1336 *J. Am. Chem. Soc.* **1995,** *117,* 1336−1343

Electrophilic Substitution of Methane Revisited[1]

George A. Olah,* Nikolai Hartz, Golam Rasul, and G. K. Surya Prakash

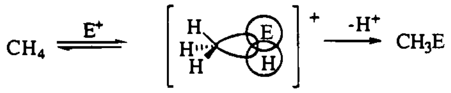
Contribution from the Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661

Received March 15, 1994[⊗]

Abstract: *Ab initio* molecular orbital theory at the correlated level of MP4SDTQ/6-31G**//MP2/6-31G** has been applied to investigate the reactions of NO^+ and NOH^{2+} with methane. Reinvestigation of the theoretical reaction of CH_4 with NO^+ showed that the reaction path involves attack on carbon instead of C−H bond insertion in accord with recent studies of Schreiner *et al.* This is, however, the consequence of the ambident electrophilic nature of NO^+ and does not represent a general electrophilic reaction pathway for methane involving its highly energetic rearrangement (via flattening) and attack on the developing nonbonded electron pair as claimed by Schreiner *et al.* In contrast to NO^+, with superelectrophilic NOH^{2+} methane preferentially reacts via proton transfer to give CH_5^+ or by hydride abstraction. The results of the reaction of methane with NO^+ were compared with such strong electrophiles as D^+, CH_3^+, $C_2H_5^+$, OH^+, and F^+, and the consequences on the reaction mechanism are discussed. The studies reaffirm the general pattern of electrophilic substitution of methane with strong electrophiles to proceed via five coordinate carbocations involving 3c−2e C−H bond insertion as previously suggested by Olah.

Introduction

The electrophilic substitution of methane and other alkanes was first established by Olah *et al.* A mechanistic model was proposed in which a strong electrophile attacks the C−H bond directly.[2] 3c−2e bonding occurs along the reaction coordinate which then cleaves with proton elimination to the products. Although 3c−2e bonding for simplicity is frequently depicted in a symmetrical way, it was pointed out that such bonding with electrophiles other than hydrogen is unsymmetrical.



Hydrogen−deuterium exchange was observed by reacting CH_4 with D^+ or CD_4 with H^+. Related theoretical calculations showed little energy difference between the different geometrical forms of CH_5^+ (except for the more energetic D_{3h} form), and this was explained by ready interconversion through what was termed bond to bond rearrangement.[2a] It was further pointed out that in higher homologous alkonium ions these involve not only C−H bonds but also C−C bonds. Experimental evidence for the proposed C−H bond insertion mechanism in methane was derived (besides hydrogen deuterium exchange studies) from the reaction of other strong electrophiles (such as carbocations). Methane was shown to be methylated by $CH_3F{:}SbF_5$, ethylated by ethylene over superacids and alkylated by stable alkyl cation salts. H_3^+ containing the symmetrical 3c−2e bond and was studied extensively by theory and experiment.[3] CH_5^+ was extensively studied theoretically[4] and was observed not only in the gas phase (by mass spectrometric[5]) but also by ESCA[6] in the condensed state. An infrared investigation of $CH_5^+{:}H_2$ complex has also been reported.[7] The complex is highly fluxional and has not shown distinct IR bands. The protonation of ethane involves both C−H and C−C bonds. The latter is an example for a 3c−2e bond involving two carbons and a hydrogen atom. Isomeric $C_2H_5^+$ ions have been observed experimentally in the gas phase and by infrared spectroscopy.[8,9] Higher alkonium ion homologues are increasingly unstable.[10]

By necessity substantially unsymmetrical structures are involved in cases where three different atoms form the 3c−2e bonding. Due to the low basicity of the aliphatic C−H bond, electrophilic reactions of methane in the condensed state can only be observed with strong (hard) electrophiles containing low nucleophilicty counterion generally under superacidic conditions where protosolvation might further enhance the reactivity of the electrophile.[11]

Schreiner *et al.* have recently theoretically[12] studied the reaction of NO^+ with methane. The nitrosonium ion[13] is a widely used synthetic reagent for electrophilic nitrosations,[14] diazotizations,[13,15] oxidations,[16] electrophilic additions to unsaturated carbon−carbon bonds,[17] hydride abstractions,[18] and halide abstractions.[19] As a weak electrophile, the nitrosonium

---

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1995.

(1) Electrophilic Reactions at Single Bonds. 28. For part 27, see: Olah, G. A.; Hartz, N.; Rasul, G.; Wang, Q.; Prakash, G. K. S.; Casanova, J.; Christe, K. O. *J. Am. Chem. Soc.* **1994**, *116*, 5671.

(2) (a) Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808. (b) Olah, G. A.; Farooq, O.; Prakash, G. K. S. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; John Wiley & Sons: 1989; Chapter 2, p 27. (c) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry;* John Wiley: New York, 1987; p 13. (d) Olah, G. A.; Prakash, G. K. S.; Sommer, J. *Superacids;* John Wiley & Sons: New York, 1985; references therein.

(3) Oka, T. In *Molecular Ions: Spectroscopy, Structure and Chemistry;* Miller, T. A., Bondyby, V. E., Eds.; North Holland Publishing Company: Amsterdam, Holland: 1983; p 73.

(4) Schleyer, P. v. R.; Carneiro, J. W. M. *J. Comput. Chem.* **1992**, *13*, 997. Schreiner, P. R.; Kim, S.-J.; Schaefer, H. F.; Schleyer, P. v. R. *J. Chem. Phys.* **1993**, *99*, 3716. Scuseria, G. E. *Nature* **1993**, *366*, 512.

(5) Jennings, K. R. *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press; New York, 1979; Vol. 2, p 123.

(6) Olah, G. A. et al. Unpublished results.

(7) Boo, D. W.; Lee, Y. T. *Chem. Phys. Lett.* **1993**, *221*, 358.

(8) Yeh, L. I.; Price, J. M.; Lee, Y. T. *J. Am. Chem. Soc.* **1989**, *111*, 5597.

(9) Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

(10) (a) Adams, N. G.; Smith, D. In *Techniques for the Study of Ion/ Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr. Eds.; Wiley: New York, 1988; p 165. (b) Farrar, J. M. In *Techniques for the Study of Ion/ Molecule Reactions*; Farrar, J. M., Saunders, W. H., Jr., Eds.; Wiley: New York, 1988; p 325.

(11) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 767.

(12) (a) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1993**, *115*, 9659. (b) Schreiner, P. R.; Schleyer, P. v. R.; Schaefer, H. F. III Personal communication.

(13) (a) Williams, D. L. H. *Nitrosation*; Cambridge University Press: Cambridge, UK, 1988. (b) Boyer, J. H. In *The chemistry of the nitro and nitroso groups; Part 1*, Feuer, H., Ed.; Interscience: New York, 1969; Chapter 5, pp 215.

0002-7863/95/1517-1336$09.00/0

ion reacts readily only with nonbonded electron pairs or reactive π-systems. Its reactivity toward aromatics in electrophilic aromatic substitution reactions, in the condensed phase, were up to this point limited to activated aromatics (*e.g.*, phenols and anilines) which give nitroso products. Reactions with benzene and toluene show mostly secondary decomposition products. Nitroso products were not yet isolated from these reactions. The reaction between NO^+ and benzene in the gas phase was previously studied experimentally with ion cyclotron resonance spectroscopy[20] and theoretically by *ab initio* calculations.[21] Weaker electron donor σ-bonds such as tertiary C−H bonds do not react with NO^+ under aprotic or low acidity conditions. However, they undergo hydride abstraction in superacidic solution where NO^+ seems to be protolytically activated (*vide infra*). No reaction of the nitrosonium ion with methane was ever observed experimentally in the condensed phase. However, based on ab intio calculations Schreiner *et al.* concluded[12] that the electrophilic substitution of methane by NO^+ does not involve C−H bond insertion involving 3c−2e bonding as previously suggested by one of us for the general electrophilic substitution of methane. They suggested that methane reacts with NO^+ by developing a nonbonded electron pair on carbon via its rearrangement. From these results they then generalized claiming that electrophiles in general react with methane on carbon and not on the C−H bonds.

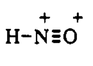
In order to revisit the question of the reaction of methane with electrophiles we have now carried out extended *ab initio* calculations on our own to further probe the mechanism. In view of Schreiner *et al.*'s conclusions involving electrophilic attack on carbon we have extended the study of the mechanism of the reaction of methane from weakly electrophilc NO^+ to superelectrophilic NOH^{2+} and other hard (strong) electrophiles. NO^+ is an ambident and relatively weak electrophile and its theoretical reaction with methane is indeed more complex, as pointed out by Schreiner *et al.* In attempts to increase the electrophilicity and to eliminate the ambident nature of NO^+, we have extended the studies to its protonated form NOH^{2+}. However, as found, the reaction of NOH^{2+} with methane preferably occurs by proton transfer, although other less favorable reaction pathways were also considered. We have further compared these studies with those of substitution of methane with strong and hard electrophiles such as D^+, CH_3^+, $C_2H_5^+$ as well as oxygen electrophiles (studied by Bach et al.[22]) and F^+.[1] These studies reaffirm the previously suggested general pattern of electrophilic substitution of methane via 3c−2e C−H bond insertion.

Results and Discussion

All calculations were performed with the SPARTAN[23] and GAUSSIAN-92[24] packages of programs. Structures were optimized by using standard basis sets (6-31G*, 6-31G**) at the Hartree−Fock level and by applying second order Møller−Plesset perturbation theory, keeping the core electrons frozen. Single point calculations at the MP4SDTQ/6-31G** level were performed on MP2/6-31G** optimized structures. Stationary points were characterized with frequency calculations at the HF/6-31G* level and in some cases at the MP2/6-31G* level. Transition states (one imaginary frequency) were treated in IRC (intrinsic reaction coordinate)[24,25] calculations to identify the minima on both sides of the TS. Calculated energetics will be given at the MP4SDTQ/6-31G**//MP2-6-31G** + ZPE//HF/6-31G* level, if not stated otherwise. The GAUSSIAN-2[26] method was used to obtain high quality estimates for the total energies and proton affinities of some critical structures in this study. The total energies of the calculated structures are shown in Table 1.

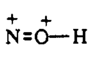
Calculation of the reaction of NO^+ with methane studied previously by Schreiner *et al.* was reinvestigated and compared with that of NOH^{2+} (*vide infra*). NO^+ is a relatively weak and ambident electrophile and is like CH_3CO^+ ion in many respects. Since the reactivity of electrophiles can be greatly enhanced by protolytic activation,[11] the reaction of protionitrosonium dication NOH^{2+} (similar to the protoacetyl dication CH_3COH^{2+}) with methane was therefore investigated by *ab initio* theory.

Protonitrosonium Ion HNO^{2+} and Its Reaction with Methane. Three structures can be envisaged for the protonitrosonium dication:



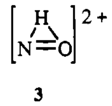
$H-\overset{+}{N}\equiv\overset{+}{O}$

1



$\overset{+}{N}=\overset{+}{O}-H$

2



3

---

(14) (a) Olah, G.; Noszko, L.; Huhn, S.; Szelke, M. *Chem. Ber.* **1956**, *89*, 2374. (b) Nagasawa, H. T.; Fraser, P. S.; Yuzon, D. L. *J. Med. Chem.* **1973**, *16*, 583. (c) Weib, R.; Wagner, K. G.; Hertel, M. *Chem. Ber.* **1984**, *117*, 1965. (d) Olah, G. A.; Olah, J. A. In *Friedel Crafts and Related Reactions;* Olah, G. A., Ed.; Interscience: New York, 1963. (e) Romea, P.; Urpi, F.; Vilarassa, J. *J. Org. Chem.* **1989**, *54*, 3209. (f) Simpon, J. M. *Synthesis* **1979**, 100. (g) Olah, G. A.; Olah, J. A.; Overchuck, N. A. *J. Org. Chem.* **1965**, *30*, 3373. (h) Prinzbach, H.; Schwesinger, R.; Breuninger, M.; Gallenkamp, B.; Hunkler, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 347. (i) Prinzbach, H.; Breuninger, M.; Gallenkamp, B.; Schwesinger, R.; Hunkler, D. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 348. Schafer-Ridder, M.; Brocker, U.; Vogel, E. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 228.

(15) (a) Olah, G. A. *Aldrich. Acta* **1979**, *12*, 43. (b) Wannagat, U.; Hohlstein, G. *Chem. Ber.* **1955**, *88*, 1839. (c) Olah, G. A.; Tolgyesi, W. S. *J. Org. Chem.* **1961**, *26*, 2319. (d) Olah, G. A.; Friedman, N.; Bollinger, J. M.; Lucas J. *J. Am. Chem. Soc.* **1966**, *88*, 5328. (e) Bott, K. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 148. (f) Bott, K. *Chem. Ber.* **1975**, *108*, 402. (g) Bachmann, G. B.; Michalowicz, W. *J. Org. Chem.* **1958**, *23*, 1800. (h) Olah, G. A.; Olah, J. A. *J. Org. Chem.* **1965**, *30*, 2386. (i) Doyle, M. P.; Whitefleet, J. L.; Bosch, R. *J. Org. Chem.* **1979**, *44*, 2923. (j) Owen, G. R.; Verheyden, J. P. H.; Moffat, J. G. *J. Org. Chem.* **1975**, *41*, 3010.

(16) (a) Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* **1977**, *42*, 561. (b) Inozemtsev, A. N.; Koshechko, V. G.; Pokhodenko, V. D. *Zh. Obshchei. Khim.* **1984**, *54*, 1160. (c) Bock, H.; Brahler, G.; Henkel, U.; Schleker, R.; Seebach, D. *Chem. Ber.* **1980**, *113*, 289. (d) Blankespoor, R. L.; Doyle, M. P.; Hedstrand, D. M.; Tamblyn, W. H.; Van Dyke, A. A. *J. Am. Chem. Soc.* **1981**, *103*, 7096. (e) Blankespoor, R. L.; Doyle, M. P.; Smith, D. J.; Van Dyke, A. A.; Waldyke, M. J. *J. Org. Chem.* **1983**, *48*, 1176. (f) Koshechko, V. G.; Inozemtsev, A. N.; Pokhpdenko, V. D. *Zh. Org. Khim.* **1983**, *19*, 751. (g) Boduszek, B.; Shine, H. J. *J. Org. Chem.* **1988**, *53*, 5142. (h) Gompper, R.; Polborn, K.; Strassberger, W. *J. Chem. Soc., Chem. Commun.* **1989**, 1346. (i) Tsubouchi, A.; Matsumura, N.; Inoue, H. *J. Chem. Soc., Chem. Commun.* **1991**, 620.

(17) (a) Scheinbaum, M. L.; Dines, M. B. *Tetrahedron Lett.* **1971**, 2204. (b) Chow, Y. L.; Iwai, K. *J. Chem. Soc., Perkin Trans. II* **1980**, 931. (c) Lee, G. H.; Lee, J. M.; Jeong, W. B.; Kim, K. *Tetrahedron Lett.* **1988**, *29*, 4437. (d) Brittelli, D. R.; Boswell, G. A., Jr. *J. Org. Chem.* **1981**, *46*, 312. (e) Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *J. Org. Chem.* **1992**, *57*, 4669.

(18) (a) Olah, G. A.; Shih, J. G.; Singh, B. P.; Gupta, B. G. B. *J. Org. Chem.* **1983**, *48*, 3356. (b) Olah, G. A.; Gupta, B. G. B. *J. Org. Chem.* **1980**, *45*, 3532. (c) Prakash, G. K. S.; Wang, Q.; Li, X. Y.; Olah, G. A. *New J. Chem.* **1990**, *14*, 791.

(19) Olah, G. A.; Gupta, B. G. B.; Narang, S. C. *Synthesis* **1979**, 274.

(20) Reents, W. D., Jr.; Freiser, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 271.

(21) Raghavachari, K.; Reents, W. D. Jr.; Haddon, R. C. *J. Comput. Chem.* **1986**, *7*, 266.

(22) (b) Bach, R. D.; Andrés, J. L.; Su, M.-D.; McDouall, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5768. for a study using OH^+ as a model electrophile (c) Bach, R. D.; Su, M.-D. *J. Am. Chem. Soc.* **1994**, *116*, 10103.

(23) SPARTAN, Version 2.0.0; Wavefunction Inc.; Irvine, CA, 1991.

(24) GAUSSIAN 92, Revision B, Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Steward, J. J. P.; Pople, J. A.; GAUSSIAN, Inc.: Pittsburgh, PA, 1992.

(25) Foresman, J. B.; Frisch, A. E. *Exploring Chemistry with Electronic Structure Methods: A Guide to Using GAUSSIAN;* Gaussian, Inc.: Pittsburgh, PA, 1993.

Table 1. *Total Energies (−Hartree) and Zero Point Vibrational Energies (kcal/mol) of Fragments and Structures **5−32** at Different Levels of Theory (**12−17** and **30** from ref 6)*

no.	HF/6-31G*// HF/6-31G*(ZPVE)[a]	HF/6-31G**// HF/6-31G**	MP2/6-31G*// MP2/6-31G*(ZPVE)[b]	MP2/6-31G**// MP2/6-31G**(ZPVE)[b]	MP4(SDTQ)/6-31G**// MP2/6-31G**
1	128.698 66 (7.9)	128.703 78	129.049 04	129.055 43	129.068 13
4 TS	128.695 56(5.4)	128.698 42	129.043 64	129.045 83	129.059 81
7	130.064 12(17.7)	130.071 89	130.399 91	130.416 28	130.441 31
8	129.955 34(15.6)	129.969 27	130.256 79	130.276 95	130.310 20
9	130.040 16(17.4)	130.050 15	130.367 47	130.385 66	130.415 69
10	130.025 73(17.2)	130.036 16	130.352 97	130.371 73	130.402 23
11 TS	129.924 25(12.6)	129.937 85	130.292 27	130.312 54	130.336 82
12	169.109 02(34.1)	169.115 78	169.581 84	169.614 02	169.656 42
13 TS	168.989 96(29.1)	169.005 09	169.470 20(28.3)	169.505 31(28.2)	169.548 27
14	168.995 52(29.9)	169.010 74	169.471 17(28.5)	169.505 96(28.3)	169.548 27
15	169.098 89(33.9)	169.11081	169.557 20	169.588 22	169.635 33
16	169.112 18(34.0)	169.213 92	169.568 32	169.600 66	169.647 30
17	169.131 91(34.7)	169.140 82	169.598 94	169.629 58	169.670 58
18	169.062 86(37.9)	169.082 93	169.536 17	169.576 93	169.620 03
19	169.057 39(37.7)	169.080 00	169.523 75	169.566 25	169.613 90
20	169.054 62(37.5)	169.077 35	169.519 93	169.562 52	169.610 23
21	169.018 78(37.0)	169.042 16	169.498 53	169.541 54	169.590 11
22 TS	168.990 41(36.1)	169.010 65			
23 TS	168.976 18(35.4)	168.998 55	169.457 21	169.500 35	169.552 69
24 TS	168.952 81(34.8)	168.974 89	169.442 62	169.484 77	169.502 16
25 TS	168.990 63(34.9)	169.016 24	169.468 39	169.514 38	169.530 30
26	169.113 98(40.0)	169.131 05	169.590 33	169.628 74	169.671 62
27	169.112 94(40.2)	169.129 97	169.588 15	169.626 43	169.669 76
28 TS	168.991 45(28.6)	169.006 09	169.468 41(28.1)	169.503 53(28.3)	169.547 61
29 TS	168.999 25(29.9)	169.013 88	169.496 79	169.530 92	169.573 56
30 TS	168.959 40(28.7)	168.977 47	169.443 62	169.481 68	169.524 37
31 TS	169.021 88(36.4)	169.043 46	169.508 18	169.551 06	169.593 66
32 TS	168.938 39(32.9)	168.962 90	169.442 23	169.485 80	169.527 68
CH_4	40.195 17(26.8)	40.201 71	40.332 55	40.364 63	40.388 64
NO^+	128.909 65(3.7)	128.909 65	129.242 59	129.242 59	129.260 93
CH_3^+	39.230 64(18.9)	39.236 30	39.325 38	39.346 63	39.368 91
CH_5^+	40.388 50(31.2)	40.406 16	40.531 86	40.575 00	40.599 80

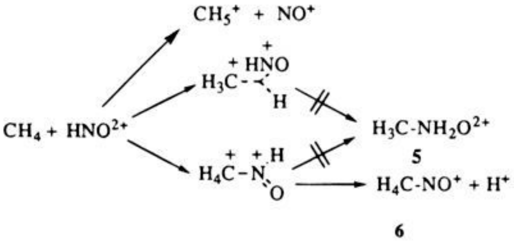
[a] Scaled by 0.893. [b] Scaled by 0.930. MP2 and MP4 in frozen core approximation.

1 ($C_{\infty}V$) **4** ($C_{\infty}V$)

Figure 1. MP2/6-31G** optimized parameters for **1** and **4** (bond lengths in Å).

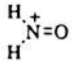
Optimization at all levels of theory employed in this study indicate that only the N-protonated form **1** corresponds to a stable minimum. The O-protonated form **2** and the bridged structure **3** are unstable and dissociate to the nitrosonium ion and a proton. The protonated nitrosonium ion is destabilized by 125.2 kcal/mol relative to NO^+. The kinetic barrier to deprotonation is only 2.7 kcal/mol at the highest level. The GAUSSIAN-2 method[26] predicts a proton affinity of −126.4 kcal/mol at 0° K and a kinetic barrier for the dissociation of 1.6 kcal/mol. (The experimental PA of methane (+130 kcal/mol at 0 K)[27] suggests, however, that HNO^{2+} cannot coexist with methane without undergoing facile proton transfer to form NO^+ and CH_5^+, *vide infra*.) The superelectrophilic protonitrosonium dication could be effectively stabilized by clustering in the condensed phase and, therefore, be in a thermodynamically more accessible region. The optimized minimum structure **1** and the TS **4** for the deprotonation are depicted in Figure 1.

The reaction of the protonitrosonium dication with methane takes place preferentially via transprotonation to give CH_5^+ and NO^+ No stable C−H insertion intermediate is found as N,N-diprotonated nitrosomethane is also unstable. All attempts to locate a stable isomer of $H_3C-NH_2O^{2+}$ **5** failed. Since all valencies of nitrogen are already filled before a H-shift can occur, the migrating proton from carbon cannot be accommodated on this center.

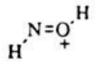


N-Deprotonation, however, leads to **6**, and the reaction would be able to continue as discussed by Schreiner *et al.*[12]

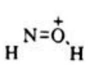
Hydride abstraction from methane by HNO^{2+}, on the other hand, would lead to the methyl cation and one of the following isomers of H_2NO^+.



7



9



10

The frontier orbitals of HNO^{2+} and thermodynamic considerations (ΔE_{7-9} = 15.8 kcal/mol; ΔE_{7-10} = 24.0 kcal/mol) suggest that **7** is most favored. The less stable O,O-diprotonated isomer **8** ($\Delta E_{7\text{-}8}$ = 80.1 kcal/mol) would not be expected due to the instability of HNO^{2+}. The rearrangement from **7** to the *trans*-isomer **9** requires an activation energy of 60.1 kcal/mol *via* the transition structure **11**. Structural details are as given in Figure 2.

---

[26] Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Phys. Chem.* **1991**, *94*, 7221.

[27] Lias, S. G.; Liebman, F. J.; Levin, R. D. *J. Phys. Chem. Ref. Data.* **1984**, *13*, 695.

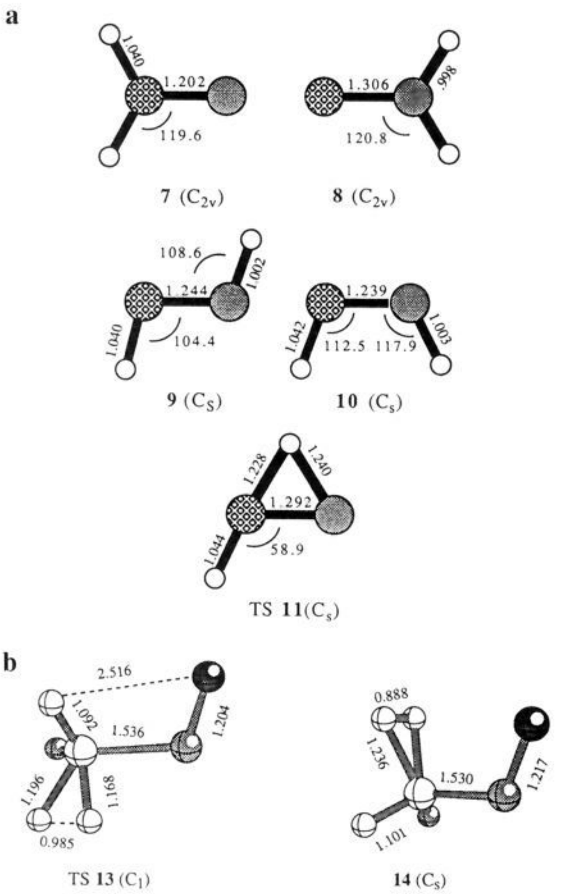
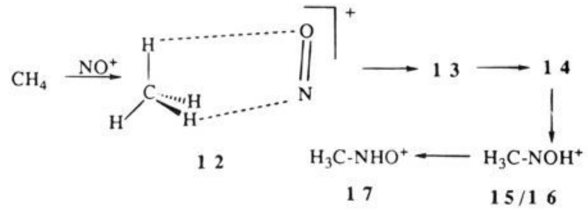


Figure 2. (a) MP2/6-31G** optimized parameters for **7**, **8**, **9**, **10**, and **11** (bond lengths in Å, angle in degree) and (b) MP2/6-31G** optimized parameters for **13** and **14** (bond lengths in Å, angles in deg) taken from ref 12a.

Comparison of the Reaction of Methane with NO$^+$ and HNO^{2+}. Schreiner et al.'s recent computational study[12] using the nitrosonium ion as a model electrophile concluded that the electrophile attacks carbon instead of a C−H bond.



It was proposed that NO$^+$ forms an initial complex with methane (**12**). This species rearranges subsequently to a five coordinate carbon species **14** (Figure 2a). The transition state **13** (Figure 2a) for this process (**12** → **14**) was located. The five-coordinate intermediate **14** was proposed to rearrange by migration of a proton to oxygen (**15**). Subsequent rotation of the N−O bond, to give **16**, and migration of the proton, to the nitrogen atom, gives **17**. The thus obtained N-protonated nitrosomethane (**17**) formally corresponds to the N-insertion product of NO$^+$ into the C−H bond.

In our study, three reaction paths were considered for the reaction of NO$^+$ as well as HNO^{2+} with methane.

(a) The hydride abstraction pathway in which the NO$^+$ first abstract a hydride and subsequently recombine with the methyl cation. In the case of HNO^{2+} it cannot only hydride abstract but also transfer a proton to methane.

$$NO^+ + CH_4 \longrightarrow HNO + H_3C^+ \qquad \Delta H_0 = 68 \text{ kcal/mol}$$

$$NO^+ + H^+ \longrightarrow HNO^{2+} \qquad \Delta H_0 = 128 \text{ kcal/mol}$$

$$HNO^{2+} + CH_4 \longrightarrow H_2NO^+ + H_3C^+ \qquad \Delta H_0 = -157 \text{ kcal/mol}$$

$$HNO^{2+} + CH_4 \longrightarrow NO^+ + CH_5^+ \qquad \Delta H_0 = -253 \text{ kcal/mol}$$

Figure 3. Energetics of the hydride abstraction from methane by the nitrosonium and protionitrosonium ions and proton transfer.

(b) The direct attack of the electrophile on the carbon atom with subsequent rearrangement to the product, as suggested by Schreiner *et al.*

(c) The attack of the electrophile on a C−H bond followed by concerted insertion to give the product.

Abstraction-Recombination and Proton Transfer. The thermodynamics of the abstraction recombination mechanistic path are as shown in Figure 3.

With NO$^+$ as electrophile the formation of the methyl cation and HNO is energetically unfavorable by 68 kcal/mol based on experiment.[28] The corresponding reaction with protosolvated HNO^{2+} is favored by −157 kcal/mol. The endothermic protonation of NO$^+$, however, still has to be taken into account (126 kcal/mol with G-2 method). The overall reaction would still be favored by −31 kcal/mol. The kinetic barriers for the hydrogen abstraction processes were not determined. The recombination of the methyl cation can, in principle, occur with H_2NO^+ **7** or an isomer of HNOH$^+$ **9**, **10**. The product of the reaction $CH_3^+ + $ **7** leads to a stable structure **18**. The isomers **19**, **20**, and **21** correspond to the reaction of the methyl cation with **8** and **9**. The fourth isomer of H_4C-NOH^{2+}, (that can be derived from the rotation around the C−N and the N-O bond), is unstable at correlated levels and converges to **21**. Structural details of the MP2(FC)/6-31G** optimized structures are as given in Figure 4.

The recombination of **7** with the methyl cation leads to **18** and the transition state (**22**) for this process was calculated. IRC calculations rule out the possibility that this TS corresponds to the insertion of HNO^{2+} into a C−H bond of methane. Structural details are as given in Figure 5.

The intermediate **18** can then react to give N,O-diprotonated nitrosomethane, *via* a proton shift from carbon to oxygen (TS **31**), followed by an H-shift from oxygen to nitrogen (TS **32**). Alternatively, a direct shift of the proton from carbon to nitrogen (TS **25**) leads to the same product (see a more detailed discussion below).

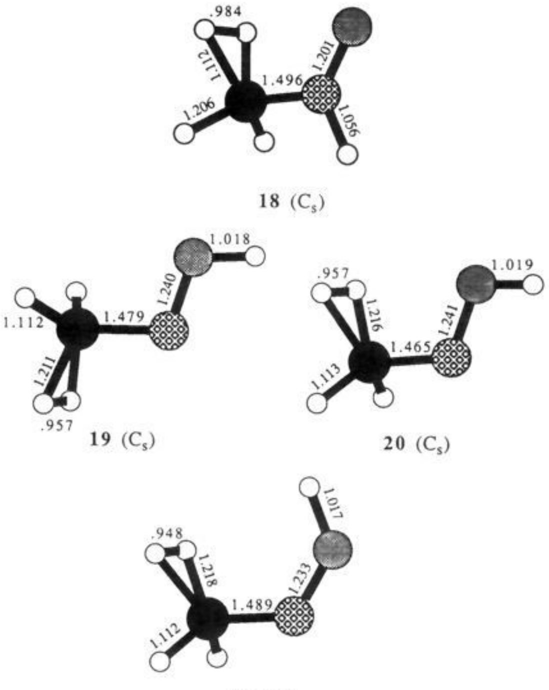
In order for the recombination to occur to give **19**, **20**, or **21**, **7** has to rearrange to **9** with a calculated activation energy of 60.1 kcal/mol.

Two transition states **23** and **24** were located for the subsequent insertion into the N−H bond ($\Delta E_{19,23} = 36.1$ kcal/mol; $\Delta E_{19,24} = 67.2$ kcal/mol) (Figure 6). The structures are energetically different, but lead to the same products, as it was demonstrated with IRC calculations. It should be noted that these transition states, involving three different types of atoms, do not correspond to an insertion of NOH^{2+} into a C−H bond of methane, as NOH^{2+} is not a stable species.

Proton shift from carbon to nitrogen leads then to diprotonated nitrosomethane **26** and **27**. The transition state **25** is located 49.7 kcal/mol above **19**. Structural details of the **25** are given in Figure 7.

---

[28] *CRC Handbook of Chemistry and Physics*, 71st ed.; Lide, D. R., ed.; CRC Press; Boca Raton: FL, 1990.



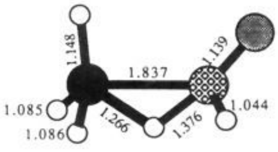
18 (C_s)

19 (C_s)

20 (C_s)

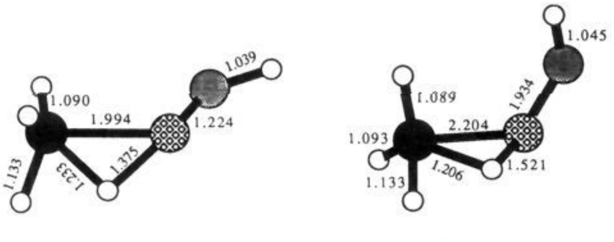
21 (C_s)

Figure 4. Selected MP2/6-31G** optimized parameters for **18, 19, 20**, and **21** (bond lengths in Å).



TS **22** (C_1)

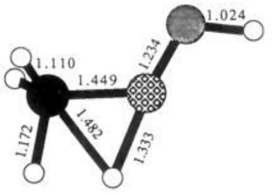
Figure 5. Selected MP2/6-31G** optimized parameters for **22** (bond lengths in Å).



TS **23** (C_1)

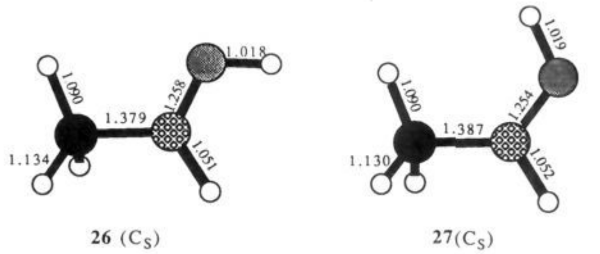
TS **24** (C_1)

Figure 6. Selected MP2/6-31G** optimized parameters for **23** and **24** (bond lengths in Å).



TS **25** (C_S)

Figure 7. Selected MP2/6-31G** optimized parameters for **25** (bond lengths in Å).



26 (C_S)

27(C_S)

Figure 8. Selected MP2/6-31G** optimized parameters for **26** and **27** (bond lengths in Å).

TS **28** (C_s)

TS **29** (C_s)

Figure 9. Selected MP2/6-31G** optimized parameters for **28** and **29** (bond lengths in Å).

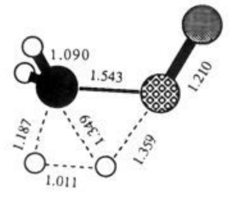
Diprotonated nitrosomethane can exist in two isomeric forms **26** and **27** ($\Delta E_{26,27}$ = 1.4 kcal/mol, $\Delta E_{18,26}$ = 30.3 kcal/mol, $\Delta E_{19,26}$ = 38.5 kcal/mol) that are shown with the structural details in Figure 8.

Hydride abstraction−recombination between CH_4 and HNO^{2+} is less likely since HNO^{2+} can proton transfer to give CH_5^+ and NO^+. In fact this reaction was found (Figure 3) to be highly exothermic by 253 kcal/mol. This is 96 kcal/mol more exothermic than hydride abstraction. Thus even if NO^+ is protolytically activated, it would preferentially transfer the proton to CH_4 to give CH_5^+.

Direct Attack on Carbon. The direct attack of NO^+ on carbon was proposed by Schreiner *et al.*,[12] followed by a cascade of rearrangements to the formal insertion product. The overall kinetic barrier through **13** for this process was calculated to be 57.6 kcal/mol at CISD+Q(FC)/TZ2P//MP2/6-31G**. None of the subsequent transition states leading to protonated nitrosomethane were reported. However, the barrier for the alternative loss of H_2 from **14** turns out to be only 2.8 kcal/mol.

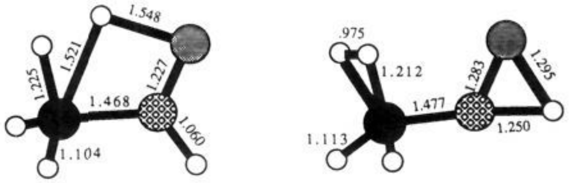
The area around **14** was subsequently explored and the transition state for the "through space" hydride shift, from carbon to oxygen **28**, was located. The energetics of the two crucial points, defining the kinetic stability of the postulated intermediate **14** (e.g., **13** and **28**), was then elucidated at MP4SDTQ/6-31G**//MP2/6-31G** + ZPE//HF/6-31G** level. Without ZPVE it turns out that the kinetic stability of **14** toward dissociation *via* **13** is less than 0.1 kcal/mol. The stability is 0.4 kcal/mol toward a H-shift *via* **28**. Taking the ZPE (scaled by 0.893) into account, it turns out, that the TS **13** and TS **28** are actually stabilized compared to **14** by 0.8 and 0.9 kcal/mol, respectively. If MP2/6-31G* frequencies (scaled by 0.930) are used, the energy differences between the TS and the minimum **14** are 0.2 kcal/mol and <0.1 kcal/mol. The potential energy surface around **14** is very flat. Once this barrier is overcome, the O-protonated nitrosomethane is obtained which can rearrange to **17**. The barrier for the rotation around the N-O bond, to bring the proton in a suitable position for the last shift, is expected to be low and was not considered. The barrier for the subsequent O-N hydrogen shift *via* **29** was found to be 46.3 kcal/mol. The optimized geometries for **28** and **29** are shown in Figure 9.

A second pathway which involves the direct hydride shift from carbon to nitrogen exists in principal for the rearrangement of **14** to protonated nitrosomethane **17**. The transition state **30**, involving a 4c−4e bonding, that was calculated for this process, turns out to be the TS previously proposed for the direct insertion



TS **30** (C_s)

Figure 10. Selected MP2/6-31G** optimized parameters for **30** (bond lengths in Å).



TS **31** (C_s) TS **32** (C_s)

Figure 11. Selected MP2/6-31G** optimized parameters for **31** and **32** (bond lengths in Å).

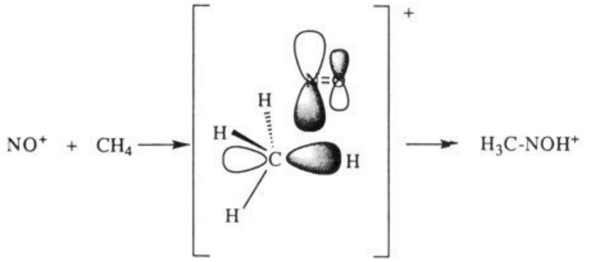
of NO^+ into the C−H bond. This structure is located 14.7 kcal/mol above the TS **28** for the H-migration from C to N. The structure **30** is 14.6 kcal/mol above the TS **13**.[12a] Thus the hydride shift from carbon to oxygen through TS **28** is more favorable than the hydride shift from carbon to nitrogen through TS **30**. The structural details of **30** are given in Figure 10.

Next we considered the theoretical attack by superelectrophilic HNO^{2+} directly on carbon. The transition state, that corresponds to protonated TS **13** for this process, converges to **19** when protonated on oxygen and dissociates upon N-protonation. We were unable to find an alternative TS for the direct attack of HNO^{2+} on methane to form **18**. This might be due to the dramatically enhanced reactivity of this electrophile compared to NO^+. Assuming that **18** is formed, the formal insertion product **26/27** can be reached from **18** *via* three different ways: (a) direct proton shift from carbon to oxygen to give **27**; (b) proton shift from nitrogen to oxygen to give **20**, followed by a proton shift from carbon to nitrogen to give **26**; (c) deprotonation−reprotonation (which is not be considered in our discussion).

The barrier for process (a) was calculated to be 15.0 kcal/mol involving the transition state **31**. The first H-shift from nitrogen to oxygen in process (b) proceeds through TS **32** *via* a barrier of 53.0 kcal/mol. The subsequent H-shift from carbon to nitrogen involves again **25** as transition structure and a barrier of 49.7 kcal/mol. Path (b) is therefore energetically highly unfavorable. The kinetic stability of **18** is still questionable since the TS for its decomposition remains unknown. Structural details of **31** and **32** are given in Figure 11.

Direct Insertion into the C−H Bond. The transition state for the direct insertion of the nitrosonium ion into the C−H bond was considered previously.[12] An IRC calculation revealed that the minima connected to this transition state correspond to the five coordinate carbon species **14** and protonated nitrosomethane. Due to the kinetic instability of **14**, it is suggested, that this structure may not be important, either for the reaction mechanism, in which the nitrosonium ion inserts directly into the C−H bond, or as an alternative rearrangement path involving **14**.

As it was demonstrated above, the overall reaction of NO^+ with methane can be described as an asynchronous insertion of the nitrosonium ion into the C−H bond involving the migration of the proton from oxygen to nitrogen. Energetically the transition states TS **28** and TS **13** and the structure **14** are almost same. This behavior can be rationalized as an interaction of the LUMO of the NO^+ and the C−H bond of CH_4. Since the electron density on carbon is higher due to the greater electronegativity, it is not surprising that the bigger coefficient of the LUMO on nitrogen approaches preferentially the carbon center. However, the process is orbital-symmetry forbidden if it occurs in a concerted fashion in C_s symmetry but tilting of NO^+ could remove the unfavorable interaction. At the level of theory employed, the proton is transferred to oxygen without the formation of an intermediate.



This reactivity is thus an extension of the general 3c−2e bonding concept, due to the modified nature of the attacking orbital.

The direct insertion of the protionitrosonium dication seems to occur in a similar fashion although, the intermediate **18** is rather stable toward the migration of the proton. The still elusive transition state for the decomposition (e.g., protonated **13**) is, however, essential for a further understanding of this system. As it was shown above, the more favorable pathway for the reaction of HNO^{2+} with methane is proton transfer and hydride abstraction.

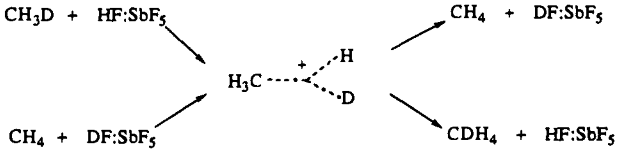
The reaction of NO^+ with methane is thus thermodynamically unfavorable, unless the electrophile is activated by protonation or Lewis-acid coordination (Figure 3). However, this is unlikely to take place in the presence of excess methane due to the much higher proton affinity of methane compared to NO^+. The activated protonitrosonium dication reacts with methane preferentially via proton transfer. However, under considered hydride abstraction pathway two different isomers of H_2NO^+ and methyl cation are formed. This system can recombine through a TS **22** involving a 3c−2e bond to form the formal insertion product into the C−H bond.

To reiterate NO^+ can interact with methane *via* an orbital-symmetry-forbidden unsymmetrical 4c−2e interaction between the LUMO of the electrophile and the electron density of the C−H bond. The orientation of the attack is such that the nitrogen interacts on the side of carbon. The N−O bond is aligned with the CH bond, and the oxygen is oriented toward the hydrogen center. The reason for this is the unsymmetrical nature of the attacking orbital as well as the electron distribution of the C−H bond and not a "nonbonded lone pair" on carbon as originally visualized by Schreiner *et al.*[12] (the reorganization of tetrahedral mthane to planar methane containing a nonbonded electron pair is energetically prohibitive). It was shown that the postulated intermediate is in fact a transition state. The ZPE was found to be slightly higher than the ZPE of the crucial transition states points **13** and **28**.

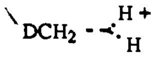
There seems to be a similar pathway for the reaction of superelectrophilic HNO^{2+}, although the kinetic stability of the intermediate **18** could not be defined. The hydride abstraction pathway for NO^+ is thermodynamically even less favored than the C−H insertion reaction and thus is expected to be even less likely to occur.

Whereas ambident polarizable electrophiles, such as NO^+ react with methane in the discussed more complex manner, this is not the case for reactive hard electrophiles, such as H^+ (D^+), R^+, HO^+, F^+, and the like.

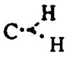
Experimental evidence for the protonation of alkanes under highly acidic (superacid) conditions was first reported by Olah and Lukas[29a,b] and Hogeveen and Bickel.[29c] The reactivity of covalent C−H and C−C single bonds of alkanes in superacids is due to the donor ability of σ-bond electron pairs via 3c−2e bond formation. The suggested[30] transition state for protolytic ionization of hydrocarbons is nonlinear. Such 3c−2e interactions in carbocations generally tend to be nonlinear (even in sterically crowded cases) in nature. Evidence for this mode of protolytic attack was obtained from concurrent deuterium−hydrogen exchange.[31] Monodeuteromethane was reported to undergo H−D exchange in $HF-SbF_5$ via hypercoordinate isotopic methonium ions without any detectable side reactions. Identical results were observed when liquid methane was reacted with $DF-SbF_5$.



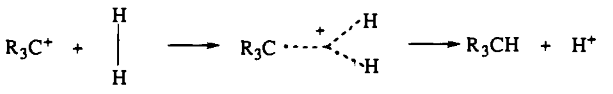
It should be emphasized that because of the very low barrier for bond to bond rearrangement in CH_4D^+ proton elimination can alternatively take place from



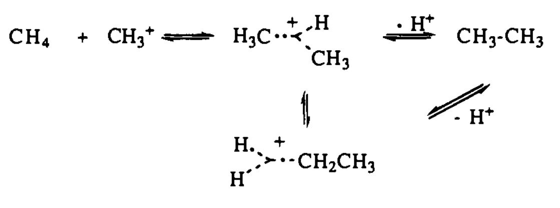
involving a more symmetrical



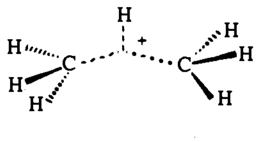
bond. The reverse reaction of the protolytic ionization of hydrocarbons to carbenium ions, that is, the reaction of carbenium ions with molecular hydrogen[32] can be considered as alkylation of H_2 by the electrophilic carbenium ion through a pentacoordinate carbonium ion. Indeed Hogeveen and Bickel have experimentally reacted stable alkyl cations in superacids with molecular hydrogen to hydrocarbons.[32]

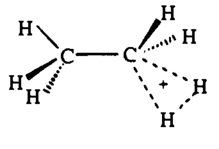


Considering the alkylation of methane with alkyl cations, the prototype reaction is the insertion the methyl cation into the methane.



As mentioned before facile bond to bond rearrangement is again possible through low barriers which could result in proton elimination from an isomeric ion. The $C_2H_7^+$ intermediates are identical with C−H or C−C bond protonated ethane. Protonated ethane, $C_2H_7^+$, has been studied both experimentally and theoretically. The kinetics and equilibrium of ethyl cation hydrogenation[9] 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 ethanes.

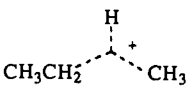


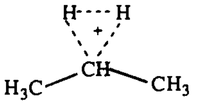


Lee *et al.* have indeed succeeded to experimentally observe the two forms of $C_2H_7^+$ by IR in the gas phase.[8]

Theoretical calculations[33] at the MP4(SDTQ)/6-31G**// MP2(FULL)/6-31G** level show that C−C protonated ethane is 4.4 kcal/mol more stable than C−H protonated ethane although at even higher levels the differences may diminish. Whereas the free methyl cation cannot be generated under long lived conditions even in superacid solutions, the strongly polarized $CH_3F{\cdot}SbF_5$ complex is a powerful alkylating agent. In its reaction with methane ethane is formed, *albeit* in low yield.[34] Using $CD_3F{\cdot}SbF_5$ in the reaction with CH_4, the hydride transfer product CD_3H predominates but some CH_3CD_3 was also formed.[34]

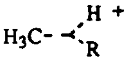
In the reaction of methane with the $C_2H_5F{\cdot}SbF_5$ complex similarly propane is formed, besides major hydride transfer (*i.e.*, C_2H_5D) and higher alkylates resulting from $C_3H_7^+$ ions.[34] These results are in accord with *ab initio* theoretical studies[35] of protonated propane, $C_3H_9^+$ intermediates.



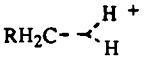


The C−C protonated structure was found to be only 1 kcal/mol more stable than the the C−H protonated structure at the HF/4-31G//HF/4-31G level.

Alkyl cations of course are of nonambident nature and their interaction with methane clearly takes place on the C−H bond and not on the carbon. Bond to bond proton migration in the intermediate carbonium ion is, however, a low energy process and proton elimination to give the alkylated product can take place not only from the



but from more symmetrical forms.



A recent theoretical study by Bach et al.[22] reported the transition states for the OH^+ insertion into a C−H bond of alkanes. It was found that the reaction occurs without the

---

(29) (a) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 2227. (b) Olah, G. A.; Lukas, J. *J. Am. Chem. Soc.* **1967**, *89*, 4739. (c) Hogeveen, H.; Bickel, A. *Chem. Commun.* **1967**, 635.

(30) Olah, G. A. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 173.

(31) (a) Olah, G. A.; Klopman, G.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1969**, *91*, 3261. (b) Olah, G. A.; Shen, J.; Schlosberg, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 3831.

(32) Hogeveen, H.; Bickel, A. F. *Recl. Trav. Chim. Pays-Bas* **1967**, *86*, 1313.

(33) Carneiro, J. W. M.; Schleyer, P. v. R.; Saunders, M.; Remington, R.; Schaefer, H. F.; Rauk, A.; Sorensen, T. S. *J. Am. Chem. Soc.* **1994**, *116*, 3483.

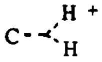
(34) Olah, G. A.; Demember, J. R.; Shen, J. *J. Am. Chem. Soc.* **1973**, *95*, 4952.

(35) Radom, L.; Poppinger, D.; Haddon, R. C. In *Carbonium Ions V*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; p 2329.

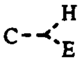
formation of an intermediate *via* transition structures that have 3c−2e bonds between the electrophile and the aliphatic C−H bond.[22] Our investigation[1] of F^+ with methane also led to C−H bond inserted product CH_3FH^+ as the global minimum.

Conclusions

Schreiner, Schleyer, and Schaefer recently[12b] reiterated their claim "We find that neither the insertion nor the addition of an electrophile to methane proceeds through an attack of the electrophile onto the electron density of one of the methane C−H bonds. Instead, methane distortion to C_s symmetry occurs and carbon is attacked directly" (i.e., on the nonbonded electron pair). They reached this conclusion based on a theoretical study of the reaction $CH_4 + NO^+$. Our reinvestigation of their hypothetical $CH_4 + NO^+$ reaction showed that indeed the reaction path is more complex than simple C−H bond insertion, but the attack on carbon is a consequence of the ambident electrophilic nature of NO^+. With superelectrophilic NOH^{2+} proton transfer to methane is the preferred pathway although less likely paths were also considered. With "hard" electrophiles as D^+ (H^+), CH_3^+, $C_2H_5^+$, OH^+, and F^+ methane preferentially reacts via 3c−2e C−H bond insertion path as previously suggested by Olah for the electrophilic substitution of methane. As all electrophilic reactions of methane go through a five coordinate carbocation (methonium ion) intermediate which involve two electron three center bonds the question of C−H bond insertion vs attack on carbon involving a simultaneous shift of a proton into a C−H bond does not represent any fundamental change in the mechanism of these reactions. Bond to bond shifts in hypercoordinate carbocations are generally facile and the higher stability of the more symmetric

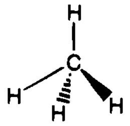


bond compared with an unsymmetrical

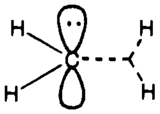


bond may account for preference for the former to be involved in the proton elimination step leading to substituted products.

As important as theoretical studies are in the study of chemical reactions, it is necessary to maintain relevance with experimental facts. Tetrahedral methane contains no nonbonded electron pair. Only through flattening (an extremely energetic, more than 100 kcal, process) can methane rearrange to acquire such C_s symmetry form (involving two 2e−2c bonds, a 2e−3c bond, and a perpendicular p-orbital containing the nonbonded electron pair).



tetrahedral methane



flat methane (C_s) with non-bonded electron pair

Even with the consideration of compensating factors involvement of a nonbonded electron pair in electrophilic reactions of methane is improbable for prohibitive energetic reasons unless strongly assisted by bipolar interactions as in the case of the hypothetical reaction with NO^+.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

JA940827R