Common Radical Cation Intermediates in Cage Hydrocarbon Activations

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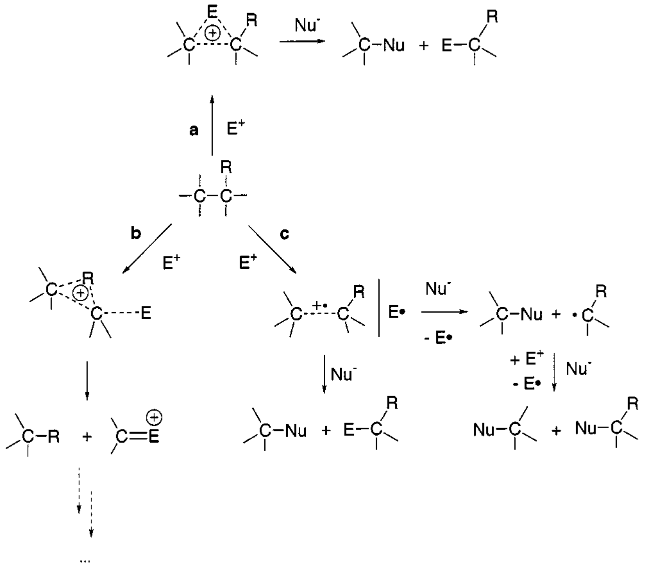
The oxidation of 3,6-dehydrohomoadamantane (**1**) was achieved under chemical ($NO^+BF_4^-$/EtOAc, NO^+OAc^-/Ac_2O, and $NO^+BF_4^-$/CH_3CN), photochemical (photoexcited 1,2,4,5-tetracyanobenzene), and electrochemical (Pt anode, CH_3CN, NH_4BF_4) conditions. Supporting ab initio [density functional theory (BLYP) and Møller–Plesset perturbation theory (MP2)] computations utilizing standard basis sets, 6–31G* (optimizations) and 6–311+G* (single-point energy evaluations), agree with the experimental results implicating the involvement of the same radical cation intermediates in the activation processes. Isomeric radical cations formed from different precursors can equilibrate with low barriers (2.0–11.7 kcal mol^{-1}) and lead to common products. The computed and experimental adiabatic ionization potential of adamantane shows that activation with $NO^+BF_4^-$ is also likely to occur through the adamantyl radical cation. Hence, the bonds need not be attacked directly by the electrophile in the C–H or C–C activation of alkanes with relatively low ionization potentials.

Introduction

Electrophilic attack at C−H or C−C single bonds is believed to proceed through 3c−2e (3-center−2-electron) species (path **a**, Scheme 1).[1−5] However, it has been shown recently[6−12] that reactive species with moderate to low electrophilicity (e.g., NO^+) may attack the carbon or hydrogen atoms directly, leading to C−C or C−H bond cleavage (path **b**, Scheme 1). A third possible pathway (**c**) involves the oxidation of the hydrocarbon; the literature is extensive.[13−22] H. D. Roth has been a leading investigator.[23−36] Indeed, we present evidence that single-electron transfer (SET),[16][17] involving oxidizing electrophiles, like nitrosonium reagents and photoexcited aromatic compounds [1,2,4,5-tetracyanobenzene (TCB)] or anodic oxidation, is the major C−C activation pathway (**c**, Scheme 1) for strained propellanic systems. These substrates are ideal models because the approach to the central C−C bond is precluded sterically, and the course of the reaction must involve attack at the carbon atoms instead.

We reported recently that the reactions of the nitronium cation ($NO_2{}^+$) at the bridgehead carbon atoms in highly strained propellanes give nitro derivatives.[37] Stable large-ring propellanes afford products of double nucleophilic addition to the consecutively formed radical cations and cation intermediates.[38] Hence, these reactions need not involve direct attack of the electrophile on σ bonds as has been suggested previously for $NO_2{}^+$ reactions with alkanes.[39] Since SET oxidation seems to be the most important pathway for propellanic σ_{C-C}-bond interactions with $NO_2{}^+$, the same reactivity may be expected for nitrosonium reagents (NO^+) which are effective in SET oxidations of organic sulfides,[40−44] urazines,[45] aromatic compounds,[46−48] and cyclopropanes.[49] NO^+-containing reagents are also reactive towards some saturated hydrocarbons, such as adamantane.[50] Considering the low electrophilicity of NO^+, these transformations are hard to rationalize by traditional alkane electrophilic substitution mechanisms.[1−5]



Scheme 1

We investigated the reactions of 3,6-dehydrohomoadamantane (**1**) with $NO^+BF_4{}^-$, photoexcited TCB, and under anodic oxidation conditions in order to achieve a more

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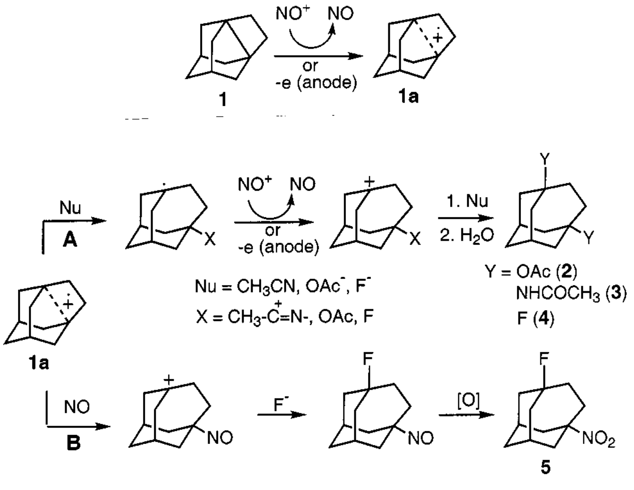
comprehensive understanding of SET pathways in the oxidation of hydrocarbons. We chose **1** since it is relatively stable in electrophilic media; e.g., **1** does not react with strong Brønsted acids. The present investigation is complemented by ab initio computations on pertinent radical cations and their rearrangement pathways.

Results and Discussion

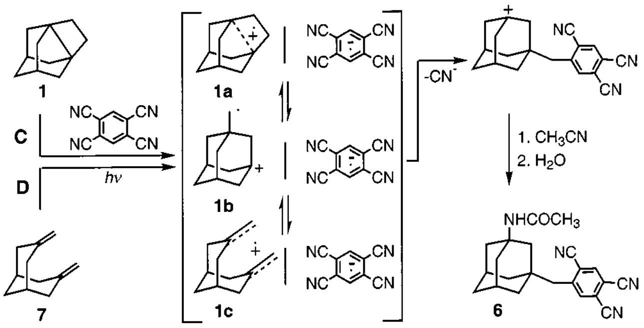
The reactions and chemical behavior of **1** with nitrosonium reagents were studied both in low-nucleophilic (EtOAc and MeOAc) and in more nucleophilic (CH_3CN and Ac_2O) solvents (Scheme 2). As observed for nitronium ion oxidations,[38][51] double nucleophilic addition to **1** resulting in diacetate **2** (NO^+OAc^- in acetic anhydride) and diacetamide **3** ($NO^+BF_4^-$ in acetonitrile) occurs with high selectivity. The reactions of **1** with $NO^+BF_4^-$ in the less nucleophilic EtOAc only gave difluoride **4** and nitrofluoride **5** in 57 and 25% preparative yields, respectively. The unrearranged structures of **2−5** indicate sequential formation of bridgehead carbocations and point to a stepwise oxidative mechanism. As the coefficients of the HOMO of **1** are located mainly on the central C−C bond, removal of an electron leads to bond elongation, from 1.60 to 2.27 Å, upon ionization.[52] The resulting radical cation **1a** either can trap a nucleophile (Scheme 2, path **A**) or a radical (e.g., NO, Scheme 2, path **B**). Two consecutive oxidation and nucleophilic addition steps lead to **2** (Nu = $^-$OAc) and to **3** (Nu = CH_3CN). In a solvent of lower nucleophilicity (EtOAc), radical cation **1a** also may react sequentially with F^- (from BF_4^-) along path **A** to give difluoride **4** (Nu = F^-). Radical-pair collapse of **1a** with NO (path **B**), followed by nucleophilic addition of F^-, and oxidation of the nitroso intermediate finally yields nitrofluoride **5**. The simultaneous formation of **4** and **5**, as well as their constant product ratio (independent of the $NO^+BF_4^-$ concentration), are strong arguments for a common intermediate (**1a**). Electrophilic attack of NO^+ on **1** does not explain the formation of **2−4**.



Scheme 2

We also examined independent ways to generate **1a**, namely electrochemical oxidation and photoinduced electron transfer (PET). Anodic oxidation (2.5 V, Pt electrodes, 20−30 mA, 2 F mol^{-1}) of **1** in the presence of NH_4BF_4 as the supporting electrolyte yielded diacetate **2** (in AcOH/Ac_2O, 1:1) and diacetamide **3** (in CH_3CN) with 65 and 87% preparative yields, respectively (Scheme 2, path **A**).

PET oxidation of **1** in CH_3CN (Scheme 3, path **C**) is induced by short-lived photoexcited TCB.[53−60] Since a CN group has to be cleaved from TCB initially in order to react with the cation radical, **1a** can rearrange to the methyleneadamantyl cation **1b**; product **6** forms after nucleophilic attack. Similarly, the PET oxidation of 3,7-dimethylenebicyclo[3.3.1]nonane (**7**)[61] yields **6** (Scheme 3, path **D**) as the sole product, strongly suggesting the same radical cations **1c** → **1b** as the critical intermediates.

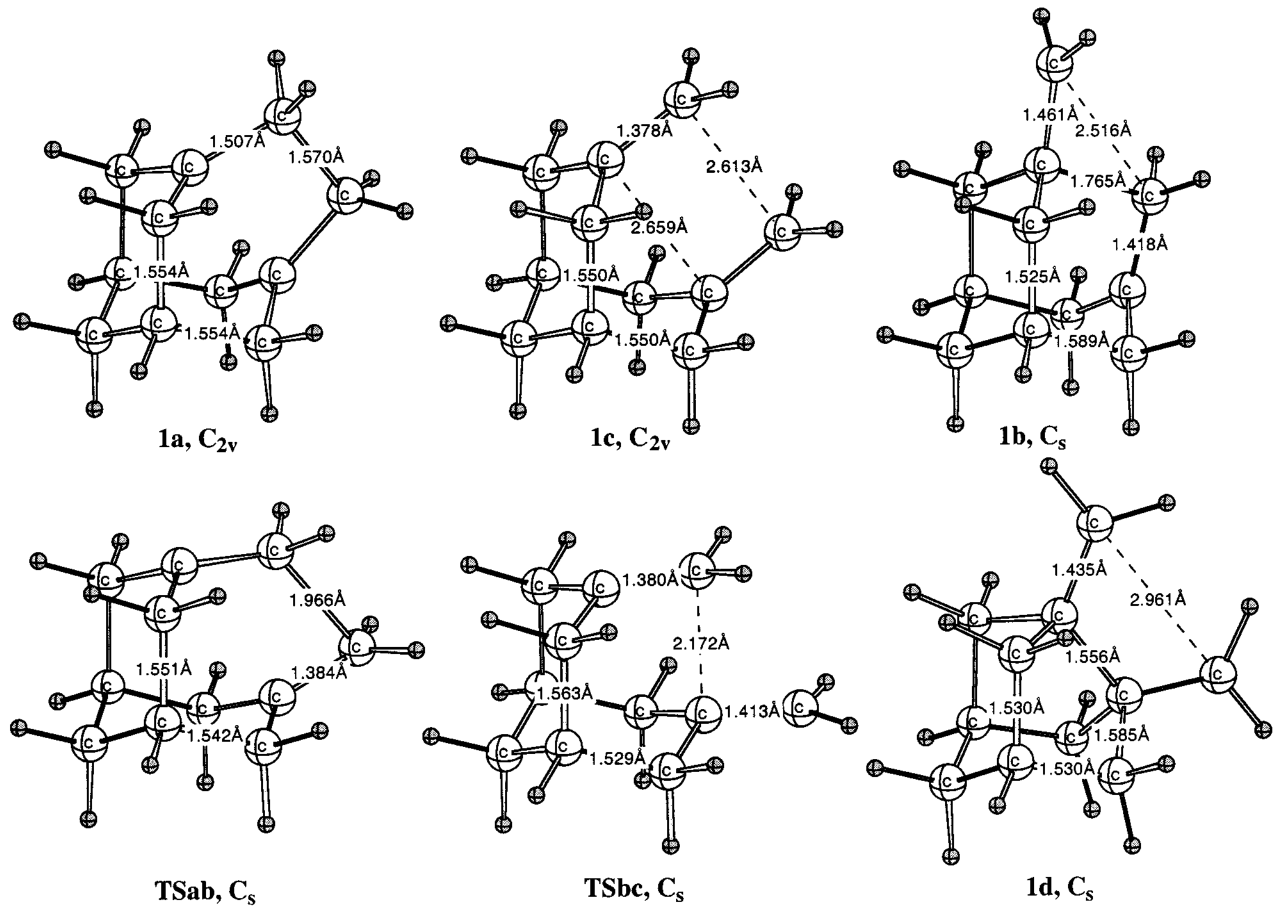


Scheme 3

Our computed potential energy surface (PES) for the **1a−1c** (Table 1) interconversions is rather flat. Three minima **1a−1c** and two transition structures **TSab** and **TSbc** were located at MP2 (Figure 1; BLYP optimizations gave only **1a** and **1b**, see below). Transition structure **TSab** separates minimum **1a** from the 1-methyleneadamant-3-yl radical cation minimum **1b** (C_s); the barrier is 11.7 kcal mol^{-1} (MP2) from **1a**. **TSbc** is involved (2.0 kcal mol^{-1} barrier) in the C−C bond fragmentation in **1b** leading to the structurally related 3,7-dimethylenebicyclo[3.3.1]nonane radical cation **1c** (C_{2v}). Optimization attempts of **1b** at BLYP/6−31G* led to **1c** which is 7.6 kcal mol^{-1} more stable than **1a**. In contrast, **1c** is 3.6 kcal mol^{-1} less stable than **1a** at MP2. The energy difference between **1b** and **1c** is negligible (0.2 kcal mol^{-1} at MP2); either or both of these species could be involved in the radical recombination step giving **6**.

SET oxidation of **1** with the nitrosonium ion is highly exothermic: the electron affinity of NO^+ (experimental: 213.5[62] and 213.6 kcal mol^{-1};[63] BLYP: 221.1 kcal mol^{-1}; MP2: 198.7 kcal mol^{-1}) is much higher than the endothermicity for radical cation **1a** formation from propellane **1** by SET (+164.6 kcal mol^{-1}).[52] These results support the formation of **1a−1c** generated from **1** by SET oxidation. Ring opening of **1** with C4−C5 bond cleavage is unfavorable energetically due to the strain of the noradamantane structure **1d** (Figure 1). The latter is 41.9 kcal mol^{-1} less stable than **1a** at BLYP and 50.1 kcal mol^{-1} at MP2.

It is very likely that SET not only is a highly important pathway for chemical oxidations of strained hydrocarbons (e.g., propellanes[64−68]) but also is a viable route for the



1a, C_{2v} **1c, C_{2v}** **1b, C_s**

TSab, C_s **TSbc, C_s** **1d, C_s**

Figure 1. UMP2/6−31G*-optimized geometries of $C_{11}H_{16}$ radical cations

activation of other alkanes with relatively low oxidation potentials. Examples are the reactions of adamantane (**8**) with $NO_2^+BF_4^-$ and with $NO^+BF_4^-$ which were viewed by Olah et al. as hydride abstraction processes, despite the rather small primary kinetic k_H/k_D isotope effects (1.2−1.3).[50] Olah et al. excluded the SET pathway on the basis that "*Single electron transfer (SET) nitration of adamantane by NO_2^+ is unlikely as the first ionization potential*

Table 1. Absolute (in hartree) and relative (in kcal mol^{-1}) energies at BLYP and MP2 levels of theory; zero-point vibrational energies (ZPVEs; in kcal mol^{-1}) are included in relative energies; in parentheses: number of imaginary frequencies (NIMAG)

	Absolute energy		ZPVE[a]	Relative energy		
Structure and point group	6−31G*	6−311+G*//6−31G*		6−31G*	6−311+G*//6−31G*	
$C_{11}H_{16}$ radical cations						
1a, C_{2v}	−428.24533	−428.28615	147.6 (0)	0.0	0.0	BLYP
	−426.99130	−427.14335	149.5 (0)	0.0	0.0	MP2
1b, C_s	–	–	–	–	–	BLYP[b]
	−426.98329	−427.13573	148.1 (0)	+3.6	+3.4	MP2
1c, C_{2v}	−428.25528	−428.29542	145.8 (0)	−8.0	−7.6	BLYP
	−426.98512	−427.13750	149.4 (0)	+3.7	+3.6	MP2
TSab, C_s	–	–	–	–	–	BLYP[b]
	−426.97017	−427.12324	148.6 (1)	+12.3	+11.7	MP2
TSbc, C_s	–	–	–	–	–	BLYP[b]
	−426.98004	−427.13227	148.0 (1)	+5.6	+5.4	MP2
$C_{10}H_{16}$						
8, T_d	−390.46992	−390.55868	146.6 (0)	0.0	0.0	BLYP
	−389.33497	−389.48032	–	0.0	0.0	MP2
8$^+$, C_{3v}	−390.16102	−390.24058	141.2 (0)	+188.4	+194.2	BLYP
	−389.00944	−389.14825	–	+198.9	+203.0	MP2

[a] BLYP and MP2 frequencies scaled by factors of 0.98 and 0.95, respectively. − [b] Structure not located at this level; all optimization attempts converged to **1a** or **1c**.

of adamantane to Ad$^+$ is too high."[50] However, since the experimental adiabatic ionization potential of adamantane [212.6[69]−213.3[70][71] kcal mol^{-1}; computed: 194.2 (BLYP) and 203.0 kcal mol^{-1} (MP2); for the adamantyl radical cation structure **8**$^{\bullet+}$ see Figure 2] is low enough for an SET pathway by oxidation with NO$^+$ and even more so with NO$_2$$^+$ (EA: experimental: 224.8 kcal mol^{-1};[63] BLYP: 221.4 kcal mol^{-1}; MP2: 203.1 kcal mol^{-1}) to be a viable alternative to electrophilic C−H attack. This conclusion also is supported by the formation of 1-fluoroadamantane and 1-fluoro-3-hydroxyadamantane, both with NO$^+$BF$_4$$^-$ and with NO$_2$$^+BF_4$$^-$.[50] The small primary kinetic isotope effect observed in Olah's nitration and nitrosation experiments is consistent with the C1−H bond elongation (by 0.03−0.04 Å) found in the computed adamantyl radical cation structure (**8**$^{\bullet+}$, Figure 2).

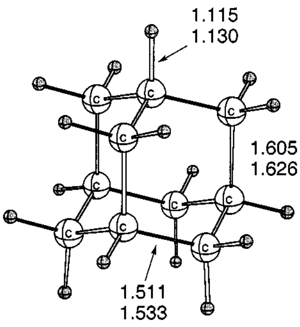


Figure 2. UMP2/6−31G*- (first line) and BLYP/6−31G*- (second line) -optimized geometry of the adamantane radical cation (**8**$^{\bullet+}$); bond lengths in Å

The electro- and photochemical behavior of adamantane (**8**) also is rather similar to that of the propellanes.[52] Anodic oxidation yields the radical cation which gives the highly stabilized 1-adamantyl cation after a second oxidation step. Subsequently, this cation is trapped in acetonitrile in a Ritter-type reaction to form 1-adamantyl acetamide;[72−74] the same product forms in the reaction of **8** with NO$_2$$^+BF_4$$^-$ in CH$_3$CN. Oxidation of adamantane with photoexcited 1,2,4,5-tetracyanobenzene also gives rise to 5-(1-adamantyl)benzene-1,2,4-tricarbonitrile.[53] Hence, adamantane follows rather similar oxidation pathways, as observed for the propellanes.

Conclusions

Our results show that the activation of propellane σ_{C-C} bonds with strong oxidizing electrophiles occurs by a sequence of single-electron transfer steps. A common radical cation intermediate is implicated in the chemical, electrochemical, and photochemical oxidation of **1**. These findings are supported by ab initio computations showing that isomeric radical cations can equilibrate with low barriers.

Analogous radical cation pathways may be followed during single-electron oxidation of larger alkanes with relatively low ionization potentials. Thus, experimental and computational data indicate that such mechanisms can be involved in the reactions of adamantane with oxidizing electrophiles.

Experimental Section

Oxidation of 1 with Nitrosonium Reagents: Under nitrogen, 296 mg (2 mmol) of **1** (in 5 mL of CH$_2$Cl$_2$) was added to 585 mg (5 mmol) of NO$^+$BF$_4$$^-$ in 10 mL of Ac$_2$O, MeCN, or EtOAc under stirring at 0°C. After 5 h, the reaction mixture was quenched with 100 mL of water; organic solvents were removed in vacuo. The aqueous part was extracted with CH$_2$Cl$_2$ (3 × 20 mL). The organic solution was concentrated in vacuo, the residue was separated by column chromatography on silica gel [eluent: CHCl$_3$/EtOAc, 1:10 for **2** (55%); Et$_2$O/CH$_3$OH, 10:1 for **3** (75%); *n*C$_6$H$_{14}$ for **4** (57%); and *n*C$_6$H$_{14}$/Et$_2$O, 5:2 for **5** (25%)]. Compounds **2−5** are identical to the products of the oxidation of **1** with nitronium reagents.[37]

Photooxidation of 1 with TCB: A solution of **1** (250 mg) and 150 mg of TCB in 90 mL of acetonitrile was irradiated under argon with a 150-W lamp (maximum emission at 350 nm) for 5 h. The reaction mixture was diluted with 5 mL of water, and solvents were removed in vacuo. Chromatographic separation on silica gel gave 105 mg of TCB (*n*C$_6$H$_{12}$/EtOAc, 1:1) and 47 mg (54%) of **6** (EtOAc/CH$_3$OH, 20:1; R_f = 0.55) as a colorless liquid. − ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.33 (2 H, m), 1.70−2.30 (10 H, m), 2.05 (3 H, s), 2,47 (2 H, m), 2.85 (2 H, s), 5.20 (1 H, m), 7.72 (1 H, s), 8.12 (1 H, s). − ^{13}C NMR (125.8 MHz, CDCl$_3$): δ = 24.6, 29.2, 35.2, 37.8, 40.6, 40.8, 45.3, 48.1, 52.4, 113.6, 114.2, 114.5, 115.4, 118.4, 119.2, 136.4, 136.9, 148.1, 169.6. − IR (CHCl$_3$, cm^{-1}): $\tilde{\nu}$ = 3420 (N−H), 2850−2990 (C−H), 2230 (C≡N), 1660, 1500 (C=O), 1590−1650 (C=C). − C$_{22}$H$_{22}$N$_4$O: calcd. C 73.72, H 6.19, N 15.63; found C 73.55, H 6.40, N 15.39.

Photooxidation of 7 with TCB: From 250 mg of **7**, according to the described photooxidation of **1**, 60 mg (53%) of **6** was obtained; NMR data are identical to those of **6**; 95 mg of TCB was recovered.

Computational Methods: All structures were optimized at unrestricted HF/6−31G* (not reported), BLYP/6−31G*, and MP2/6−31G* levels of theory as implemented in Gaussian 94.[75] Single-point energies were evaluated utilizing the more flexible 6−311+G* basis set. As electron correlation is important for spin/charge delocalized systems,[76−81] details of the results differ from level to level but are nevertheless quite illustrative. The choice of the theoretical level is not straightforward as Hartree−Fock-based methods like MP2 generally describe carbocations rather well but are prone to spin contamination in case of radical cations. We found expectation values for the spin operator $<S^2>$ of 0.76−0.85 (expected: 0.750) at UMP2. Density functional methods, on the other hand, show much less spin contamination [$<S^2>$ = 0.750−0.751].[82][83] Despite our good experience with DFT for radical cations[52] or even multi-reference biradicals,[84] both MP2 and BLYP results are presented. Standard notation is used: "//" means "energy computed at the // optimized geometry".[85] Energies refer to the BLYP/6−311+G*//BLYP/6−31G* level of theory, unless noted otherwise.

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