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Mechanism of the Oxidation of Alkanes with Nitronium Tetrafluoroborate in Acetonitrile. Evidence for a Carbenium Ion Intermediate

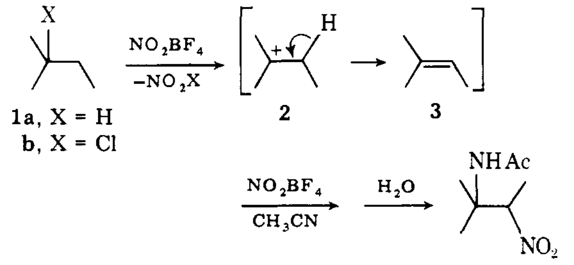
Sir:

It is becoming increasingly evident that electrophilic attack at a carbon σ bond is an important reaction despite the low reactivity often associated with completely saturated molecules. Since σ-bond cleavage via this type of mechanism has only recently been noted,[1] the scope and utility of this class of reactions remain to be defined. Protolytic reactions of alkanes by superacids,[2] nitration by nitronium salts,[3] Lewis acid catalyzed halogenation by elementary halogen,[4] hydroxylation with dry ozone,[5a] and oxyfunctionalization with ozone and hydrogen peroxide in superacid media[5b] are among the more interesting transformations involving σ bonds that have been reported to date.

Early efforts to oxidatively functionalize hydrocarbons frequently utilized the nitrogen oxides. Both solution and gas-phase chemistry at high temperatures often favored free-radical reactions.[6] At lower temperatures, heterolytic σ-bond cleavages are observed with NO_2PF_6 in methylene chloride-sulfolane solvent.[3] For example, the oxidation of ethane afforded both nitroethane and nitromethane, while adamantane afforded nitroadamantane in about 10% yield. In general, the heterolytic cleavage of carbon-hydrogen and other σ bonds requires a highly reactive electrophile, which is commonly generated in situ under harsh conditions. As a consequence, yields are often low and complex mixtures of products common.

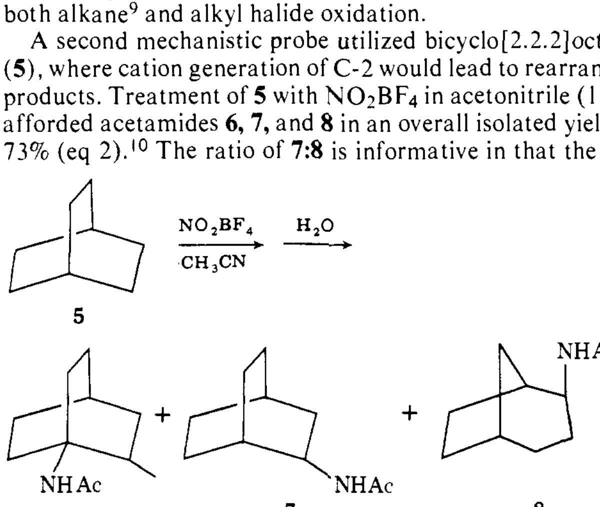
We recently demonstrated that the reaction of alkyl halides and alkyl ethers with NO_2BF_4 in acetonitrile resulted in efficient abstraction of halide or alkoxide ion and formation of a nitrilium ion, which afforded the corresponding acetamide upon hydrolysis.[7a] Mechanistic studies[7b] with optically active *exo-* and *endo-*2-bromonorbornane provided convincing evidence that the reaction of NO_2^+ with the nonbonding electron pairs of the halogen forms a nitronium complex that effects heterolysis of the C–X bond. In the present study, we provide conclusive evidence that a related mechanism is operating in alkane oxidation. The reaction of selected hydrocarbons with NO_2BF_2 results in a formal hydride ion abstraction, leading to the formation of transient carbenium ion intermediates.

We have noted that tertiary alkyl halides frequently afforded highly substituted thermodynamically stable alkenes as intermediates upon reaction with NO_2BF_4. This observation prompted a comparative study between halide and hydride abstraction. A common carbenium ion (**2**) is implicated in the oxidation of 2-methylbutane (**1a**) and 2-chloro-2-methylbutane (**1b**). *Both* compounds afforded 2-acetamido-2-methyl-3-nitrobutane (**4**) (55%) as the major product. The vicinal nitroacetamide **4** was identical in every respect with the product obtained from the electrophilic addition of NO_2BF_4 to trimethylethylene (**3**) in acetonitrile.[8] The reaction sequence given in eq 1, involving alkene formation from a cationic species, provides a rational explanation for these observations. These data cannot exclude a concerted elimination from a complex consisting of **1b** and NO_2^+. Significantly, the results do strongly suggest that parallel mechanisms are operating in both alkane[9] and alkyl halide oxidation.



1a, X = H
b, X = Cl
2
3
4
(1)

A second mechanistic probe utilized bicyclo[2.2.2]octane (**5**), where cation generation of C-2 would lead to rearranged products. Treatment of **5** with NO_2BF_4 in acetonitrile (16 h) afforded acetamides **6**, **7**, and **8** in an overall isolated yield of 73% (eq 2).[10] The ratio of **7**:**8** is informative in that the sol-



5
6
7
8
65 : 22 : 13
(2)

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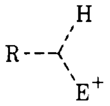
volysis of bicyclo[2.2.2]octyl-2-*p*-bromobenzenesulfonate has been reported to afford a 65:35 ratio of unrearranged (**7**) to rearranged products (**8**).[11] The formation of a preponderance of the tertiary bridgehead cation is significant in that it provides a clear example when σ nucleophilicity is more important than the stability of the resulting carbenium ion in electrophilic attack at a C–H bond. The importance of σ basicity in this electrophilic addition is further exemplified by the facile oxidation of adamantane (**9**), which is readily converted (5 h) to *N*-(1-adamantyl)acetamide in 88% yield. In contrast, norbornane (**10**) gave only *N*-(*exo*-2-norbornyl)acetamide (78%), with no evidence of involvement of the highly destabilized 1-norbornyl cation. The relative ease of hydrogen transfer from the bridgehead positions of **5, 9,** and **10** does reflect the stability of the incipient tertiary cations.[12]

Rate-limiting hydrogen transfer to NO_2^+ is further supported by an observable primary deuterium kinetic isotope effect. Previously reported oxidative hydride transfer reactions have exhibited a k_H/k_D range from 1.6 to 11.7 for organic substrates.[13] The isotope effect is expected to be largest when hydrogen is half transferred in a linear transition state, where the summation of vibrational energy differences will be maximized (eq 3). Oxidation of 1-adamantane-d_1 with NO_2BF_4 in acetonitrile was accompanied by a kinetic isotope effect of 1.86 at 20 °C. The same experiment with nitrosonium tetrafluoroborate resulted in a k_H/k_D of 2.30 at 82 °C.[14] The higher temperature for $NOBF_4$ was required because of the substantially diminished efficacy of NO^+ as an electrophilic reagent in this solvent system.[15] Both salts are most likely highly solvated by the donor solvent, which both increases the selectivity of the oxidant and stabilizes carbenium ion formation.

$$R{-}H + E^+ \rightarrow [R{-}{-}{-}H{-}{-}{-}E]^+ \rightarrow R^+ + H{-}E \quad (3)$$

Our data demonstrate that the nitronium ion is a fairly discriminant oxidant (in acetonitrile), whose reactivity is influenced by both σ basicity and incipient carbenium ion stability. This selectivity would tend to exclude a reactant-like transition state. The formation of bridgehead acetamide **6** as the major product from **5** argues against a late transition state with appreciable carbenium ion character. In order to explain the relatively small k_H/k_D, we therefore invoke the nonlinear transition state **11.** Such a "triangular"[3,16] transition state would be expected to exhibit a smaller iostope effect, since less energetic bending vibrational modes may be the major contributor to the observed isotope effect. Significantly, kinetic isotope effects for hydrocarbon nitration with nascent protonated NO_2^+ ($O{=}N^{2+}{-}OH$) generated in concentrated HNO_3/H_2SO_4 are also small ($k_H/k_D = 2.0$).[17] This suggests that similar transition states may be involved. Olah initially suggested that nitronium ion nitration of alkanes with NO_2PF_6 proceeds via a three-center bond transition state (**11**) involving the electron pair of the σ C–H bond and an empty p orbital of the bent nitronium ion. The apparent dichotomy between these studies,[3,17] which afford nitroalkanes (nitration), and the present results may be attributed to our use of acetonitrile solvent, a very efficient carbenium ion trap. Control experiments have rigorously excluded nitroalkanes as the kinetic product in acetonitrile.[18,19]



11

In summary, this study has provided the most effective method to date for functionalizing hydrocarbons with nitronium salts. This is the first example of rate-limiting hydrogen transfer to a nitronium salt that affords a carbenium ion intermediate. Evidence is presented that the transition state closely resembles that for nitration with the donor solvent strongly influencing cation formation.

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(9) In a typical experiment, 10 mmol of substrate in 20 mL of dry CH_3CN was added to 13 mmol of NO_2BF_4 under a nitrogen atmosphere. After the solution was stirred at room temperature for 1 to 16 h, the reaction was quenched by the addition of water and the acetamide product was isolated by simple extraction.

(10) The ^{13}C and ^1H NMR and mass spectral data for **6, 7,** and **8** were consistent with their assigned structures. In addition, **7** and **8** were converted to their respective quarternary ammonium hydroxides and subjected to Hoffmann pyrolysis. Isolation of bicyclo[2.2.2]oct-2-ene and bicyclo[3.2.1]oct-2-ene confirmed the skeletal structures of **7** and **8.** All other acetamides reported were independently synthesized.

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(14) The adamantane (7.6% d_0, 92.4% d_1) was purified by preparative GLC and treated with NO_2BF_4 (1.1 equiv) for 30 min. Experiments with $NOBF_4$ were performed at reflux. In the latter reaction the yield of *N*-(1-adamantyl)acetamide is essentially quantitative if allowed to react for 4 h.

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(18) The formation of 1-nitroadamantane (<1%) could not be detected by GLC during the oxidation of adamantane. 2-Nitropropane, 2-methyl-2-nitropropane, and 1-nitroadamantane were found to be inert to NO_2BF_4 in CH_3CN at 25 °C for 1.5 h. Equimolar mixtures of 2-methyl-2-nitropropane and *tert*-butyl bromide showed >95% reaction of the bromide with no measurable loss of nitroalkane. Inclusion of $HClO_4$ effected a 32% loss of nitro compound. Equimolar mixtures of 1-nitroadamantane and adamantane (or 1-bromoadamantane) and 1.3 equiv of NO_2BF_4 in CH_3CN at 25 °C showed <20% loss of nitroadamantane in 5.5 h. Complete reaction of adamantane (or its bromide) and formation of the corresponding acetamide were noted.

(19) We have also observed this dichotomy with NO_2OCOCF_3, formed in situ by the reaction of NH_4NO_3 and trifluoroacetic anhydride in trifluoroacetic acid. Cyclooctane gave the trifluoroacetate, the nitrate, and nitrocyclooctane.

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Primary Processes in the Photochemistry of $Co(NH_3)_5Cl^{2+}$

Sir:

Extensive photochemical studies of Co(III) complexes have been carried out.[1] In particular the charge-transfer photo-

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