J. Am. Chem. Soc. 1990, 112, 3225-3226

Table II. Variation in the Computed Hydrogen Free Valence Index (f_H) along the Photodissociation Path of HNO ($^3A''$)^a → H + NO

r_{NH}, Å	f_H	r_{NH}, Å	f_H
0.6	0.033	1.6	0.866
0.8	0.058	2.0	0.974
1.0	0.090	4.0	0.999
1.2	0.154	8.0	1.000
1.4	0.606	10.0	1.000

[a] The dissociation in the $^1A''$ state also shows similar behavior.

in their lowest $^{1,3}A''$ states. The excited-state calculations have been carried out by applying a variant of the orthogonal gradient method of orbital optimization[11-16] in an INDO-MCSCF framework. The method has been shown to perform well in the calculation of molecular structure in excited states.[17,18] The quantum chemical valence parameters (bond order, free valence, etc.) have been calculated by adopting[23,24] definitions proposed by Mayer.[19-22]

Figure 1 shows the section of the potential energy surface along the reaction path for the isomerization of HNO to NOH in the lowest $^3A''$ state. The transition state has been located by optimizing the two bond lengths for different values of the HNO angle till the maximum is reached.

The left well corresponds to N–O–H and the right one to H–N–O in the lowest $^3A''$ state. The computed energies, bond order, and structural parameters of each are reported in Table I. The transition state corresponds to a triangular arrangement of the H, N, and O atoms. The barrier height from the reactant (HNO) side is 53 kcal/mol. From the product side, it is 50% less. Figure 2 displays the profiles of the computed N–H and O–H bond orders along the reaction path. In each case, the plot exhibits a point of inflection at $\theta = \theta_c$ (critical HNO angle), 55.5°. At this point, both the N–H and O–H bond orders are approximately 0.5, while beyond this point, N–H bond order rapidly falls to 0 and O–H bond order registers a sharp rise to the value 1. We conjecture that the points of inflection noted in the BO plots may be identified with the actual saddle point revealed in the energy profile (Figure 1). A close examination shows that the inflection points in Figure 2 and the saddle point in Figure 1 both occur at $\theta_c \sim 55.5$. The structural parameters and quantum chemical bond order indices of the transition state are recorded in Table I. It is heartening to note that an identical transition-state structure is predicted by the two methods. In the example just discussed, the process involves the breaking and simultaneous making of a single bond. However, even for a simple bond-breaking process, the BO profile may often reveal identical features. As an example, we consider the behavior of the N–H bond order as HNO photochemically dissociates into H + NO, in the lowest $^3A''$ state. Here also, the plot of B_{NH} against R_{NH} (Å) (HNO angle and N–O length have been optimized for each value of R_{NH}) shows the occurrence of a similar inflection point (Figure 3). We have observed that the corresponding energy profile (figure not shown here) is rather flat around the transition point, making it difficult to trace the bond-breaking point.[25] Similar features have been noted in an ab initio CI calculation[26] of the potential energy surfaces of H–N–O in $^{1,3}A''$ states. The BO method, on the other hand, locates the bond-breaking point rather sharply. As a further check on the wave function, we have reported the computed free valence index of the H atom for different points on the reaction path (Table II). For large values of N–H distance, the free valence index of the H atom smoothly becomes unity, as it should. Similar behavior has also been noted in the photoisomerization of X–N–O-type molecules into N–O–X in the lowest A states (singlet as well as triplet) and in the photochemical dissociation of X–N–O → X + NO. The details of these calculations will be published shortly.[27]

Very recently, Lendvay[28,29] has studied the behavior of BO and valence indices in some chemical reactions (thermal) involving metathesis. These studies tend to confirm the validity of the bond order conservation principle invoked in BEBO calculations. The BO plots, however, reveal lack of coincidence of the inflection point in the BO profile with the saddle point in the corresponding energy plot in some unsymmetrical atom-transfer reactions. We feel that one of the key factors that determines the extent of this coincidence is the similarity between the bond being broken and formed. The significance of Hammond's postulates is worth investigating in this connection. A closer analysis of these phenomena may lead to a better understanding and wider generalization of the basic tenets of the BEBO method.

Acknowledgment. We sincerely thank the CSIR, Government of India, New Delhi, for providing computational facilities [Grant No. 5(136)188-EMR-II] and awarding a fellowship to D.K.M. We acknowledge partial financial support received from the National Bureau of Standards, U.S.A. [Grant No. NBS(a-004)].

Cubyl Cation[1]

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Everything about cubyl cation seems unfavorable.

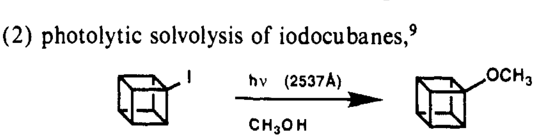
1. The geometry about the cation carbon is very far from the preferable planar arrangement. A planar cation has a pyramidalization angle of 0 °C; if the cubyl cation carbon had the same geometry as a carbon in the parent hydrocarbon its pyramidalization angle would be 35°.[2] Even the 1-norbornyl cation is "flatter"; its pyramidalization angle would be 24° if the geometry were the same as at the norbornane bridgehead.[3]

2. The exocyclic orbitals in cubane are s-rich. Forming a cation from a hybrid orbital is more difficult the greater the s character therein. The carbon orbital in the central CH bond of isobutane, that in the bridgehead CH bond of norbornane, and those in the CH bonds of cubane are estimated from $J_{^{13}C-H}$ to have about 25%, 28%, and 31% s character, respectively.[4,5]

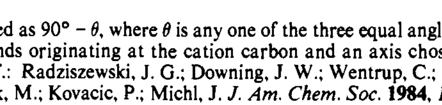
3. Although the vicinal CH bonds eclipse the empty orbital in cubyl cation, hyperconjugation would require high-energy, cubene-like structures.[6]

4. Ab initio calculations (6-31G*, but without electron correlation) place cubyl cation about 20 kcal/mol higher in energy than *tert*-butyl cation and about 5 kcal/mol above 1-norbornyl cation.[7]

Nevertheless, numerous reactions have been observed that might involve the intermediacy of cubyl cation: (1) decomposition of cubyl diazonium salts,[4a,8]



(2) photolytic solvolysis of iodocubanes,[9]



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(1) Dedicated to Prof. Christoph Rüchardt on the occasion of his 60th birthday.

(2) Defined as 90° − θ, where θ is any one of the three equal angles between the three bonds originating at the cation carbon and an axis chosen to pass through it (cf.: Radziszewski, J. G.; Downing, J. W.; Wentrup, C.; Kaszynski, P.; Jawdosiuk, M.; Kovacic, P.; Michl, J. *J. Am. Chem. Soc.* **1984**, *106*, 7996).

(3) Calculated from the MM2 optimized geometry of norbornane.

(4) (a) Cole, T. W., Jr. Ph.D. Dissertation, The University of Chicago, 1966. (b) Della, E. W.; Hine, T. W.; Patney, H. K. *J. Org. Chem.* **1977**, *42*, 2940.

(5) Tori, K.; Muneyuki, T.; Tanida, H. *Can. J. Chem.* **1963**, *41*, 3142.

(6) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

(7) Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.*, second of three papers in this issue.

(8) Klunder, A. J. H.; *Zwanenburg*, B. *Tetrahedron* **1972**, *28*, 4131.

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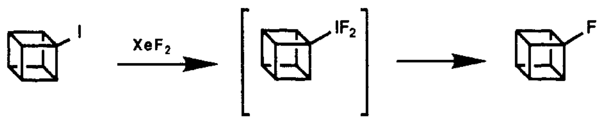
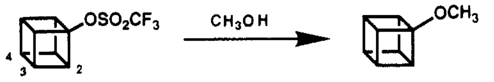
and (3) decomposition of hypervalent derivatives of iodocubanes,[10]



Some of these reactions do not have clearly defined mechanisms, and the possibilities of "front-side attack", "hot intermediates", etc. might weaken the case for involving cubyl cations. To investigate the matter further, we have examined the solvolysis of cubyl triflates. Accepting the usual caveats about solvation, cage effects, ion separation, and the like, the solvolysis of triflates in alcohols seems to us commonly recognized as proceeding through the intermediacy of a carbenium ion or carbenium ion like species.

Cubyl triflate and its relatives were prepared from the appropriate cubane carboxylic acids.[11] Reaction of each acid with methyllithium followed by *m*-chloroperbenzoic acid oxidation of the resulting methyl ketone gave the corresponding cubyl acetate. Careful reductive cleavage of each acetate with diisobutylaluminum hydride in toluene at low temperature followed by addition of trifluoromethanesulfonic anhydride gave the required triflate directly. Each was purified carefully by chromatography and characterized spectroscopically.

Solvolysis of cubyl triflate in pure dry methanol is facile and very clean. No rearrangement is observed;[12] the only significant product is cubyl methyl ether.



Kinetic parameters were determined by following reactions of 0.12 M solutions of triflate in methanol using calibrated GLC or NMR (perdeuteriated methanol). The reaction is pseudo first order over at least 3 half-lives. At 50.1 °C, $k = 7.72 \times 10^{-5}$ s^{-1} (unchanged if 1 equiv of triethylamine is added). This is *at least* 10^{13} *times faster* than predicted by molecular mechanics type calculations.[13] The appearance of the methyl ether mirrors the disappearance of the triflate. Over the temperature range 50–70 °C, $\Delta H^{\ddagger}$ = 24.6 kcal/mol and $\Delta S^{\ddagger}$ = 1.5 eu.

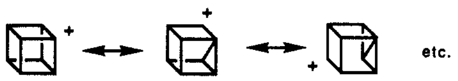
The half-life of cubyl triflate in methanol at 70 °C is only 15 min. *Cubyl triflate is much more reactive than 1-norbornyl triflate*, which is not solvolyzed noticeably by methanol even after 250 h at 70 °C.[14] In hexafluoro-2-propanol at 60 °C, 1-norbornyl triflate is 90% solvolyzed in 85 h, whereas cubyl triflate is converted completely in this solvent to cubyl hexafluoroisopropyl ether *within 5 min at room temperature*. If we extrapolate using the usual rough rules of thumb to bring these reactions to the same temperature, cubyl triflate is solvolyzed at least 100 000 times faster than norbornyl triflate in hexafluoro-2-propanol.

Why is cubyl cation more easily reached than expected? The matter is handled quantitatively in the accompanying paper by Hrovat and Borden.[7] We raise here several qualitative points worth consideration.

1. The internuclear lines give a false picture for the bonding and geometry in cubane. Bent bonding is important. The endocyclic interorbital angle is not 90°. It has been estimated to be 107° by calculation[15] and is, on average, 105° by difference Fourier synthesis from X-ray analysis of the 1,4-diacid.[16] If the pyramidalization angle is defined by using orbital vectors rather than internuclear lines, it is reduced substantially.

2. The s character in the exocyclic orbital estimated from the CH bond in cubane is not properly extensible to the cubyl cation. The balance of factors is different.[17]

3. Delocalization of the positive charge might occur via interaction with the strained cubane CC bonds. A resonance hybrid like that in the familiar cyclopropylcarbinyl–cyclobutyl cation system might be significant.[18]



Rüchardt and co-workers have suggested a similar possibility to account for the "fast" solvolysis at 120 °C of 4-bromohomocubane in hexafluoro-2-propanol.[19]

To probe the significance of delocalization, we have examined the solvolysis of some substituted cubyl triflates. The 2- and 4-methylcubyl triflates are solvolyzed in methanol at 50 °C cleanly to the corresponding methyl ethers. The 2-methyl substituent accelerates the reaction 3-fold over the desmethyl compound, whereas the 4-methyl depresses the rate by a factor of about 2. The symmetry of the HOMO of a π donor like methyl at position 4 does not allow effective stabilization of the cation at 1; this limitation does not apply to such donors at position 2.[7,20] Electron-withdrawing groups at position 4 depress the rate of solvolysis enormously. We were unable to detect *any* significant solvolysis of cubane-1,4-diol bis(triflate) after it was heated in methanol at 85 °C for 5 days, in aqueous 80% ethanol at 100 °C for 5 days, or in hexafluoro-2-propanol at 100 °C for 6 days. 4-Chlorocubyl triflate is solvolyzed, but only in small part (about 25%), during 9 days in hexafluoro-2-propanol at 60 °C. These observations are in qualitative accord with expected resonance and inductive substituent effects, and we conclude that delocalization to the 2- and 4-positions plays a critical role in making the cubyl cation accessible.

Lest we leave the impression that cubyl cation is easy to reach, rather than just easier than expected, we note that our extensive NMR attempts to "see" the cation at low temperature in various superionizing media failed. Fluorocubane does not ionize in SbF_5/SO_2 nor SbF_5/SO_2ClF at -90 °C; at higher temperatures, decomposition sets in. Cubyl triflate decomposes in either medium immediately at −100 °C; the 4-chloro triflate is stable therein up to −80 °C, whereupon it decomposes.

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Registry No. Cubyl triflate, 125762-86-9; cubyl methyl ether, 125764-02-5; 2-methylcubyl triflate, 125764-03-6; 4-methylcubyl triflate, 125762-87-0; 2-methylcubyl methyl ether, 125764-04-7; 4-methylcubyl methyl ether, 125764-05-8; 4-chlorocubyl triflate, 125762-90-5; hexafluoro-2-propanol, 920-66-1.

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