Organic and Biological Chemistry

A Quantum Mechanical Approach to the Classical Nonclassical Problem in Norbornyl Cation

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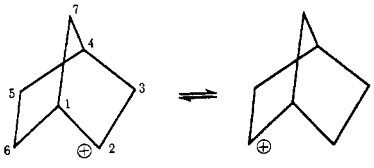
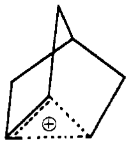
Abstract: The LCAOSCF method (PNDDO approximation) has been used to determine among several possible structures the one which is most likely to be the intermediate in the solvolysis of norbornyl derivatives. The corner- and edge-protonated nortricyclenes were found to be the most stable species. This result seems to be compatible with most pertinent experimental data.

Since the discovery of the unique behavior of norbornyl-like derivatives and the subsequent proposal of the existence of carbonium ions,[1] a controversy has occurred as to whether this carbonium ion exists as a rapidly equilibrating pair of classical ions[2] (I) or whether the intermediate is a mesomeric or σ bridged "nonclassical" species[3] (II).

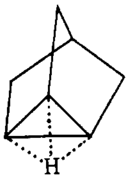


I



II

Both lines of thought are directed toward finding an explanation for the basic experimental fact that the *exo*/*endo* rate ratio for solvolysis is very large and that the return reaction occurs predominately to the *exo* position. In addition, the interpretation must be compatible with the experimental-labeling results which showed that extensive ^{14}C isotopic rearrangement occurs between the 1, 2, and 6 positions. A face-protonated nortricyclene (III) intermediate was suggested in order to account for the latter observation.[4] A similar conclusion was reached from tritium tracer experiment.[5]



III

It was also shown that at low temperature in SbF_5, the nmr spectra of the 2-norbornyl cation could be resolved into three peaks of relative intensity 4:1:6 which suggests the equivalence of four protons in the stable 2-norbornyl cation.[6] Raman-spectroscopic studies of the long-lived norbornyl cation seem to indicate that the observed stable ion indeed is protonated nortricyclene.[7]

I would like to report here some calculations which have been made possible by the recent development of quantum mechanical SCF treatment of σ-bonded molecules.[8]

The method which was described in a previous paper[9] was shown to give good estimates of heats of formation of hydrocarbons providing that the interatomic distances are kept at 1.534 Å for a CC bond and 1.093 Å for a CH bond. As long as no distances in the molecule become shorter than the values given above (in which case the theory does overestimate the bonding energy), the theory leads to a general agreement with experimental heats of formation of the order of ±3 kcal. The method was recently tested also for carbonium ions[10] and the agreement there again appears to be of the same order of magnitude.

The coordinates of the various atoms of the systems which are investigated have been determined following the previous rule and allowing all strained angles to be as large as possible at the same time.[11]

Several compounds have been calculated belonging to three structural classes: (a) norbornane, 2–6 CC distance = 2.42 Å; (b) norbornane, 2–6 CC distance shortened to 1.8 Å; (c) nortricyclene, 2–6 CC distance = 1.534 Å. The calculated heats of formation of the various species are assembled in Table I.

As was pointed out above, the confidence one might have in the calculations is that the results are usually within 3 kcal of the experimental ones. This value probably remains valid when one compares the heat of formation of compounds belonging to the same class

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(1) H. Meerwein and K. Van Emster, *Ber.*, **55**, 2507 (1922).

(2) H. C. Brown, *Chem. Brit.*, **2**, 199 (1966).

(3) T. P. Nevell, E. deSalas, and C. L. Wilson, *J. Chem. Soc.*, 1192 (1939); S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **74**, 1147 1154 (1952).

(4) J. D. Roberts and C. C. Lee, *ibid.*, **73**, 5009 (1951); J. D. Roberts, C. C. Lee, and W. H. Saunders, *ibid.*, **76**, 4501 (1954).

(5) C. C. Lee and L. K. M. Lam, *ibid.*, **88**, 2831 (1966).

(6) P. von R. Schleyer, W. E. Watts, R. C. Fort, Jr., M. B. Comisarow, and G. A. Olah, *ibid.*, **86**, 5679 (1964); M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964).

(7) G. A. Olah, A. Commeyras, and C. Y. Lui, *ibid.*, 90, 3882 (1968).

(8) G. Klopman, *ibid.*, **86**, 4550 (1964).

(9) M. J. S. Dewar and G. Klopman, *ibid.*, **89**, 3089 (1967).

(10) G. A. Olah, R. H. Schlosberg, and G. Klopman, in preparation.

(11) After completion of this work, an electron diffraction study of norbornane was published: J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Am. Chem. Soc.*, 90, 3149 (1968). The agreement between the experimental and our assumed coordinates is excellent; no atom–atom distance differed by more than 3%.

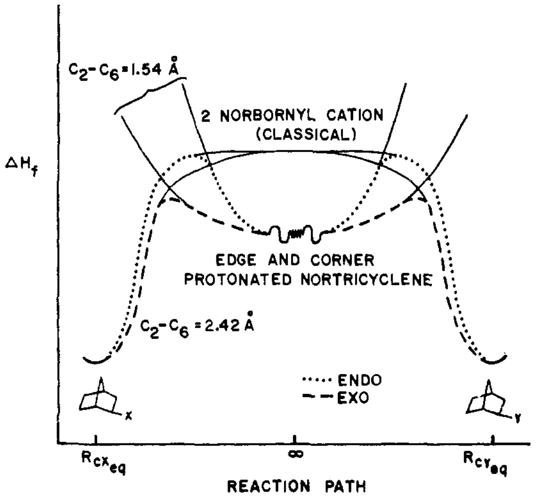


Figure 1.

(only one atom is being displaced at the time). However, in view of the uncertainty of the exact geometries of these compounds, this discrepancy may become larger when compounds of different classes are compared. A maximum error of 10 kcal may then be considered more reasonable.

Table I. Heats of Formation (from Graphite and H_2) at 25°

	Compd	ΔH_f, kcal
	Class a	
(1)	Norbornane	−12.9
(2)	Norbornane C_{sp^2}–H *exo* bond is 1.4 Å	45.0
(3)	Norbornane C_{sp^2}–H *endo* bond is 1.4 Å	51.4
(4)	Norbornyl cation ("classical")	247.7
	Class b	
(5)	Norbornane	56.8
(6)	Norbornane C_{sp^2}–H *exo* bond is 1.4 Å	54.5
(7)	Norbornane C_{sp^2}–H *endo* bond is 1.4 Å	174.8
	Class c	
(8)	Nortricyclene	33.4
(9)	Face-protonated nortricyclene (distance proton to plane = 1 Å)	244.9
(10)	Edge-protonated nortricyclene (distance proton to bond = 1 Å)	203.0
(11)	Corner-protonated nortricyclene	206.0

A further restriction which has to be considered is that the intermediates whose heats of formation have been calculated represent only "reasonable guesses." By no means is this list complete nor the real occurrence of these species certain.

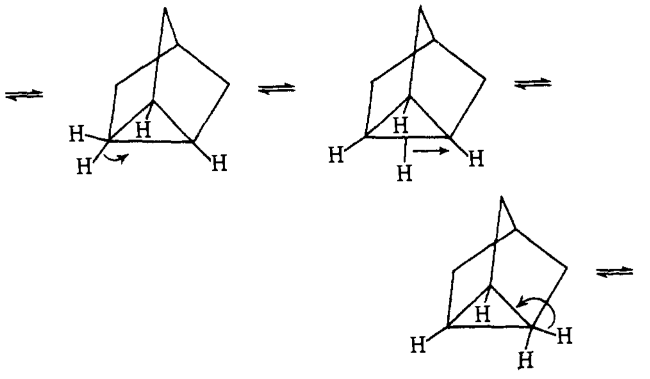
As long, however, that we are unable to calculate directly the transition states, and this would also involve a real estimate of the solvation energy, calculations of that kind provide the most reasonable theoretical approach to the problem.

A possible check of the results is provided by the heats of formation of norbornane and nortricyclene. For norbornane, the heat of formation is found to be −12.9 kcal and this compares with −15.8 kcal calculated by Allinger.[12] Our value is slightly larger than his, and this might represent the combined effect of our assumed coordinates and his overestimation of bonding for strained hydrocarbons.

The heats of formation of norbornane and nortricyclene calculated by a simple additivity procedure lead respectively to −20.5 and −15.5 kcal/mol. We, therefore, deduce a strain energy of 7.6 kcal for norbornane and 48.9 kcal for nortricyclene.

Several possible structures for the free carbonium ion have also been calculated (**4**, **9**, **10**, and **11**). The less stable ones appeared to be the "classical" cation (**4**) and the face-protonated nortricyclene (**9**) which are found to be about 40 kcal less stable than the edge-protonated and the corner-protonated nortricyclene. This difference is very large by our standards and in our opinion therefore, none of species **4** or **9** can be formed.

It thus appears that, under thermodynamic-controlled conditions, the ion which is predicted to be predominant is either the edge- or the corner-protonated nortricyclene and this, in spite of the fact that a large steric strain was found for nortricyclene itself. The difference in energy between the edge- and the corner-protonated nortricyclene is found to be only of the order of 3 kcal. Providing thus that the assumed geometries have some physical reality, and that the real barrier remains of the order of magnitude of that calculated in our models, the 4 hydrogen atom will appear equivalent and be scrambled over the whole system.



It is also clear that the opening of the ring by the nucleophilic agent can now occur at any of the three cyclopropane bonds and this might explain the extensive ^{14}C isotopic rearrangement observed in these compounds.

The final property we were trying to interpret is the large *exo*/*endo* rate ratios. Two sets of structures, representative of possible transition states were calculated, in which either the *endo* or the *exo* CH bond was elongated to 1.4 Å. The fact that the leaving group here was a H^- does probably not affect the normal electronic behavior very much, but the steric strains are probably underestimated.

In the first set of calculations, the norbornane skeleton is maintained undistorted but carbon 2 takes an sp^2 configuration representative of the transition state. It is found that the compound with an elongated *exo* bond is now more stable by 6.4 kcal than that with a long *endo* bond. The 2–6 bond index remains very small for both derivatives, and the difference in stability has probably to be assigned to a steric interaction of the leaving group with the 6-*endo* hydrogen.

The second set of calculations was done for a distorted norbornane, the 2–6 CC distance being shortened to 1.8 Å (**6** and **7**). In this case the *exo* derivative lost 10 kcal from the previous case but the stability of the

[12] N. L. Allinger, personal communication.

endo derivative decreased by more than 120 kcal. The latter result was to be expected from simple steric consideration. An analysis of the bond indices reveals at this point that the observed differences are produced both by a *steric inhibition for the endo derivative* and *a σ participation for the exo derivative* (Figure 1). However, even the *exo* derivative appears to be less stable than his analog with a 2–6 CC distance of 2.4 Å indicating that the closing of the cyclopropane ring (σ assistance) occurs later in the process. These results are tentatively interpreted as in the Figure 1 where the *exo* derivative appears to react faster and its transition state involves more σ participation than the *endo* position whose reactivity is inhibited by steric hindrance. Similarly, the formation of a new bond, C–Y, to form the product is more favorable in the *exo* position. In a very nucleophilic medium the quenching of the carbonium occurs very fast and before any extensive rearrangement of the ^{14}C occurs whereas in a less nucleophilic medium the longer life of the protonated nortricyclene permits the tautomeric rearrangement of the protons. In this case, a complete scrambling of the hydrogen and the carbon atoms may occur.

Acknowledgment. I wish to thank Professor G. A. Olah for his interest and stimulating suggestions. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

The Oxibase Scale and Displacement Reactions. XVII. The Reaction of Nucleophiles with Ethyl Tosylate and the Extension of the Oxibase Scale[1]

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Abstract: The rate constants of ten nucleophiles reacting with ethyl tosylate have been measured in aqueous solution. From these rate constants the oxibase scale parameters for ethyl tosylate have been obtained; α = 1.48 and β = 0.03 at 25° in water. The nucleophilic constants of several nucleophiles have been obtained for the temperature range of 0–100° in water. The uses of the oxibase scale are extended to include the energetics of isotopic exchange reactions as well as the relationship between the oxidation potential and the basicity.

The tosylate group, $^{-}OSO_2C_6H_4CH_3$-*p*, is an often used leaving group to study structure–reactivity effects in physical-organic chemistry. In the present study ethyl tosylate has served as the substrate for ten nucleophiles in aqueous solution (see section I below).

The data of McCleary and Hammett[3] on the SN2 reaction of water, hydroxide, and halide ions with ethyl *p*-toluenesulfonate (or ethyl tosylate) were determined in 60% aqueous dioxane (by volume) at 50°. Edwards[4] computed α to be 1.68 and β to be 0.014. However, the plot[5] of $E^{-1}\log(k/k_0)$ *vs.* H/E has a large amount of scatter. The scatter is due to several factors; an important factor is the requirement of accurate pK_a values of the halide ions. A second problem is that kinetic data in dioxane–water at 50° should not necessarily correlate well the thermodynamic values in water[7] at 25° or with empirical kinetic constants[8] obtained in water at 25°.

In parts II and III, the oxibase scale is extended as the result of theoretical work to cover the temperature range of 0–100° in water. Further theoretical work on the oxibase scale relates the parameters to more fundamental properties of the reacting species.

Results

I. The Present Investigation. The use of the oxibase scale on ethyl tosylate in pure water at 25° has been made so that the substrate can be used as a convenient substrate for determining the kinetic E values of the mercaptoethylamine and other nucleophiles (see the following paper).

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[1] Paper XVI: R. E. Davis in "Inorganic Sulphur Chemistry," G. Nickless, Ed., Elsevier Publishing Co., The Netherlands, in press.

[2] (a) Postdoctoral Fellow, 1962–1963. (b) Undergraduate Research Thesis Student, 1963–1964. (c) Taken in part from the Ph.D. Thesis, August 1967.

[3] H. R. McCleary and L. P. Hammett, *J. Amer. Chem. Soc.*, **63**, 2254 (1941).

[4] J. O. Edwards, *ibid.*, **76**, 1540 (1954).

[5] The equation now called the oxibase scale[6] is

$$\log(k/k_0) = \alpha E + \beta H \qquad \text{(i)}$$

with

$$X^- + AY \xrightarrow{k} AX + Y^-$$

$$H_2O + AY \xrightarrow{k_0} AOH + Y^- + H^+$$

$$E \equiv \epsilon^0 + 2.60\ \mathrm{V}$$

$$2X^- \rightleftharpoons X_2 + 2e^- \quad \epsilon^0$$

$$X^- + H^+ \rightleftharpoons HX \quad \mathrm{p}K_a$$

$$H \equiv \mathrm{p}K_a + 1.74$$

A plot can be prepared from (i) by dividing by E.

$$E^{-1}\log(k/k_0) = \alpha + \beta(H/E) \qquad \text{(ii)}$$

[6] R. E. Davis in "Survey of Progress in Chemistry," A. Scott, Ed., Academic Press, New York, N. Y., 1964, pp 189–238.

[7] The same problem of using nucleophilic data obtained in one solvent at one temperature with data in other solvents at different temperatures is wide spread. Lack of data forces such correlations to be tried, nevertheless.

[8] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, **75**, 141 (1953).