

# The Electrophilic Reactions of Aliphatic Hydrocarbons: Substitution and Cleavage of Ethane by NO<sup>+</sup>

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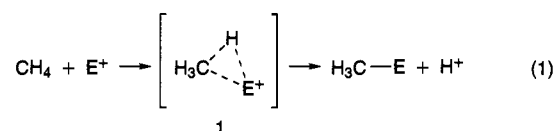
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**Abstract:** The reactions of ethane with the nitrosonium cation, a model electrophile, were investigated computationally at the Hartree–Fock as well as the correlated MP2(frozen core) and CISD levels of theory. In agreement with the experimentally observed electrophilic reactions of alkanes, the substitution (yielding protonated nitrosoethane) and C–C bond cleavage pathways (leading to the loss of methane) are competitive energetically. Standard basis sets (6-31G(d), 6-31G(dp), and 6-31+G(dp)) were used for geometry optimizations and triple- $\zeta$  plus polarization (TZP, and with the inclusion of diffuse functions: TZP+) for single point energies on the MP2/6-31G(dp) optimized structures. Vibrational frequencies were computed through the MP2/6-31G(d) level. A complex of ethane and the nitrosonium cation forms first [the complexation energy is 4.0 kcal mol<sup>-1</sup> at CISD+Q/TZP+//MP2/6-31G(dp) + ZPVE(MP2/6-31(d))]. Although several plausible pathways leading to nitrosomethane, to nitrosoethane, to loss of hydrogen after addition of NO<sup>+</sup> to ethane, as well as insertion of the electrophile into the C–C or a C–H bond of ethane were examined, only two viable pathways were located. These lead to (a) the nitrosomethylene cation and methane through C–C bond cleavage and to (b) protonated nitrosoethane via abstraction of a hydride followed by addition of HNO to the ethyl cation. The computed activation energies of the two reactions are similar (33.5 and 31.1 kcal mol<sup>-1</sup>, respectively). We found no evidence for a mechanism involving direct insertion of the electrophile into a C–H or a C–C bond of ethane. Computations of the vibrational frequencies for the H/D isotopically substituted complex and the transition structures yield relatively small primary H/D isotope effects for both mechanisms (2.6 and 2.9, respectively), due to nonlinearity of the transition structures. These results, like those we have reported earlier for methane, do not support the generally discussed mechanisms for the electrophilic substitution of alkanes. Our evidence suggests that some electrophiles may attack carbon directly, rather than C–H or C–C bonds, and that three-center transition structures with the electrophile need not be involved.

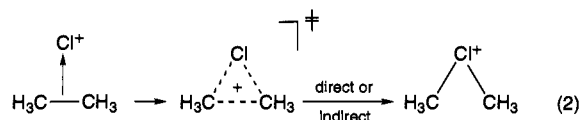
## Introduction

Aliphatic electrophilic substitution reactions, explored and developed extensively by Olah and his associates,<sup>2,3</sup> afford alternatives to nonspecific radical methods for derivatizing alkanes. The conversion of lower hydrocarbons to higher molecular weight alkanes and to other derivatives is important, since low boiling components in natural raw materials can account for major fractions. For example, both methane and adamantane can be nitrated (using, for instance, NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>/HSO<sub>3</sub>F) to give nitromethane<sup>3a</sup> and 1-nitroadamantane,<sup>3b</sup> respectively. Mechanisms involving three-center two-electron

(3c-2e) C, H, E<sup>+</sup> (the electrophile) bonding have been proposed (eq 1).



Surprisingly, the electrophilic substitution reactions of ethane (the subject of the present paper) were found to give methyl as well as ethyl products.<sup>3</sup> Thus, the reaction of Cl<sub>2</sub> and ethane, catalyzed with SbF<sub>5</sub> in SO<sub>2</sub>ClF solution at room temperature, gave CH<sub>3</sub>Cl and C<sub>2</sub>H<sub>5</sub>Cl in a 7:3 ratio.<sup>3b</sup> Likewise, a 2.9:1 ratio of CH<sub>3</sub>NO<sub>2</sub> and C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub> was obtained from ethane with NO<sub>2</sub><sup>+</sup>PF<sub>6</sub><sup>-</sup>.<sup>3a</sup> These C–C cleavage reactions, which are generally observed for higher alkanes as well, were formulated as proceeding through E<sup>+</sup> attack on the C–C single bond (eq 2).



Electrophilic chlorination of ethane at lower temperatures gave (CH<sub>3</sub>)<sub>2</sub>Cl<sup>+</sup> as a directly observable product, but such chloronium ions also may form via secondary reactions.

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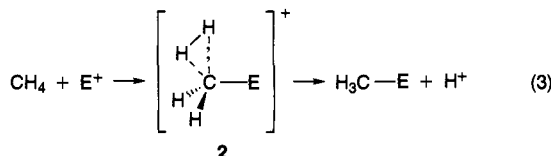
(1) (a) University of Georgia. (b) Universität Erlangen-Nürnberg.

(2) For reviews see: (a) Olah, G. A.; Farooq, O.; Prakash, G. K. S. In Hill, C. L., Ed.; *Activation and Functionalization of Alkanes*; John Wiley: New York, 1989; Chapter II, p 27 and references cited therein. (b) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987. (c) Olah, G. A.; Prakash, G. K. S.; Summer, J. *Superacids*; Wiley-Interscience: New York, 1985.

(3) (a) Olah, G. A.; Lin, H. C. *J. Am. Chem. Soc.* **1971**, *93*, 1259. Olah, G. A.; Friedman, M. *J. Am. Chem. Soc.* **1966**, *88*, 5330. Dunbar, R. C.; Shen, J.; Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 6864. Olah, G. A.; Schilling, P. *J. Am. Chem. Soc.* **1973**, *95*, 7680. (b) Olah, G. A.; Ramaiah, P.; Rao, C. B.; Sandford, G.; Golam, R.; Trivedi, N. J.; Olah, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 7246. Note that NO<sup>+</sup>BF<sub>4</sub><sup>-</sup> also reacts with adamantane. The initial product, 1-nitroadamantane, is transformed to 1-nitroadamantane by a series of steps.

Olah's mechanistic suggestions (eqs 1 and 2)<sup>2,3</sup> were based on the well-established protonation reactions as well as the reactions of the methyl and other alkyl cations with alkanes.<sup>4</sup> Thus, ethane and propane are known to be protonated both on the C–H and the C–C bonds. Nevertheless, the proton or alkyl cations are exceptionally strong electrophiles, and their behavior may not be representative for, e.g., NO<sub>2</sub><sup>+</sup> and more highly stabilized electrophiles.

Indeed, our recent investigation of the reaction of methane with the nitronium ion (NO<sup>+</sup>)<sup>5</sup> suggested that the mechanisms for the reactions of the proton (H<sup>+</sup>) and carbenium ions (R<sup>+</sup>) as electrophiles<sup>2–5</sup> were not applicable in cases involving these more stable electrophiles. Our computations suggested that carbon rather than hydrogen is attacked by NO<sup>+</sup> and similar electrophiles (eq 3).<sup>5</sup> A 3c-2e intermediate **2** is formed, but



this does not involve the electrophile, E<sup>+</sup>, which is fully bonded to the carbon. The distortion of methane is concomitant with NO<sup>+</sup> attack; the electrophile binds to the developing lone pair on carbon. Part of the energy required for the methane distortion is recovered from the new bonding interaction.

Methane certainly is an exceptional hydrocarbon and may not be suitable as a model for other alkanes. We have stressed recently that the methonium ion (CH<sub>5</sub><sup>+</sup>) is unique rather than being *the* nonclassical carbonium ion prototype.<sup>6</sup> Thus, the reactions of higher hydrocarbons with electrophiles may well be different from those of methane.

We now report on our investigation of the reactions of ethane with NO<sup>+</sup>. This serves as a model for the electrophilic substitution reactions of higher alkanes with relatively stable electrophiles. A number of reaction pathways are plausible (Scheme 1). Their relevance depends on the thermodynamics and on the activation barriers leading to various products. We compare our results to the reactions of methane + NO<sup>+</sup>, and to the reactions of ethane with H<sup>+</sup>.

## Methods

The *ab initio* program GAUSSIAN 92,<sup>7a</sup> running on an Indigo Iris XS-24 workstation, was employed to fully optimize geometries within the designated symmetry constraints at the restricted Hartree–Fock

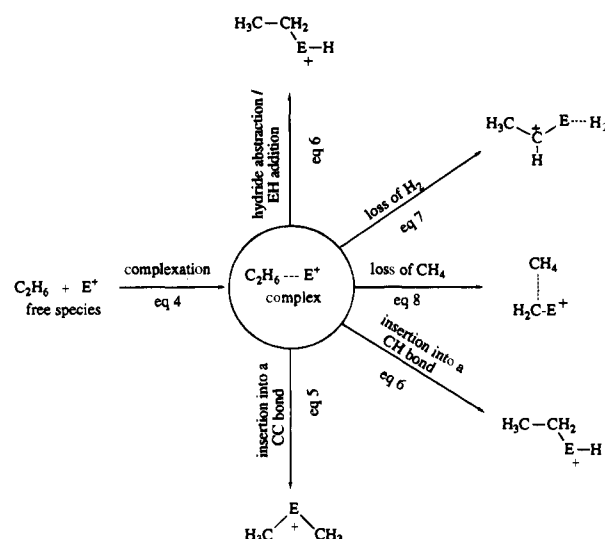
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## Scheme 1



(HF)<sup>8</sup> level using gradient optimization techniques<sup>8</sup> and standard basis sets [6-31G(d), 6-31G(dp), 6-31+G(dp), TZP, and TZP+]. Optimizations explicitly including electron correlation were carried out at the second-order Møller–Plesset level (MP2)<sup>8</sup> keeping the core electrons frozen (MP2-fc). CISD/TZP single-point energy calculations (using the PSI<sup>7b</sup> program on IBM RS 6000 workstations) were carried out on all MP2/6-31G(dp) optimized structures. The effect of unlinked quadrupole excitations on the CISD energies was estimated by incorporating the Davidson correction.<sup>9</sup> The corresponding energies are denoted CISD+Q. For the separated ethane and NO<sup>+</sup> species, the "supermolecule" approach, composed of the two molecules separated by about 500 Å, was used to avoid the size-consistency problem. The Huzinaga–Dunning triple- $\zeta$  basis set<sup>10</sup>—designated 10s6p/5s3p for C, N, and O and 5s/3s for H—with one set of polarization functions (TZP) on all the nuclei was employed for the CISD single-point calculations. The polarization function exponents for basis functions with  $l = l_v + 1$  (where  $l_v$  represents the  $l$  angular momentum value for the outermost valence shell) were  $\alpha_p(\text{H}) = 0.75$  and  $\alpha_d(\text{C}) = 0.75$ ,  $\alpha_d(\text{N}) = 0.80$ , and  $\alpha_d(\text{O}) = 0.85$ . These augmented basis sets employed six-component spherical harmonic d functions. For the initial weakly bound complex, we also used an additional set of diffuse s-type functions (denoted as "+" in the basis set:  $\alpha_+( \text{H} ) = 0.0302$ ,  $\alpha_+( \text{C} ) = 0.0481$ ,  $\alpha_+( \text{N} ) = 0.0438$ , and  $\alpha_+( \text{O} ) = 0.0845$ )<sup>11</sup> on all atoms. Analytic vibrational frequencies were obtained through the MP2/6-31G(d) level of theory to determine the number of imaginary frequencies (NIMAG) and to characterize stationary points (minima have NIMAG = 0 and transition structures have NIMAG = 1). Vibrational frequencies and zero-point vibrational energies (ZPVE) were scaled by the empirical factors 0.91<sup>12</sup> at the Hartree–Fock level and 0.93 at MP2, to correct for anharmonicity and correlation effects. All reaction enthalpies are based on CISD+Q/TZP//MP2/6-31G(dp) + ZPVE//MP2/6-31G(d) energies, unless stated otherwise. Standard notation<sup>8</sup> is used; "//" means "at the geometry of."

## Results and Discussion

**General Considerations.** The computed energies (Tables 1 and 2) of the reactions of ethane with NO<sup>+</sup> depicted in Scheme

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**Table 1.** Relative Energies (in -au) of C<sub>2</sub>H<sub>6</sub>NO<sup>+</sup> Species Involved in the Reaction of Ethane with NO<sup>+</sup>. Zero-Point Vibrational Energies (in kcal mol<sup>-1</sup>, scaled by 0.91) Given in Parentheses

species [point group]	HF/6-31G(d)	HF/6-31G(dp)	MP2/6-31G(d)// MP2/6-31G(d)	MP2/6-31G(dp)// MP2/6-31G(dp)	CISD/TZP// MP2/6-31G(dp)	CISD+Q/TZP// MP2/6-31G(dp)
C <sub>2</sub> H <sub>6</sub> + NO <sup>+</sup>	208.137 91 (48.4)	208.147 89 (48.0)	208.737 33 (47.0)	208.785 99	208.789 48 <sup>a</sup>	208.876 81 <sup>a</sup>
<b>3</b> <sup>b</sup> [C <sub>2</sub> ]	208.144 04 (49.7)	208.153 89 (49.4)	208.748 72 (49.4)	208.797 51	208.799 04	208.887 17
<b>TS</b> <sub>2</sub> [C <sub>1</sub> ]	208.042 57 (48.0)	208.084 24 (47.7)	208.667 54 (46.0)	208.720 66	208.739 56	208.828 34
<b>TS</b> <sub>3</sub> [C <sub>s</sub> ]	208.084 23 (46.0)	208.095 88 (45.7)	208.669 06 (43.5)	208.717 24	208.741 48	208.828 22
<b>TS</b> <sub>4</sub> [C <sub>s</sub> ]	208.115 73 (47.7)	208.128 02 (47.3)	208.694 12 (45.0)	208.747 08	208.764 66	208.849 34
<b>4</b> [C <sub>2v</sub> ]	208.192 12 (52.4)	208.202 51 (52.1)	208.790 29 (50.1)	208.835 70	208.848 73	208.933 52
<b>5</b> [C <sub>s</sub> ]	208.177 75 (52.8)	208.184 20 (52.4)	208.771 08 (49.5)	208.817 84	208.833 82	208.919 47
<b>6</b> [C <sub>s</sub> ]	208.094 86 (44.0)	208.106 79 (44.0)	208.708 70 (41.5)	208.752 65	208.765 48	208.854 30
<b>7</b> [C <sub>1</sub> ]	208.106 71 (47.7)	208.117 46 (47.2)	208.713 91 (45.2)	208.760 48	208.776 10	208.865 33
<b>16</b> <sup>c</sup> [C <sub>s</sub> ]	208.114 09 (47.7)	208.128 71 (45.4)	208.702 46 (45.4)	208.751 16	208.771 54	208.853 35

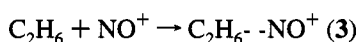
<sup>a</sup> Supermolecule (consisting of ethane and NO<sup>+</sup> at a distance of about 500 Å). Energies with diffuse functions: CISD/TZP+//MP2/6-31G(dp) = -209.994 52; CISD+Q/TZP+//MP2/6-31G(dp) = -209.092 12. <sup>b</sup> Energies at CISD/TZP+//MP2/6-31G(dp) = -209.014 40; CISD+Q/TZP+//MP2/6-31G(dp) = -209.102 32. <sup>c</sup> Energies of the ethyl cation with the MP2/6-31G(dp) basis set: CISD/TZP = -78.626 50, CISD+Q/TZP = -78.652 48, ZPVE = 36.0. NO<sup>+</sup>: CISD/TZP = -128.959 53, CISD+Q/TZP = -128.962 45, ZPVE = 2.7. HNO: CISD/TZP = -130.170 72, CISD+Q/TZP = -130.204 56, ZPVE = 8.0.

**Table 2.** Relative Energies<sup>a</sup> of C<sub>2</sub>H<sub>6</sub>NO<sup>+</sup> Species Involved in the Reaction of Ethane with NO<sup>+</sup>

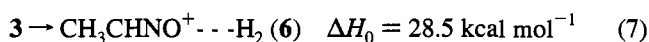
species [point group]	HF/6-31G(d)	HF/6-31G(dp)	MP2/6-31G(d)// MP2/6-31G(d)	MP2/6-31G(dp)// MP2/6-31G(dp)	CISD/TZP// MP2/6-31G(dp)	CISD+Q/TZP// MP2/6-31G(dp)
C <sub>2</sub> H <sub>6</sub> + NO <sup>+</sup>	2.5	3.8	4.7	4.8	3.6	4.1
<b>3</b> [C <sub>2</sub> ]	0.0	0.0	0.0	0.0	0.0	0.0
<b>TS</b> <sub>2</sub> [C <sub>1</sub> ]	62.0	42.0	47.5	44.8	33.9	33.5
<b>TS</b> <sub>3</sub> [C <sub>s</sub> ]	33.8	32.7	44.1	44.5	30.2	31.1
<b>TS</b> <sub>4</sub> [C <sub>s</sub> ]	15.8	14.1	29.9	27.2	17.2	19.3
<b>4</b> [C <sub>2v</sub> ]	-27.5	-27.8	-25.4	-23.3	-30.5	-28.4
<b>5</b> [C <sub>s</sub> ]	-18.0	-16.0	-13.9	-12.7	-21.7	-20.2
<b>6</b> [C <sub>s</sub> ]	25.2	24.2	17.2	20.2	13.2	12.7
<b>7</b> [C <sub>1</sub> ]	21.4	20.7	17.6	18.9	10.2	9.5
<b>16</b> [C <sub>s</sub> ]	16.8	11.8	25.0	25.1	13.3	17.2

<sup>a</sup> In kcal mol<sup>-1</sup>, including zero-point vibrational energies (scaled by 0.91).

1 are summarized in eqs 4 to 8. Each of these reactions is



$$\Delta H_0 = -4.1 \text{ kcal mol}^{-1} \quad (4)$$



discussed in detail below, but it is useful to keep an overview in mind. The initial C<sub>2</sub>H<sub>6</sub> · NO<sup>+</sup> (**3**) complex is only weakly bound. The steps (eqs 5 and 6) leading from **3** to the methyl (**4**) and ethyl (**5**) derivatives are exothermic, but processes which result in the loss of hydrogen (**6**, eq 7) and the loss of methane (**7**, eq 8) are endothermic. Nevertheless, we find (see below) that the methyl products arise via the endothermic pathway **8** rather than from exothermic reaction **5**.

**The Initial Complex (3, Eq 4, Figure 1).** A weakly bound complex of ethane with the nitrosonium ion is formed first. The binding energy [-4.0 kcal mol<sup>-1</sup> at CISD+Q/TZP+//MP2/6-31+G(dp) + ZPVE(MP2/6-31G(d))] is only slightly larger than that of the H<sub>4</sub>C · · NO<sup>+</sup> (**8**, Figure 6) complex [3.6 kcal mol<sup>-1</sup> at MP2/6-31+G(dp)//MP2/6-31+G(dp)+ZPVE(MP2/6-31G-

(dp))].<sup>5</sup> As in **8**, the binding in **3** is mainly due to the polarization of ethane by the charged NO<sup>+</sup>. Since NO<sup>+</sup>, isoelectronic with CO, is a very stable, delocalized electrophile,<sup>5</sup> its complexation energy is much less than the proton affinity of ethane (-146.9 kcal mol<sup>-1</sup>).<sup>13</sup>

The exothermicity of reaction **4** increases somewhat from the Hartree-Fock level (HF/6-31G(d)//HF/6-31G(d) + ZPVE(HF/6-31G(d)): -2.6 kcal mol<sup>-1</sup>) to the correlated level (CISD+Q/TZP+//MP2/6-31+G(dp) + ZPVE(MP2/6-31G(d)): -4.0 kcal mol<sup>-1</sup>). The inclusion of diffuse functions should largely overcome<sup>14</sup> basis set superposition errors (BSSE). Nevertheless, we estimated the magnitude of the BSSE for our reference level using the counterpoise method.<sup>15</sup> For the initial complex **3**, we computed a correction to the binding energy of 0.7 kcal mol<sup>-1</sup> due to the BSSE. This value is a measure of basis set incompleteness,<sup>16</sup> and it may be considered as the error margin for the upper limit of the binding energy of **3** within the employed method.<sup>14</sup> Therefore, the BSSE corrected binding energy of **3** is 3.3 kcal mol<sup>-1</sup>.

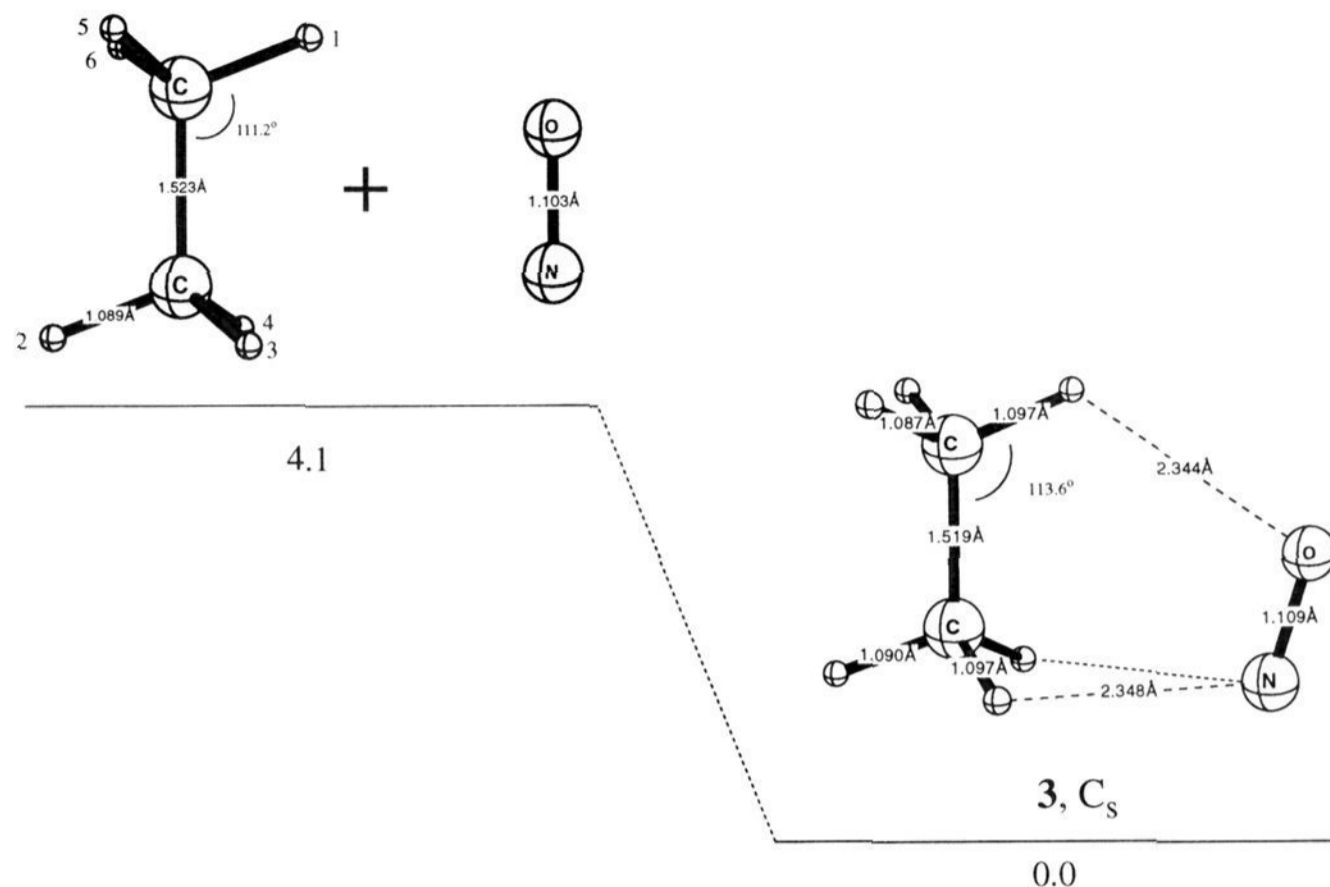
**Insertion into a CC Bond (Eq 5).** Although eq 5 is the most favorable pathway thermodynamically, we could not locate a first-order transition structure, either at HF/6-31G(d) or at

(13) At the MP2(full)/6-31G(dp)//MP2/6-31(dp) level.

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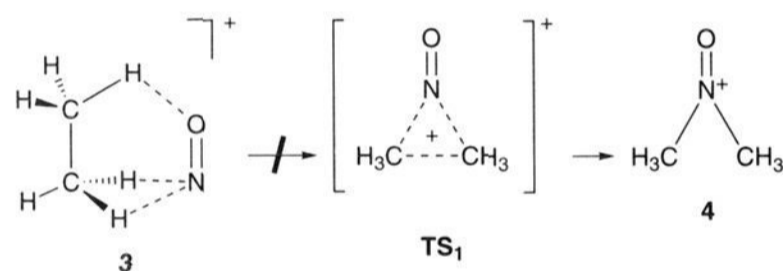
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**Figure 1.** The complexation of ethane with the nitronium cation to give the weakly bound complex **3** ( $C_s$ ). The geometries were optimized at MP2/6-31G(dp); relative energies were obtained at CISD+Q/TZP//MP2/6-31G(dp) + ZPVE//MP2/6-31G(d). We used a supermolecule approach for the energy single-point calculations at the CISD level. Relative energies in kcal mol<sup>-1</sup>.

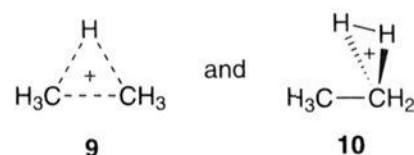
MP2/6-31G(d), for the direct insertion of NO<sup>+</sup> into the carbon-carbon bond of ethane. However, optimizations using  $C_2$



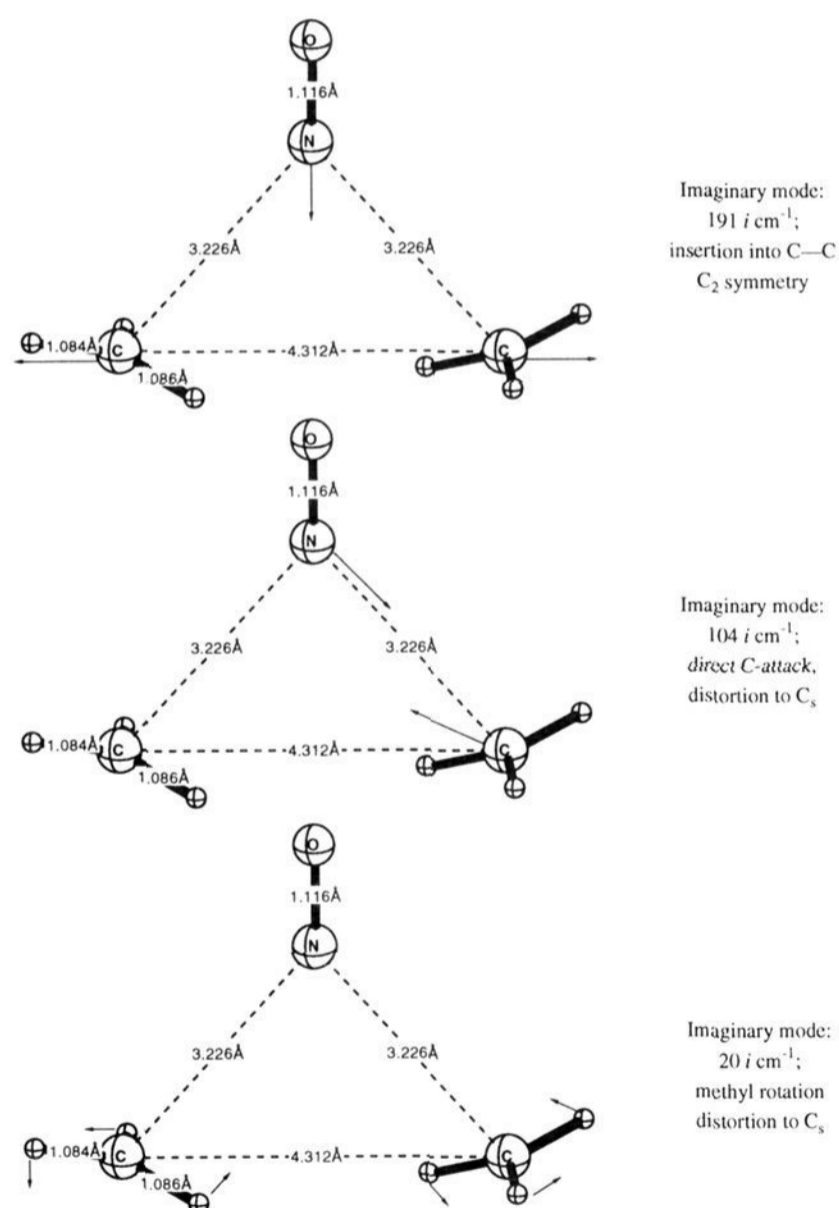
symmetry yielded a higher order saddle point (Hessian index three). The largest magnitude imaginary frequency of  $191i$  cm<sup>-1</sup> corresponds to the insertion motion of NO<sup>+</sup> into the C-C bond (Figure 2), maintaining  $C_2$  symmetry. Symmetry reduction is indicated by the second imaginary frequency of  $104i$  cm<sup>-1</sup> which describes the motion of the nitronium cation toward one of the carbon atoms. The imaginary frequency of  $20i$  cm<sup>-1</sup> corresponds to a rotation of the methyl groups. In summary, two of the three imaginary frequencies indicate a distortion to the  $C_s$  point group, and thus to the transition state for the direct carbon attack by NO<sup>+</sup>. This reaction mode is discussed below.

We also searched for the transition state for C-C insertion in the reverse direction (starting from **4**), but with negative results. Although the inability to locate a particular transition structure does not necessarily mean that it does not exist, we conclude from our results that direct C-C insertion is not a viable pathway.

This finding is in contrast to the reactions of, for instance, the much more electrophilic proton which easily forms three-center two-electron (3c-2e) structures<sup>4</sup> with either the C-C or one of the C-H bonds of ethane (**9** and **10**):

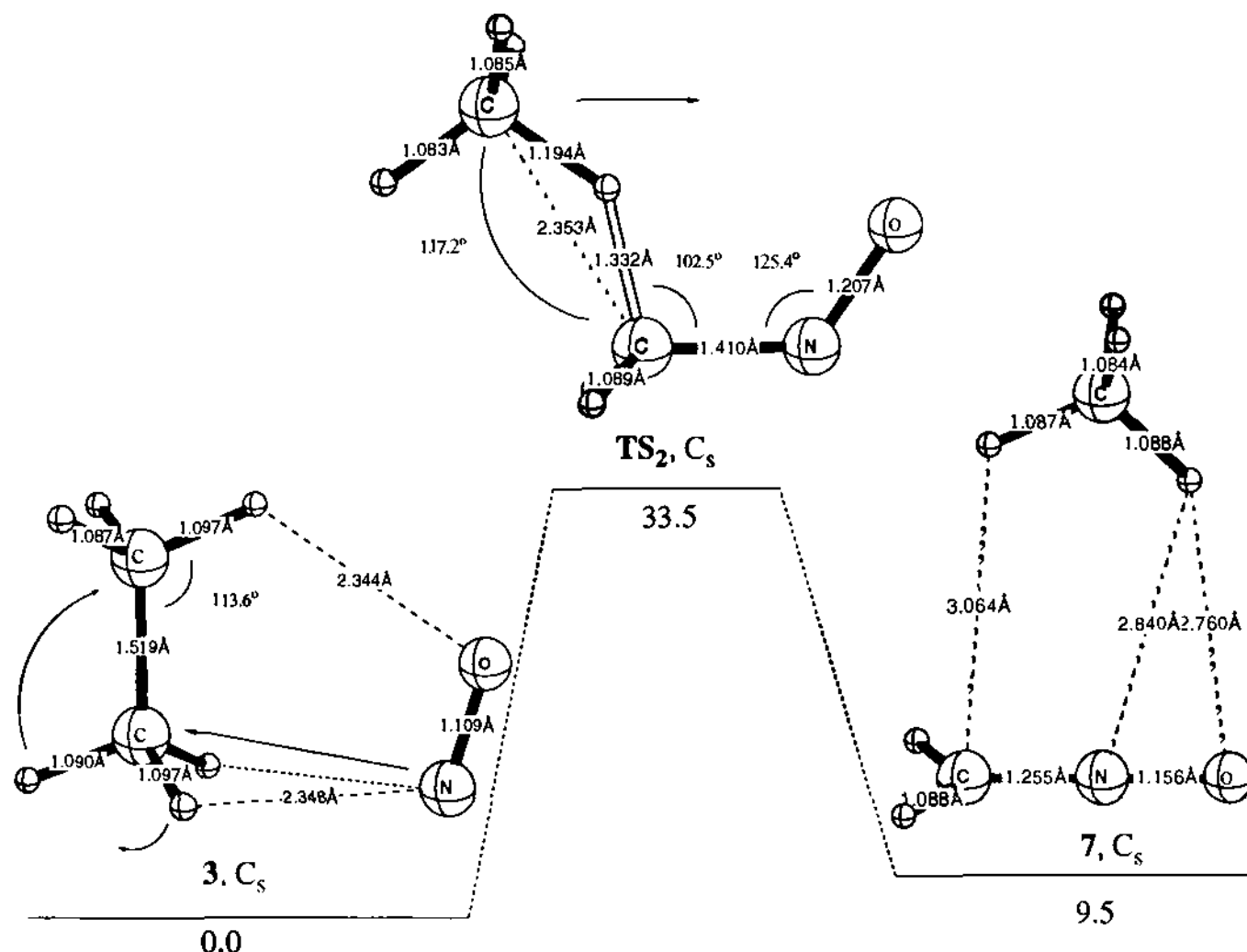


The stability of **4** versus **3** (eq 5) is easy to understand. One C-C bond is replaced by two, albeit weaker, C-N bonds. The



**Figure 2.** Analysis of the three imaginary vibrational modes of  $(CH_3)_2NO^+$  (**4**), a higher order saddle point.

positive charge in species **4** is delocalized via hyperconjugation, which also is reflected in the  $C_2$  point group (Figure 6) of the minimum energy structure at our highest level. Inclusion of polarization functions on the hydrogens describes the  $\sigma(C-H) \rightarrow p(N=O)$  overlap better in the lower, less restricted symmetry. The  $C_{2v}$  form of **4** is a minimum at MP2/6-31G(d), but has an



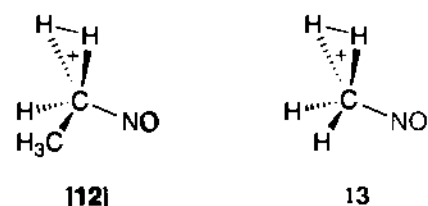
**Figure 3.** The reaction pathway leading to the loss of methane from the complex **3** at the CISD+Q/TZP//MP2/6-31(dp) + ZPVE//MP2/6-31G(d) level. Relative energies in kcal mol<sup>-1</sup>.

imaginary frequency at MP2/6-31G(dp), indicating a distortion to C<sub>3</sub> symmetry.

**Insertion into a CH Bond (Eq 6).** In Olah's familiar mechanistic model (depicted in eq 1),<sup>2,3</sup> a C-H bond is attacked by the electrophile. This is reasonable for strong electrophiles like H<sup>+</sup> or R<sup>+</sup> (e.g., CH<sub>3</sub><sup>+</sup>) since a symmetrical 3c-2e CH<sub>2</sub><sup>+</sup> (e.g., **10**) or CHR<sup>+</sup> (e.g., **9**) bonding arrangement can result. However, NO<sup>+</sup> is more stable (based on, e.g., its hydride affinity) than H<sup>+</sup> or R<sup>+</sup> and is *unlikely* to engage in such 3c-2e CHE<sup>+</sup> bonding since the necessary balance among the three bonding interactions is lacking.<sup>17</sup> As in our earlier study on the reaction of NO<sup>+</sup> with methane,<sup>5</sup> we found no indication that NO<sup>+</sup> inserts directly into a C-H bond of ethane (as shown in eq 1). Instead, NO<sup>+</sup> attacks a carbon or a hydrogen atom of ethane. This leads to loss of methane or to hydride ion abstraction, respectively (see discussion below).

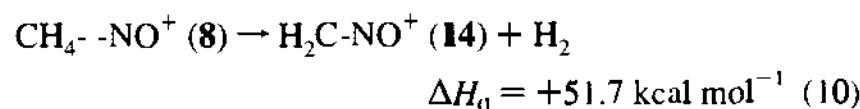
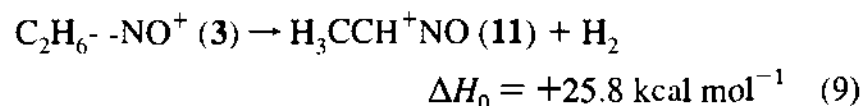
**Loss of Molecular Hydrogen (Eq 7).** Although we found a stable structure (**6**, Figure 6) comprised of H<sub>2</sub> attached to the H<sub>2</sub>C-CH<sup>+</sup>-NO cation (**11**, Figure 6), the loss of hydrogen from **3** is unfavorable thermodynamically ( $\Delta H_0 = 28.5$  kcal mol<sup>-1</sup>). We searched for, but could not locate, a transition structure that connects **3** and **6**. Most likely, if there is a transition structure at all, it occurs very late on the potential reaction hypersurface and is thus structurally very close to the product.

Interestingly, there is no stationary point like **[12]** where an H<sub>2</sub> subunit is more strongly bound (i.e., at a much shorter

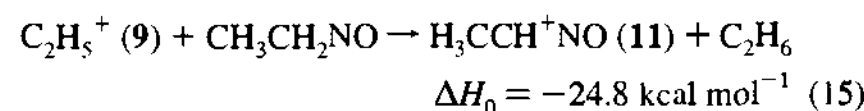
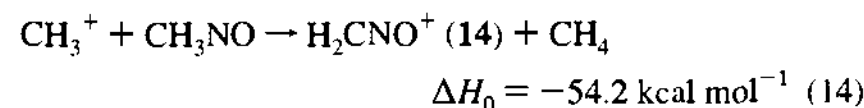
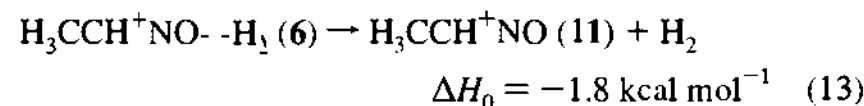
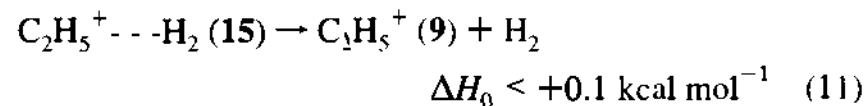


distance than in **6**) to **11**. Such a stable structure does exist for methane + NO<sup>+</sup> (**13**, Figure 6).<sup>5</sup>

Cation **11** is 25.9 kcal mol<sup>-1</sup> (eq 9 minus eq 10) more stable than the H<sub>2</sub>C-NO<sup>+</sup> cation (**14**), with respect to the initial complexes **3** and **8**.



While the dissociation of the hydrogen complex of the bridged ethyl cation C<sub>2</sub>H<sub>5</sub><sup>+</sup>-H<sub>2</sub> (**15**, eq 11)<sup>13</sup> is essentially thermoneutral, the hydrogen complex of the H<sub>2</sub>C-CH<sup>+</sup>-NO cation (**6**) dissociates in a weakly exothermic reaction (eq 13), demonstrating the higher stability of **11** versus **9**. This is due to the stabilizing effect of NO<sup>+</sup> which is also much smaller for **11** than for **14** (eqs 14 and 15), owing to the hyperconjugative stabilization of 25.9 kcal mol<sup>-1</sup> (eq 9 versus 10) through the adjacent methyl group.



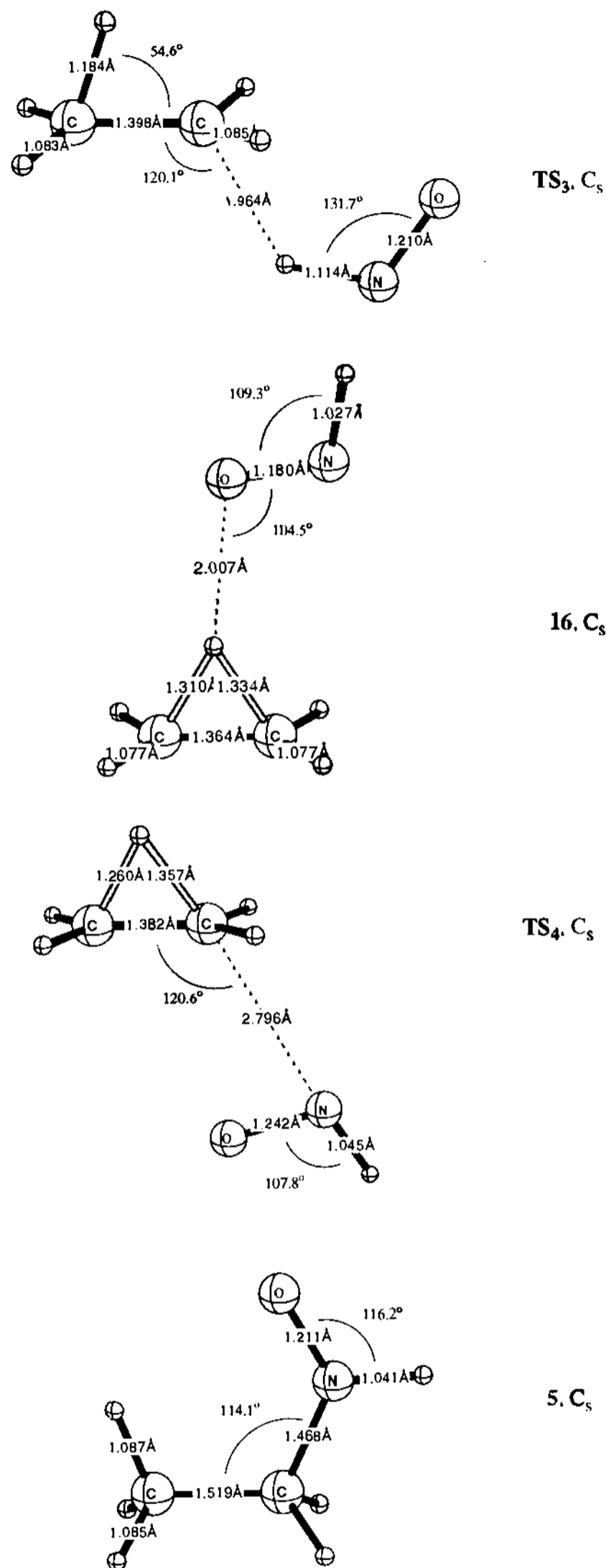
**Loss of Methane (Eq 8, Figure 3).** In contrast to the unsuccessful search for the hypothetical insertion reactions, where the electrophile would attack the electron density comprising a bond between two atoms, we did find a continuous potential energy hypersurface for the loss of methane and the for abstraction of a hydride ion from ethane (discussed below), where the electrophile attacks an atom (carbon or hydrogen) directly. This observation is in agreement with analogous experimental observations on the electrophilic derivatizations<sup>2,3</sup> of ethane or its reaction with the nitronium ion, where ethyl and methyl derivatives were the only products.

The pathway<sup>18</sup> for the loss of methane is depicted schematically in Figure 3. The overall reaction is somewhat endothermic (9.5 kcal mol<sup>-1</sup>). Some intriguing features are associated with **TS<sub>2</sub>** which also has 3c-2e bonding. This is in agreement with our results on methane + NO<sup>+</sup>, where we also found an intermediate with a CHH 3c-2e bond of type 2 (eq 2) rather than a 1-type structure (where the electrophile is incorporated in the electron-deficient bond). The linear nitrosomethylene (H<sub>2</sub>CNO<sup>+</sup>) cation (**14**) (which is isoelectronic with ketene) can be regarded as a single methylene complex NO<sup>+</sup> bound to the lone pair.

In the reaction medium, nitrosomethane may arise from H<sub>3</sub>CNO<sup>+</sup> - -CH<sub>4</sub> (**7**) by abstraction of a hydride ion from an appropriate hydride ion donor (such as nitrosoethane, which would form the more stable H<sub>3</sub>C-CH<sup>+</sup>-NO cation (**11**)).

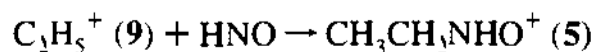
**Abstraction of a Hydride Ion and Addition of HNO to C<sub>2</sub>H<sub>5</sub><sup>+</sup> (Eq 6, Figures 4 and 5).** While we found no evidence for NO<sup>+</sup> insertion into an ethane C-H bond, the abstraction of a hydride and subsequent addition of HNO to the ethyl cation is a plausible alternative pathway that accounts for the formation of nitrosoethane. Several ground and transition structures along this pathway were located. Figures 4 and 5 depict the optimized structures and the relative energies. As the C-H distance of the hydride being transferred is quite long, the transition structure (**TS<sub>3</sub>**) must occur relatively late on the potential energy hypersurface. The activation barrier (31.1 kcal mol<sup>-1</sup>) for this abstraction of a hydride ion from ethane is similar to the activation barrier for the loss of methane (eq 8, 33.5 kcal mol<sup>-1</sup>). Thus, the activation barriers for the rate-determining steps that eventually lead to both products (nitrosoethane and nitrosomethane) are computed to be close in energy ( $\Delta\Delta H_0 = 2.4$  kcal mol<sup>-1</sup>). This is in general agreement with the experimental findings for the reactions of other electrophiles with ethane, e.g., with NO<sub>2</sub><sup>+</sup>, where nitromethane and nitroethane were formed in a ratio of 2.9:1.0, or upon electrophilic chlorination, where methyl and ethyl chloride were obtained in a ratio of 7:3.<sup>3a</sup>

We found only one possible complex (**16**) of the bridged ethyl cation and HNO. An alternative possibility with HNO *anti* to the bridging hydrogen optimizes either to N-protonated nitrosoethane or to N-protonated isonitrosoethane. The complexation energy of **16** is +2.3 kcal mol<sup>-1</sup> [+2.9 kcal mol<sup>-1</sup> including BSSE (0.6 kcal mol<sup>-1</sup>)], indicating that **16** is thermodynamically unstable. Because of the exothermicity (-33.7 kcal mol<sup>-1</sup>) of the reaction of the ethyl cation with HNO



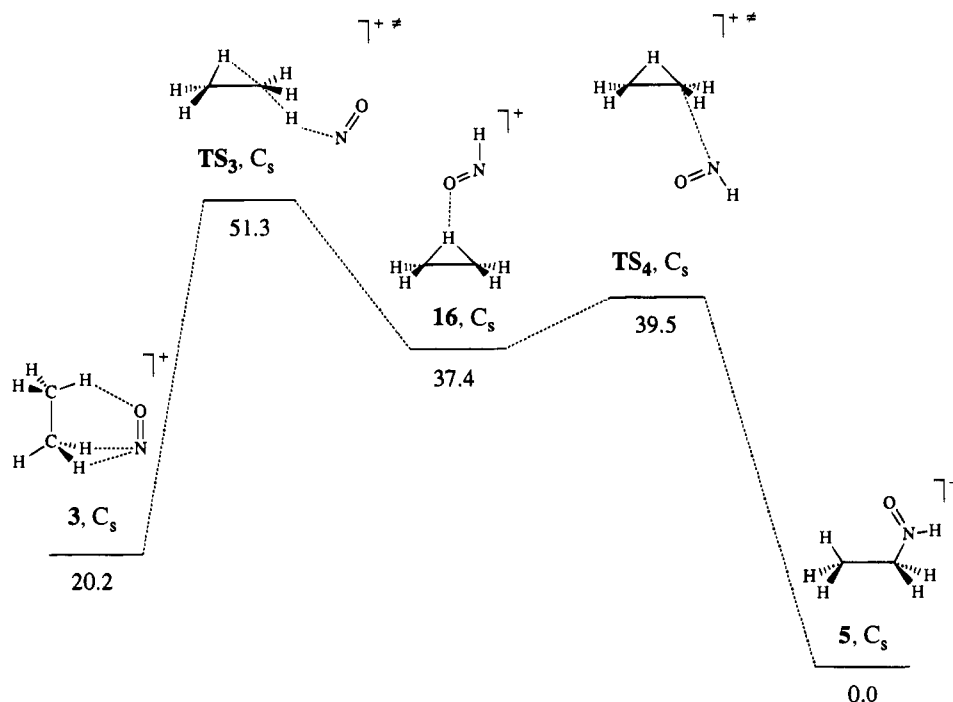
**Figure 4.** Structures (optimized at MP2/6-31G(dp)) involved in the pathway for the abstraction of a hydride ion / addition of HNO to ethane. The relative energies are depicted in Figure 5.

(eq 16), the activation barrier of **TS<sub>4</sub>** for the addition of HNO to the ethyl cation is quite small (2.1 kcal mol<sup>-1</sup>).



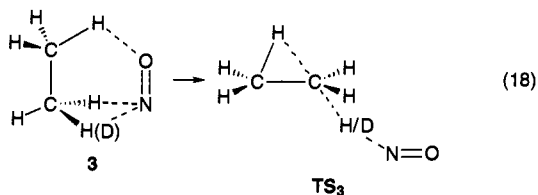
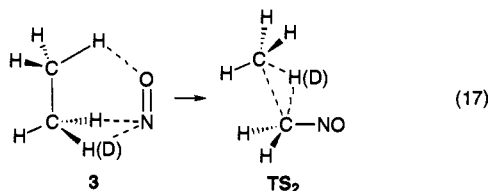
$$\Delta H_0 = -33.7 \text{ kcal mol}^{-1} \quad (16)$$

(18) Note that the Hartree-Fock potential energy surface does not entirely agree with the results at electron correlated levels of theory. While the initial complex C<sub>2</sub>H<sub>6</sub> - -NO<sup>+</sup> (**3**) is directly converted into **7** at the correlated levels, we found an additional minimum and a transition structure (**TS<sub>5</sub>**) at the SCF level. These two structures connect **TS<sub>2</sub>** with **7** going through a complex of **14** and methane. The transition structure **TS<sub>5</sub>** completes the loss of methane from **7** and eventually also leads to **5**. This behavior is not unusual. Carbocation geometries depend very much upon correlation (see ref 8), and one should be careful interpreting structures computed exclusively at SCF levels.



**Figure 5.** The reaction pathway (at the CISD+Q/TZP//MP2/6-31G(dp) + ZPVE//MP2/6-31G(d) level, in kcal mol<sup>-1</sup>) for the abstraction of a hydride ion / addition of HNO to ethane.

**H/D Kinetic Isotope Effects.** We computed the H/D isotope effects and the activation barriers for the loss of methane ( $3 \rightarrow \text{TS}_2$ , eq 17) and for the hydride abstraction ( $3 \rightarrow \text{TS}_3$ , eq 18) at



MP2/6-31G(d), using standard conditions ( $T = 298.15$  K,  $p = 1.0$  atm). According to general definitions,<sup>19</sup> both  $\text{TS}_2$  and  $\text{TS}_3$  should exhibit primary H/D kinetic isotope effects since C-H bonds are being broken. Several assumptions were made for the computation of these kinetic effects. First of all, we began with complex **3** as the reactant, rather than ethane and the nitronium ion. This assumption is certainly valid for the isolated state. In solution (e.g., super acid), however, the solvation energy of the ion probably is larger than the complexation energy, and one would not *a priori* expect the existence of a complex. All reactants and products belong to the same point group ( $C_s$ ), and therefore no symmetry correction has to be made with respect to rotational symmetry numbers.<sup>20,21</sup> We used RRKM theory,<sup>22</sup> assuming the high-pressure limit for the calculation of the  $k_H/k_D$  ratios. Tunneling effects were not included. The individual rates can be computed

(19) Westheimer, F. H. *Chem. Rev.* **1961**, *61*, 265.

(20) Davidson, N. *Statistical Mechanics*; McGraw-Hill: New York, 1962. Laidler, K. J. *Chemical Kinetics*; Harper & Row: New York, 1987.

using the rate expression (eq 19):

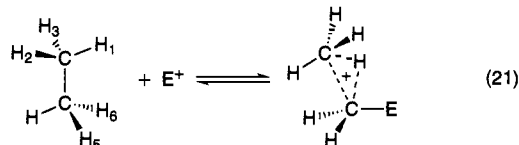
$$k(E) = A \left( \frac{E - V_0}{E} \right)^{s-1} \quad (19)$$

where  $E$  is the total energy (which is also defined relative to the minimum of the potential energy hypersurface). While  $A$  is the frequency factor (eq 20, in s<sup>-1</sup>),  $s$  is the number of

$$A = \left( \prod_{i=0}^s \omega_i \right) \left[ 2\pi \left( \prod_{i=0}^{s-1} \omega_i^\ddagger \right) \right]^{-1} \quad (20)$$

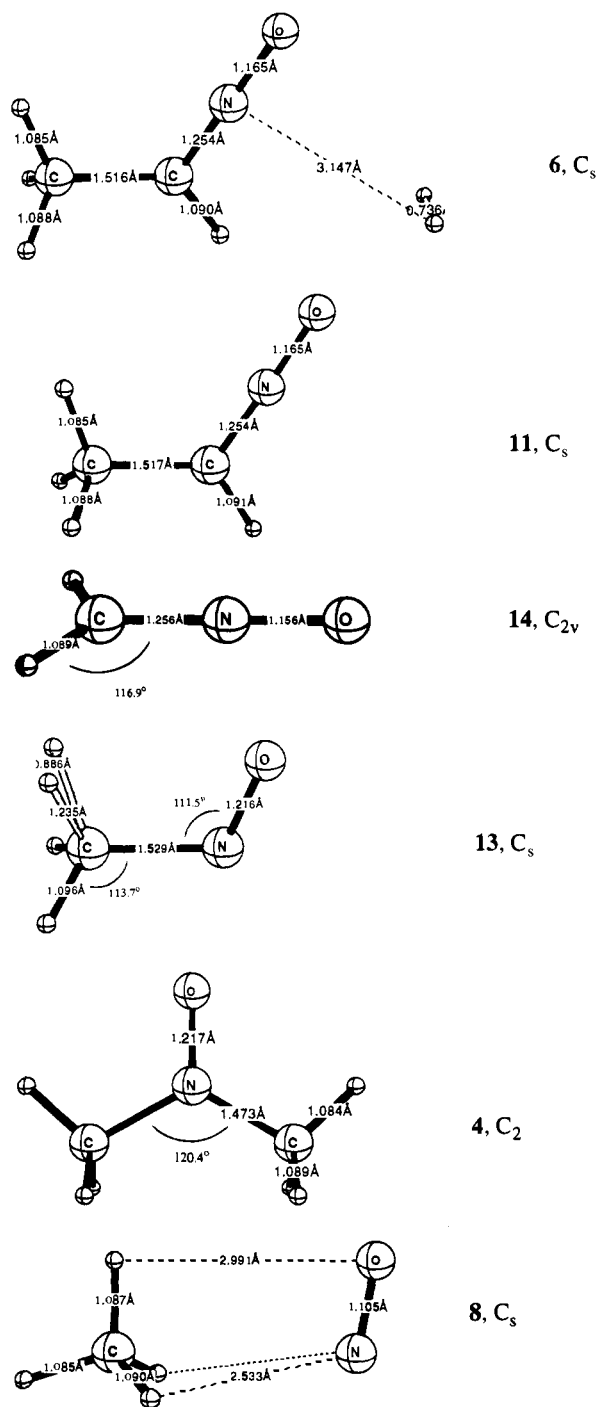
vibrational degrees of freedom of the stable molecule,  $\omega_i$  and  $\omega_i^\ddagger$  are the normal mode frequencies of the reactant and the

(21) If the initial formation of a complex between the hydrocarbon and the electrophile is not assumed, symmetry considerations lead to much larger kinetic H/D kinetic isotope effects. This is exemplified for the reaction of ethane with an electrophile, leading to C-C cleavage (eq 21).



Since any of the six hydrogens of ethane can be transferred, there could be six possible products if the hydrogens were distinguishable (in other words, the rotational symmetry number<sup>20</sup> of  $D_{3d}$  ethane is six). For the reverse reaction, however, there is only one possibility for a particular hydrogen to be transferred (the symmetry number of the product is one). Consequently, the forward reaction has a 6-fold higher statistical probability. The situation is quite different if one of the hydrogens in ethane, e.g.,  $H_1$ , is substituted by a deuterium atom to give  $C_2H_5D$ , which has a rotational symmetry number of one. In this case, no statistical correction is needed. Taking these symmetry considerations into account, the H/D kinetic isotope effects would be larger than for the reaction of the initial complex by a considerable factor. Nevertheless, we cannot predict the kinetic isotope effect in solution, where the initial complex may not be present.

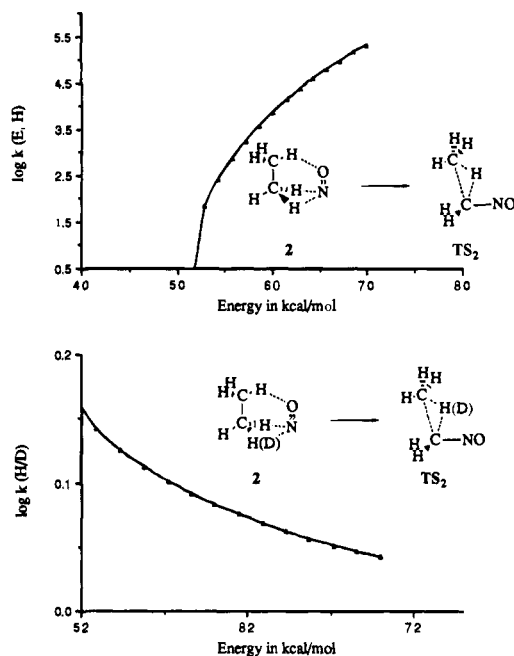
(22) Ric, O. K.; Ramsperger, H. C. *J. Am. Chem. Soc.* **1927**, *49*, 1616. Kassel, L. S. *J. Phys. Chem.* **1928**, *32*, 225. Marcus, R. A. *J. Chem. Phys.* **1952**, *20*, 359. Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley: New York, 1972. Gardiner, W. C., Jr. *Rates and Mechanisms of Chemical Reactions*; W. A. Benjamin: New York, 1969.



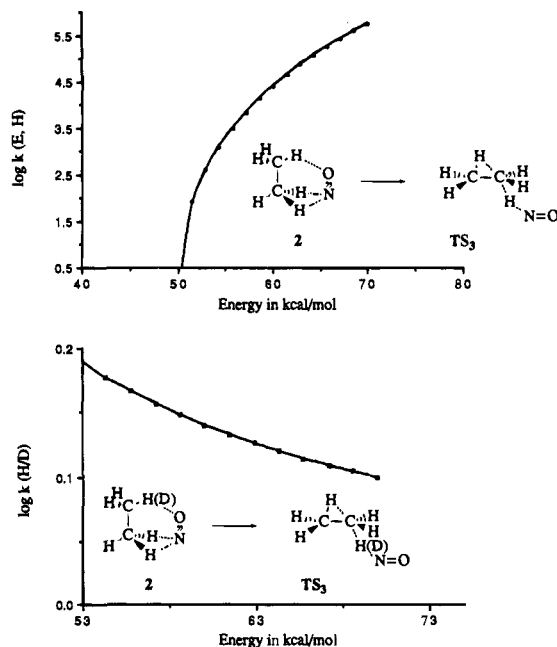
**Figure 6.** Additional stationary points discussed in the text; optimized at MP2/6-31G(dp).

transition state, and  $V_0$  refers to the activation barrier including the zero-point vibrational energy correction. Following this treatment,<sup>23</sup> we obtained  $k_H/k_D$  kinetic isotope effects of 2.6 and

(23) The level of dynamics theory used here to predict the rate constants and the kinetic isotope effects inherits certain limitations. First of all, we assume an equilibrium between the reactants and the products, even though this condition does not always pertain. We also assume that the chemical system can be treated in terms of classical motion, not including quantum effects, e.g., tunneling. Also, the accuracy of determination of the barrier height is limited by the basis set and methods used. However, errors due to inadequacies in the basis set or the method employed may largely cancel when relative energies or relative rates are compared. Nevertheless, a few kcal mol<sup>-1</sup> difference in the activation energy may lead to a large change of the rate constant, due to the exponential dependence of the rate on  $\Delta G^\ddagger$ .



**Figure 7.** (Top) Unimolecular rate constants for the C-C bond cleavage reaction (eq 17), as a function of the total energy. (Bottom) Logarithm of the ratio of hydrogen to deuterium rate constants for eq 17, as a function of the total energy.



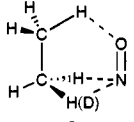
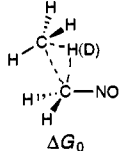
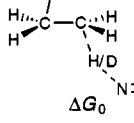
**Figure 8.** (Top) Unimolecular rate constants for the abstraction of a hydride from ethane by  $\text{NO}^+$  (eq 18), as a function of the total energy. (Bottom) Logarithm of the ratio of hydrogen to deuterium rate constants for eq 18, as a function of the total energy.

2.9 for eqs 17 and 18, respectively. From the kinetic rate/energy relationship as well as the evolution of the H/D kinetic isotope effects (Figures 7 and 8), it is apparent that both pathways are similar energetically (eqs 17 and 18). Explicit values for  $E$ ,  $\Delta G$ , and the zero-point vibrational energies are summarized in Table 3.

The compound isotope effects are relatively small, owing to the nonlinearity of both transition structures.<sup>19</sup> This is apparent from the relatively small imaginary frequencies for  $\text{TS}_2$  (262i) and  $\text{TS}_3$  (604i), leading to small changes in vibrational frequen-



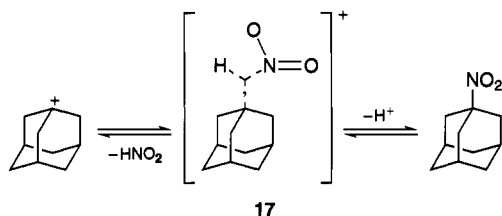
**Table 3.** Isotopic Labeling Studies on the Complex (3) of Ethane and NO<sup>+</sup>, the Transition State Leading to the Loss of Methane (TS<sub>2</sub>), and the Transition State for the Abstraction of a Hydride Ion by NO<sup>+</sup> from Ethane (TS<sub>3</sub>)<sup>a</sup>

species	MP2/6-31G(d)	ZPVE (H)	ZPVE(D)	k <sub>H</sub> /k <sub>D</sub>
<b>3</b> 	208.74872	47.2	45.4	
$\Delta G_0$	0.0	0.0	0.0	
<b>TS<sub>2</sub></b> 	208.66754	46.0	44.9	2.6
$\Delta G_0$	50.9 (E <sub>rel</sub> )	47.6	48.1	
<b>TS<sub>3</sub></b> 	208.66906	43.5	42.1	2.9
$\Delta G_0$	50.0 (E <sub>rel</sub> )	46.3	46.7	

<sup>a</sup> Zero-point vibrational energies (in kcal mol<sup>-1</sup>) scaled by 0.91. Temperature = 298.15 K; pressure = 1.0 atm. Absolute energies in -au, relative energies in kcal mol<sup>-1</sup>. The k<sub>H</sub>/k<sub>D</sub> ratios were determined using RRKM theory (see text).

cies of the transition structures versus the ground states. Hence, the total H/D kinetic isotope effects are modest in magnitude.

Although the comparison involves a primary and a tertiary substrate, our findings for ethane may be discussed in relationship to the recently experimentally determined H/D kinetic isotope effect on the nitration of adamantane with nitronium tetrafluoroborate.<sup>3b</sup> In this truly remarkable reaction, the 1.2–1.3 H/D isotope effect was interpreted to be “in all probability primary in nature due to a nonlinear transition state in the rate limiting step (as depicted by 17)” and “to be indicative of an unsymmetrical, nonlinear transition state in the ionization step” leading to the 1-adamantyl cation intermediate.<sup>3b</sup> Olah *et al.* also found that the formation of 1-nitroadamantane was reversible under the reaction conditions, and employed the following depiction.



Hence, 17 could correspond to an insertion of the electrophile into the bridgehead C–H bond as well as to the abstraction of

a hydride ion by the nitronium cation. Our optimized transition-state geometries for the reactions of ethane and of methane<sup>5</sup> do not seem to support representation 17 for the abstraction transition structure, at least if NO<sup>+</sup> is the electrophile. The observed H/D kinetic isotope effect for the electrophilic nitration of adamantane (1.2–1.3) is much smaller than our computed value (2.9) for the abstraction of a hydride from ethane. This suggests either that different types of transition states are involved, or that the rate-determining step for the electrophilic nitration of adamantane is not hydride abstraction.

## Conclusions

Two reactions of ethane with the nitronium cation have been computed *ab initio*. In general agreement with experiments of reactions with other electrophiles, which yielded methyl and ethyl products in similar amounts, we compute the formation of (a) the nitrosomethylene cation and methane (through C–C bond cleavage) and (b) protonated nitrosoethane (via hydride abstraction followed by addition of HNO to the ethyl cation) to have very similar activation energies (33.5 and 31.1 kcal mol<sup>-1</sup>, respectively). The computed H/D primary kinetic isotope effects (calculated via RRKM theory) are small for both pathways (2.6 and 2.9, respectively), owing to the nonlinearity of the transition states. The loss of molecular hydrogen from ethane by attack of the nitronium ion does not appear to be a viable reaction pathway. We found no evidence for a direct insertion of the NO<sup>+</sup> electrophile into a C–H or the C–C bond of ethane.

Hence, these results, like those we have reported earlier for methane,<sup>5</sup> do not support the generally discussed mechanisms for the electrophilic substitution of alkanes.<sup>2,3</sup> Our evidence suggests that some electrophiles may attack carbon directly, rather than C–H or C–C bonds, and that three-center transition structures with the electrophile need not be involved.

However, we note that NO<sup>+</sup> is a relatively stable electrophile and that CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> also may not be representative models for the behavior of branched alkanes and, e.g., adamantane. Our studies with other electrophiles and with larger alkanes will be reported subsequently.

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