYP/6-31G*	$\Delta_{rxn}E$ BLYP/6-311+G**	$\Delta_{rxn}H°_{298}$[b] BLYP/6-311+G**
$R + 2CH_4 \rightarrow RH_2 + C_2H_6$ (1)[a]				
cyclopropane	−25.3	−20.2	−22.4	−17.3
cyclobutane	−22.8	−18.4	−21.5	−17.1
cyclopentane	−4.7	−0.9	−3.5	0.3
1	−21.3	−16.7	−19.5	−14.9
2	−8.7	−1.3	−7.7	−0.3
3	−48.2	−41.4	−48.7	−41.9
4	−24.9	−18.6	−23.8	−17.5
5	14.0	20.7	15.4	22.1
$R + C_nH_{2n+2} \rightarrow RH_2 + \text{cyclo-}C_nH_{2n}$ (2)				
1	3.8	7.0	2.9	6.1
2	13.9	16.9	13.8	16.8
3	−23.0	−21.0	−26.1	−24.1
4	−2.3	−0.1	−2.4	−0.2
5	18.7	21.8	18.8	21.9
$kC(CH_3)_4 + lCH_3CH_2CH_3 + mHC(CH_3)_3 \rightarrow R + nCH_3CH_3$ (3)				
cyclopropane, $k = m = 0, l = n = 3$	27.4	27.2	24.7	24.5
cyclobutane, $k = m = 0, l = n = 4$	25.4	26.4	23.8	24.8
cyclopentane, $k = m = 0, l = n = 5$	6.9	9.3	6.0	8.9
1, $k = 2, l = 7, m = 0, n = 11$	32.5	36.1	30.3	33.9
2, $k = 2, l = 8, m = 0, n = 12$	30.0	34.0	28.6	32.6
3, $k = 2, l = 6, m = 2, n = 13$	55.6	55.5	55.3	55.2
4, $k = 2, l = 7, m = 2, n = 14$	40.1	41.1	38.9	39.9
5, $k = 2, l = 9, m = 0, n = 13$	13.4	19.0	12.2	17.8

[a] Experimental $\Delta_{rxn}H°_{298}$ for cyclopropane −22.2; cyclobutane −20.8; cyclopentane −1.1. [b] Optimized geometries at BLYP/6-31G*; thermochemical corrections and ZPE at HF/6-31G*.

Reactions: Oxidation. Removal of an electron from **1**−**5** (eq 4, Table 4) to give the corresponding singly positively charged radical cations $\mathbf{1}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ (Figure 3) models single electron transfer to an oxidizing reagent (see also eq 8 below). Some of the radical cations were difficult to optimize (problems with wavefunction convergence), in particular when the central C−C bond lengthened considerably (e.g., **5**). This problem, however, is not found for the parent ethane radical cation.[62] Also, we found that the UBLYP spin contaminations for $\mathbf{1}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ were very low (S^2 should be 0.75; found, e.g., 0.754 for $\mathbf{1}^{\bullet+}$ and 0.755 for $\mathbf{5}^{\bullet+}$).[63]

$$R \xrightarrow{-e^-} R^{\bullet+} \qquad (4)$$

Since an electron is removed from the propellane HOMOs (which generally describe the propellanic C−C bond, Figure 4),[62] oxidation lengthens the central C−C bond (compare Figures 1 and 3) and shortens the neighboring C−C bonds. This is consistent with the diminished antibonding character of the HOMO's coefficients between the bridgehead and the adjacent carbons. We note that the HOMOs of propellanes **1**−**5** are very different from the [1.1.1]propellane HOMO.[37] Since the latter is exceptional in being nonbonding or slightly antibonding, removal of an electron leads to very little change of the propellane bond.[64]

The *adiabatic* ionization potentials (designated as IP throughout the text, eq 4, Table 4) of **1**−**5** are lower than those of acyclic hydrocarbons (the experimental vertical IP of 2,2,3,3-tetramethylbutane is 225.8 kcal mol^{-1};[64] our computed IP is 211.8 kcal mol^{-1}).[65] Since **5** is less strained than $\mathbf{5H_2}$, the IP of **5** (182.8 kcal mol^{-1}) is larger than those for the other compounds (152.5−177.4 kcal mol^{-1}).

The lengthening of the central C−C bond upon ionization leads to strain relief. Hence, an inversely proportional relationship between strain energy and the IPs can be expected. Indeed, the order of increasing IP's is **3** < **4** < **1** < **2** < **5** which mirrors the relative strain energies evaluated above.

Protonation. Although protonation is inherently too exothermic to model the mechanisms of the reactions of electrophiles with hydrocarbons generally, the proton affinities (PA's) of **1**−**5** (eq 5) help understand some aspects of propellane chemistry. The trends in stability of **1**−**5** should be reflected well by the protonation energies (there are no protonation barriers due to the large exothermicity of eq 5).

$$R + H^+ \rightarrow RH^+ \qquad (5)$$

As expected (Table 4), **3** has the highest PA (252.8 kcal mol^{-1}), while the protonation of **5** is much less exothermic (198.8 kcal mol^{-1}). The differences in reaction enthalpies are larger for protonation (eq 5, $\Delta\Delta H$ **3** vs **5** = 54.0 kcal mol^{-1}) than for single electron oxidation (eq 4, $\Delta\Delta H$ **3** vs **5** = 30.3 kcal mol^{-1}) because the central bond is only "half broken" in the radical cations. As with the IP's, the PA ordering also is parallel to the relative stabilities and to the strain energies. The larger the strain of the propellane, the higher the PA; **3** has the highest proton affinity, **5** the lowest: **3** > **4** > **1** > **2** > **5**.

How do the PA's of **1**−**5** (Table 4, eq 5) compare to those of other hydrocarbons: saturated, olefinic, and cyclic? The most stable structure obtained on protonation of isobutane (PA = 169.9 kcal mol^{-1}) involves a weakly bound complex between the *tert*-butyl cation and dihydrogen (eq 6). In contrast, propellanes behave very much like tetraalkyl-substituted olefins and not like saturated hydrocarbons, which have much lower values. The PAs

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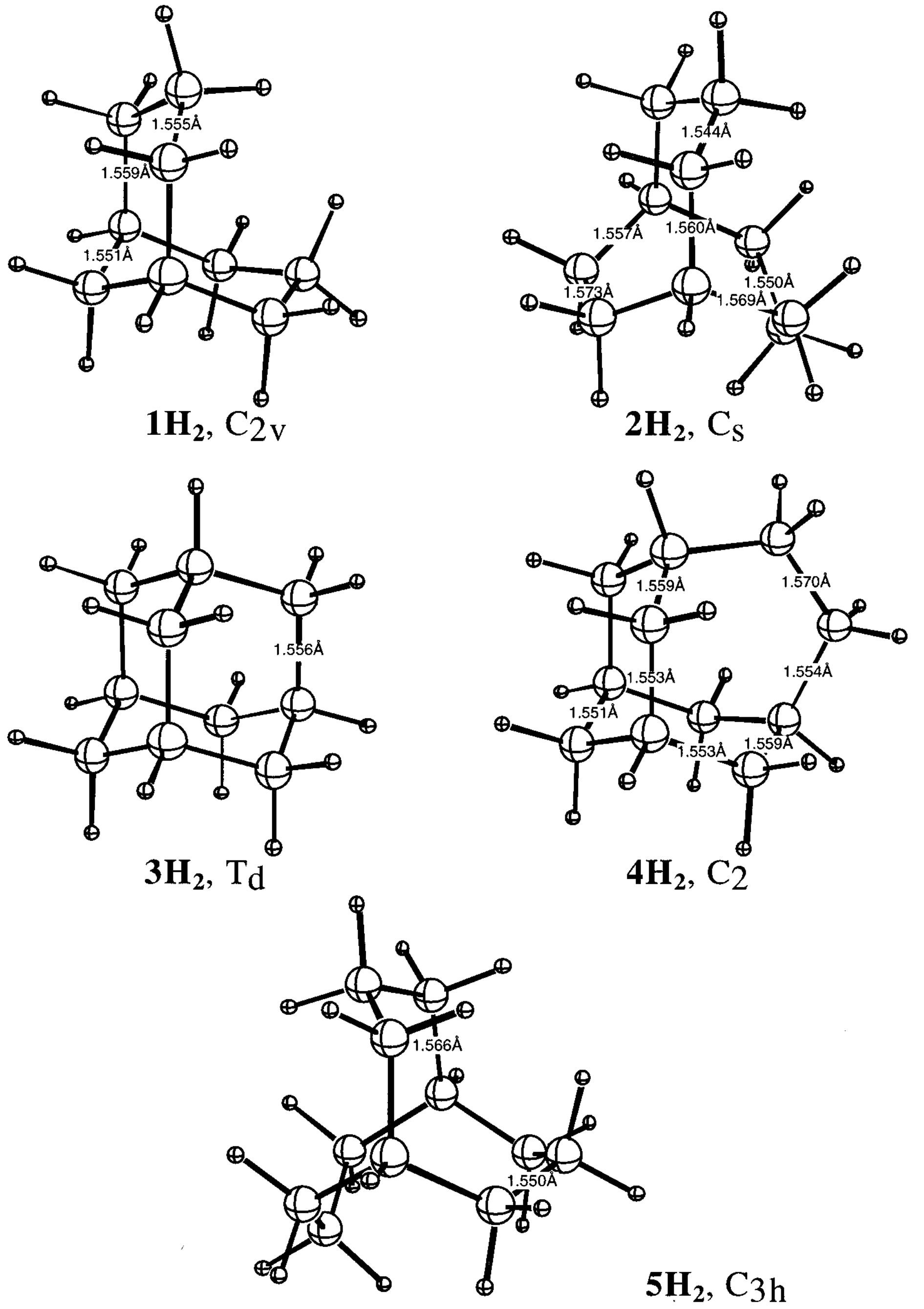
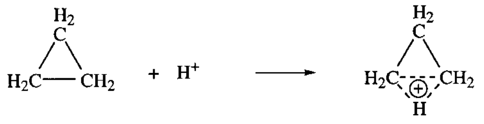


Figure 2. Optimized geometries of hydrocarbons $\mathbf{1H_2}$−$\mathbf{5H_2}$.

are 205.7 kcal mol^{-1} (we computed 202.8 kcal mol^{-1}) for 2,3-dimethylbut-2-ene (eq 7) and 188.4 kcal mol^{-1} (exptl: 179.8 kcal mol^{-1} [66]) for cyclopropane (eq 8).

$$(CH_3)_3CH + H^+ \longrightarrow (CH_3)_3C^{+}\cdots H_2 \qquad (6)$$

$$(CH_3)_2C{=}C(CH_3)_2 + H^+ \longrightarrow (CH_3)_2CH\text{-}C(CH_3)_2^+ \qquad (7)$$



(8)

Experimental data for the reactions of **1**−**4** with electrophiles and oxidizing agents are instructive. In general, propellanes with inverted geometries at the central carbons (such as **3**) are highly reactive toward electrophilic attack, even at low temperatures (e.g., $\Delta H = -43.5$ kcal mol^{-1} has been measured for the reaction of **3** with HOAc).[67] In contrast, **1** is less reactive,[68] and **2**, **4**, and **5** are recovered unchanged when heated (100 °C) with HOAc.

Propellanes **1**−**4** react with nitronium ion reagents (e.g., $NO_2^+BF_4^-$); nitro derivatives **6** are formed from **3** (Scheme 4). In **1**, **2**, and **4**, however, the propellane bond is oxidized, leading to products **7**−**9**, which do *not* contain a nitro group.

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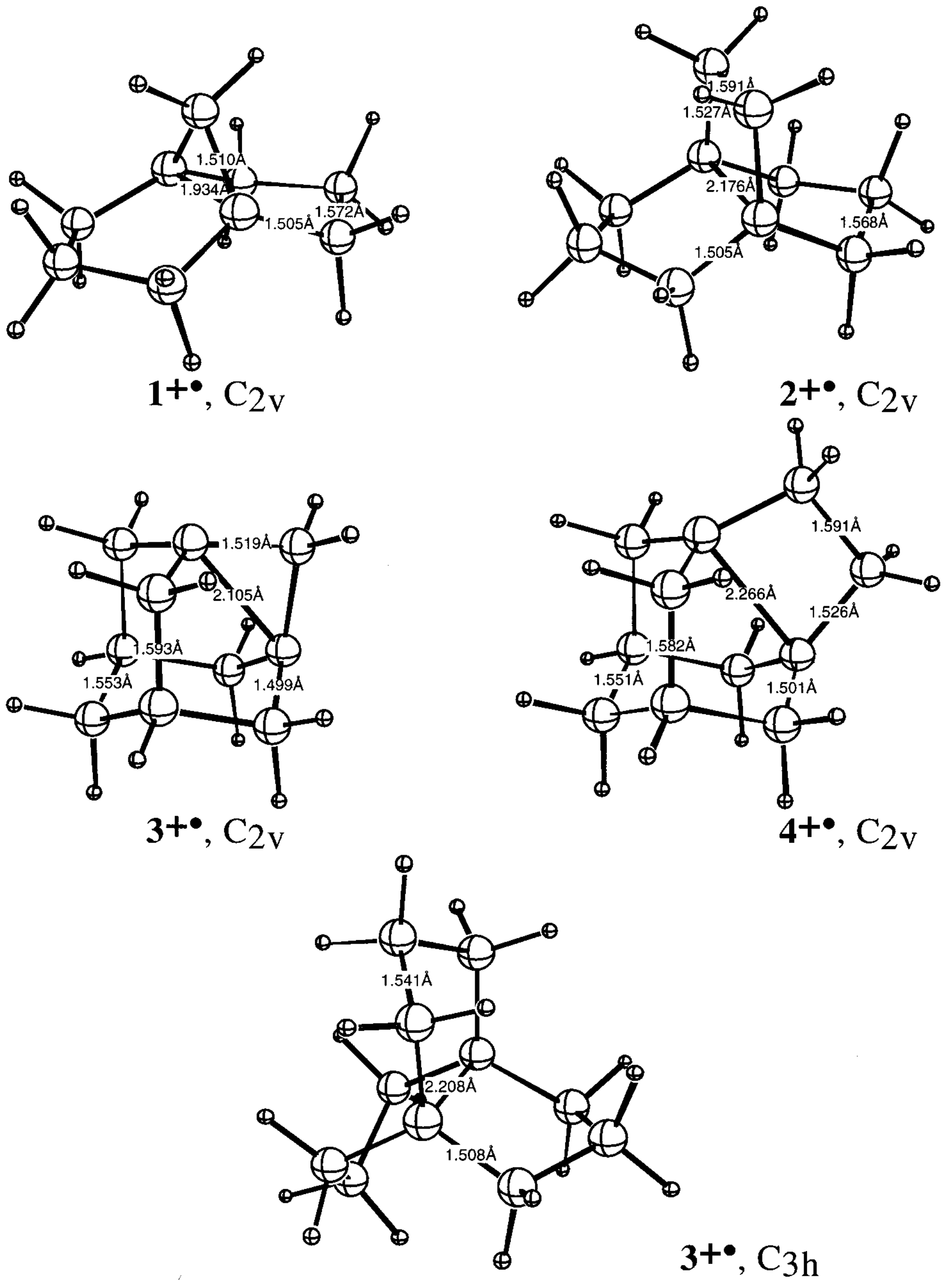

Figure 3. Optimized geometries of propellane radical cations $\mathbf{1}^{\bullet+}$–$\mathbf{5}^{\bullet+}$.

In analogy with recent experimental reports on the single electron oxidation of adamantane (either enzymatic[23] or photochemically with 1,2,4,5-benzenetetracarbonitrile[69,70]), which gives 1- and 2-substituted adamantyl derivatives, the first step in the reactions of propellanes **1**, **2**, and **4** with nitronium reagents is suggested to be the oxidation to the radical cation (eq 9). As a consequence of the large electron affinity (223.1 kcal mol^{-1}) of the nitronium ion, **1**-**5** should be oxidized easily by NO_2^+ (eq 9, Table 4). The resulting radical cations can be captured by nucleophiles (Y^-, e.g., Y = F, OAc, NO_3). A similar second oxidation step yields disubstituted isolable products.[29,30] This oxidative mechanism of propellane transformations under NO_2^+ treatment is supported experimentally by the electrochemical oxidation of **4** in acetonitrile to give **8** (Y=$NHCOCH_3$);[71] the same product was obtained with $NO_2^+BF_4^-$ in CH_3CN. For **3**, direct electrophilic attack by NO_2^+ must be faster than SET-oxidation.

$$R + NO_2^+ \rightarrow R^{\bullet+} + NO_2^{\bullet} \qquad (9)$$

The reactions outlined in Scheme 4 compare favorably with SET oxidations of activated arenes that may occur *via* a "nitrous acid catalyzed" reaction[24-27] as outlined in eqs 10–12 (eq 11 only conserves the stoichiometry but does not imply that "free" NO_2^+ is present in the reaction mixture; the active oxidizer is not yet clearly identified).[24-27] Hence, in the case of electrophiles with high oxidation potentials (like NO^+ and NO_2^+),[18] the activation

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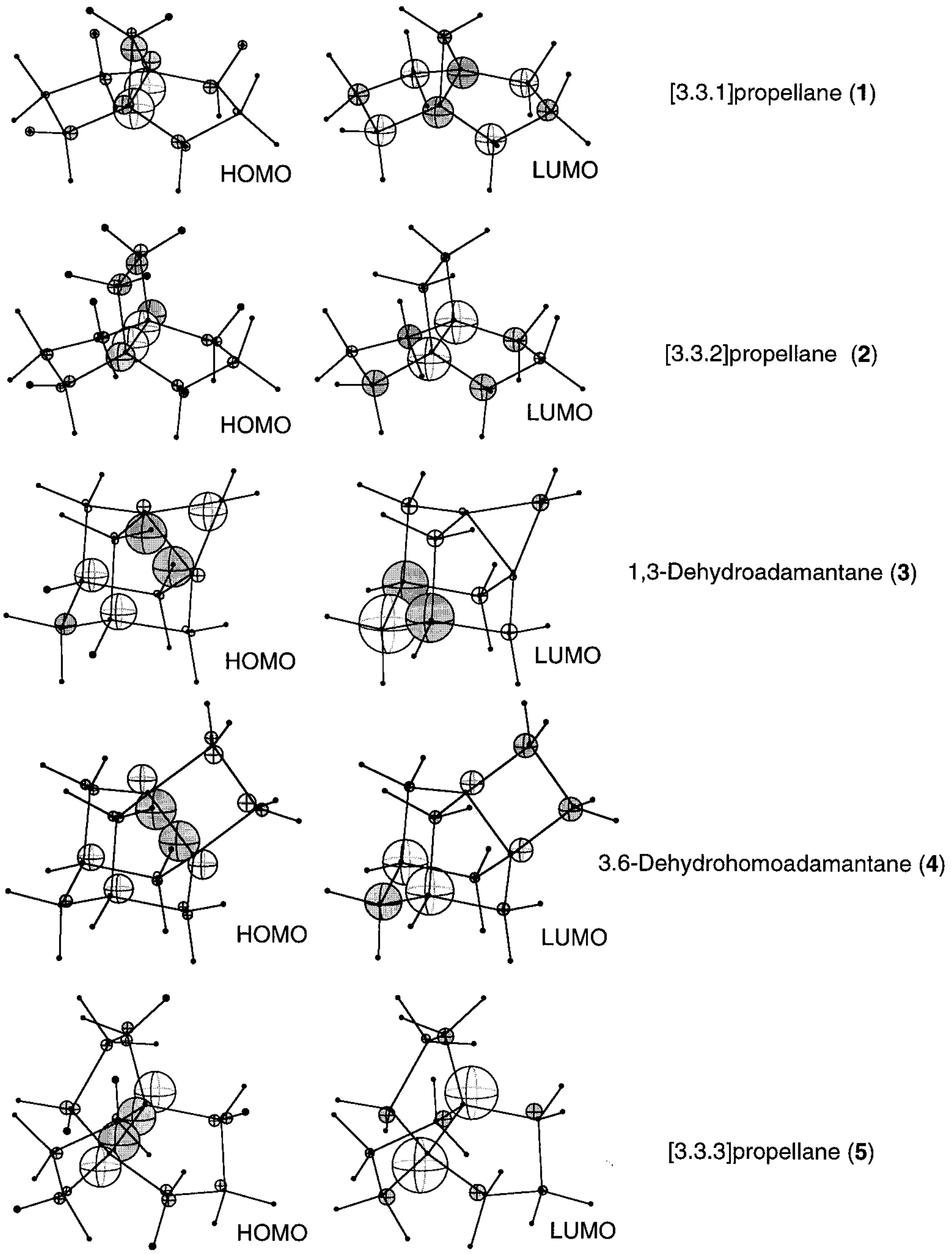

Figure 4. FMOs of propellanes **1**−**5**.

of aromatic as well as aliphatic hydrocarbons possibly may follow rather similar pathways.

$$\mathrm{ArH} + \mathrm{NO}^{+} \rightarrow \mathrm{ArH}^{\bullet+} + \mathrm{NO}^{\bullet} \qquad (10)$$

$$\mathrm{NO}^{\bullet} + \mathrm{NO_2}^{+} \rightarrow \mathrm{NO}^{+} + \mathrm{NO_2}^{\bullet} \qquad (11)$$

$$\mathrm{ArH}^{\bullet+} + \mathrm{NO_2}^{\bullet} \rightarrow \mathrm{ArNO_2} + \mathrm{H}^{+} \qquad (12)$$

Concluding Remarks

The strain in [3.3.*n*]propellanes **1** and **2** is increased by bridging the 4 and 4′ positions by a CH_2 group to give cage hydrocarbons **3** and **4**, respectively. These additional CH_2's also change the conformations (from double-boat in propellanes **1** and **2** to double-chair in **3** and **4**). While propellanes **1**−**4** are *more* strained than their hydrogenated counterparts $\mathbf{1H_2}$−$\mathbf{4H_2}$, dehydromanxane **5** is *less* strained than manxane $\mathbf{5H_2}$ and is far less reactive than **1** − **4**.

Highly exothermic protonation occurs at the bridgehead carbon *atom* directly, not necessarily at the region of highest electron density, i.e., the propellanic bond. Electrophilic attack of NO_2^+ directly at the bridgehead carbon is possible in highly strained propellanes such as **3**; nitro products form.

Compounds **1**−**5** have relatively low adiabatic ionization potentials; hence, they undergo SET easily. This is confirmed experimentally: the reactions of **1**, **2**, and **4** with $NO_2^+Y^-$ salts (e.g., $NO_2^+BF_4^-$) do not yield nitro compounds[29,30] but products resulting from nucleophilic addition of Y^- to cationic or radical cation intermediates. Recent studies on hydrocarbon activation by photoinduced SET or electrochemical oxidation in the presence

Scheme 4. Suggested Mechanisms for Some Propellanes Reacting with NO_2^+ via SET (1, 2, and 4) or via an Electrophilic Pathway (3)

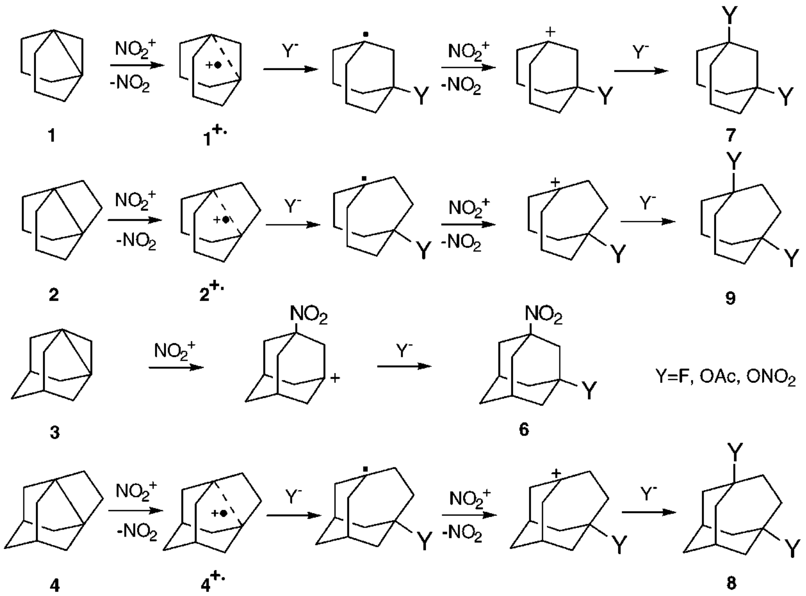

Table 3. Heats of Formation Obtained from BLYP/6-311+G//BLYP/6-31G* + ZPE (HF/6-31G*) Calculations and Strain Energies of Propellanes 1–5 and Their Hydrogenated Products $1H_2$-$5H_2$ (All Energies in kcal mol^{-1})**

R	$\Delta_fH°_{298}$[a] BLYP	$\Delta_fH°_{298}$ exptl[b]	strain energy[c] BLYP
1	2.3		36.1
2	−4.6		34.0
3	21.8		55.5[d]
4	2.6		41.1
5	−24.4		19.0
cyclopropane	12.0	12.7	27.2
cyclobutane	6.1	6.4	26.4
cyclopentane	−16.1	−18.4	9.3
$1H_2$	−27.6	−29.8	12.5
$2H_2$	−20.9	−24.9	23.7
$3H_2$	−32.1	−32.9	6.3
$4H_2$	−27.8		15.3
$5H_2$	−17.8	−21.3	30.3

[a] Calculated via eq 3 $\Delta_{rxn}H°_{298}$'s (see Table 2) and experimental $\Delta_fH°_{298}$[56] of C_2H_6, C_3H_8, $HC(CH_3)_3$, and $C(CH_3)_4$. [b] From ref 56. [c] Calculated *via* eq 3. [d] Experimental value (64 kcal mol^{-1}) estimated via a calorimetric determination of the reaction energy of **3** with acetic acid.[66]

of nucleophiles support this assumption.[70,72–74] Thus, both SET and direct carbon attack may be important pathways for hydrocarbon reactions with oxidizing electrophiles, especially for strained species.[69] Attack at the C–H or C–C bonds need not be involved.

Table 4. Reaction Energies of Oxidative and Electrophilic Activation of Propellanes 1–5 at Two DFT Levels (All Energies in kcal mol^{-1})

R	BLYP/6-31G*	BLYP/6-311+G**
	$R \xrightarrow{-e^-} R^{\bullet+}$ (4)	
1	168.3	173.2
2	172.4	177.4
3	149.2	152.5
4	164.6	169.4
5	177.9	182.8
	$R + H^+ \rightarrow RH^+$ (5)	
1	−221.0	−217.4
2	−214.5	−211.0
3	−254.3	−252.8
4	−235.2	−231.5
5	−202.2	−198.8
	$R + NO_2^+ \rightarrow R^{\bullet+} + NO_2^{\bullet}$ (9)	
1	−49.9	−50.0
2	−45.8	−45.7
3	−69.1	−70.7
4	−53.6	−53.8
5	−40.3	−40.3

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie (Liebig-fellowship to P.R.S.), the Deutsche Forschungsgemeinschaft, and Fundamental Research Foundation of the Ukraine. A.A.F. is grateful to the Deutscher Akademischer Austauschdienst and the Alexander von Humboldt Foundation (fellowship) for research support in Erlangen. P.R.S. thanks Prof. A. de Meijere for his support.

Supporting Information Available: Cartesian coordinates (in Ångstrom) for all computed species (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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