can be seen that small differences in the relaxation energies for the three core hole states has yielded IE differences which agree with experiment, within the experimental uncertainty.

The shifts in the O 1s IEs are well reproduced by Koopmans' theorem and are determined to a large extent by the Coulombic potential arising from neighboring atoms, being the second term in eq 1. Thus, the oxygen charges for all three isomers are very similar, although the meta-substituted molecule has the greatest oxygen electron density in line with the smallest nitrogen density found for this molecule. The similar O 1s IEs in 3- and 4-hydroxypyridine and the smaller value found for 2-hydroxypyridine may be attributed to the Coulombic effect of neighboring atoms. Thus, in 2-hydroxypyridine, although C2 is more positively charged than the corresponding atoms (C3, C4) in 3- and 4-hydroxypyridine, the O 1s IE in 2-hydroxypyridine is reduced, due in part to the neighboring nitrogen atom having a large negative charge, an effect absent for the other two isomers. For these latter two molecules, the effective atomic charges suggest that the Coulombic effect of the neighboring atoms is approximately the same, leading to similar O 1s IEs. the measured and calculated O 1s and N 1s IEs for 2-hydroxypyridine and 2-pyridone correlate well, but are not in line with the respective atomic charges. This may be attributed to the Coulombic effect of the positively charged hydrogen atom bonded respectively to the oxygen and nitrogen atoms, leading to an increased IE from that expected from self-charges alone.

Conclusions

With the higher level of theory reported in this paper, we have achieved an energy difference for the tautomers involved in equilibrium I close to the experimental value, and far better than that previously reported. The energy differences between the three isomeric hydroxypyridines studied here are within 10 kJ mol^{-1} of the experimental values. The effect of correlation on these energetics remains to be studied. For oxygen the measured core electron IEs are found to reflect the small changes in the charge distributions of the three isomers, and to be interpreted by calculations at the Koopmans' theorem level of approximation. For nitrogen, ΔSCF calculations are needed to predict the correct ordering of the core electron IEs.

Acknowledgment. We thank the Science and Engineering Research Council and the Royal Society for financial support and Professor H. A. Skinner and Dr. R. H. Davies for helpful discussions.

Registry No. 2-Hydroxypyridine, 72762-00-6; 2-pyridine, 142-08-5; 3-hydroxypyridine, 109-00-2; 3-pyridone, 58064-43-0; 4-hydroxypyridine, 626-64-2; 4-pyridine, 108-96-3.

Isotopic Perturbation Effects on a Single Averaged NMR Peak: Norbornyl Cation

Martin Saunders* and Mandes R. Kates

Contribution from the Department of Chemistry, Yale University, New Haven, Connecticut 06520. *Received December 14, 1982*

Abstract: A variant of the isotopic perturbation method for investigating questions of whether molecules are rapidly equilibrating over low barriers or have symmetric, single-minimum surfaces is reported. To apply it, the ^{1}H NMR spectrum of monodeuterated norbornyl cation was examined over a higher temperature range than that used previously. It shows an additional peak on the high-field side of the averaged 1,2,6 signal due to perturbation of the average shift of the remaining three protons by an equilibrium isotope effect in the fraction of molecules containing deuterium on carbons 1, 2, or 6. K_{iso} was found to vary from 1.66 to 2.14 over the temperature range from −105 to −43 °C, yielding a value for ΔH of 310 ± 20 cal/mol. Using a model of the equilibrating classical ions and the reported kinetic isotope effects on solvolysis leads to a prediction of a *downfield* shift for this peak, while the nonclassical ion structure readily accommodates an upfield shift.

The isotopic perturbation method for investigating questions of whether molecules are rapidly equilibrating over low barriers or have symmetric, single-minimum surfaces has yielded valuable information in carbonium ion and noncarbonium ion cases. In the applications reported,[1,2] asymmetric introduction of an isotope has resulted in the splitting of peaks in the NMR spectrum, the magnitude of the splitting values being compared with splittings in reference compounds known to have single- and double-minimum energy surfaces. Cases involving rapid equilibrium (double-minimum cases) have shown large values of splitting in the ^{13}C NMR in contrast with nonequilibrating systems (single-minimum cases).

It is our present purpose to report a case where a rapid rearrangement process completely scrambles a group of protons among a group of carbons, producing all possible permutations of the hydrogens. Introduction of deuterium, in such a molecule, cannot cause splitting of the corresponding carbon NMR signal since the rapid rearrangements of deuterium and hydrogen give each carbon the same averaged environment and frequency. Nevertheless, introduction of deuterium can cause a *shift* in the single averaged peak of the remaining *protons*, compared with its position in the nondeuterated material. Since the frequency of any peak in a system undergoing rapid rearrangement is the weighted average of the separate frequencies being averaged, the magnitude and direction of this shift can be used to decide among various structural possibilities by comparison with the predicted shifts for the different possibilities.

We report the application of this variant of the isotopic perturbation method to the case of the stable norbornyl cation. This ion was previously investigated by isotopic perturbation through investigating the *low-temperature* ^{13}C NMR spectra of species where deuterium was introduced to break the symmetry.[2] We concluded from the results that the ion has the nonclassical, bridged, protonated-cyclopropane structure with high likelihood.

---

(1) (a) M. Saunders, M. R. Kates, K. B. Wiberg, and W Pratt, *J. Am. Chem. Soc.*, **99**, 8072 (1977); (b) M. Saunders in "Stereodynamics of Molecular Systemsrqt, R. Sarma, Ed., Pergamon Press: New York 1979, p 171; (c) L. R Schmitz and T. S. Sorensen, *J. Am. Chem. Soc.*, **102**, 1645 (1980); (d) M. Saunders and H.-U. Siehl, *ibid.*, **102**, 6868 (1980); (e) P. Ahlberg, C. Engdahl, and G. Jonsall, *ibid.*, **103**, 1583 (1981); (f) H. Hogeveen and E. M. G. A. van Kruchten, *J. Org. Chem.* **46**, 1350 (1981); (g) R. P. Kirchen, K. Ranganayakula, A. Rauk, B. P. Singh, and T. S. Sorensen. *J. Am. Chem. Soc.*, *103*, 588 (1981).

(2) M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, **102**, 6867 (1980).

0002-7863/83/1505-3571$01.50/0

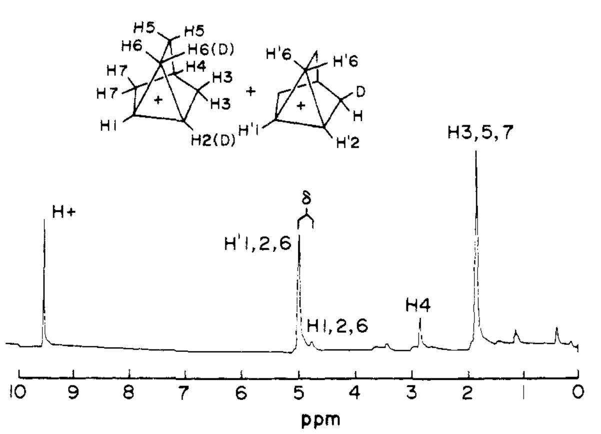


Figure 1. 270-MHz proton spectrum of a mixture of monodeuterated and nondeuterated norbornyl cation at −76 °C.

Our new results both illustrate the method and also offer an additional, independent piece of evidence concerning the structure of the norbornyl cation. Since our earlier work, Yannoni has published a very-low-temperature solid-state ^{13}C NMR spectrum consistent with the single-minimum nonclassical structure or requiring an extremely low limit on the barrier for a classical rapidly equilibrating structure.[3]

Results

At temperatures above −130 °C, the ^{1}H NMR spectrum of norbornyl cation has only three peaks due to a rapid process that averages the environments of protons of carbons 1, 2, and 6 (four protons) and also 3, 5, and 7 (six protons) and leaves the proton on carbon 4 unaffected.[4] A barrier for this process (a corner-to-corner proton shift in the nonclassical structure) of 5.9 kcal/mol has been reported.[5] At these temperatures, deuterium is equilibrated among all positions in a few minutes due to the slow (at these temperatures) 3,2 hydride shift.[4] When a deuterium is introduced, approximately four-elevenths of the molecules have this deuterium on carbons 1, 2, or 6. The distribution of the deuterium among these carbons is affected by equilibrium isotope effects, which in turn affect the averaged shift of the remaining three protons on these carbons. The averaged peak due to these hydrogens can thus change frequency. Since the averaged environments of carbons 1, 2, and 6 are the same due to the rapid exchange of hydrogens and deuterium, no change in the ^{13}C NMR peak of these carbons is expected. In any event, the ^{13}C NMR spectrum would be expected to be broad in this temperature range, since the chemical shift differences for carbon, which are much larger than those in the proton spectrum, require a much greater rate of scrambling for sharp averaging.

Norbornanone was reduced with $LiAlD_4$ and the resulting monodeuterated norbornanol converted to norbornyl cation by use of procedures identical with those reported earlier.[2,6] In the higher temperature range, a new peak shifted upfield from the averaged 1,2,6 peak in the deuterated ion was observed in the proton spectrum (Figure 1). This peak was strongly temperature dependent, which is an important diagnostic characteristic of systems affected by equilibrium isotope effects. Assuming that one deuterium and three hydrogens are exchanging between two different sites each having two positions we obtain

$$K_{\text{iso}} = (\Delta + 6\delta)/(\Delta - 6\delta)$$

where K_{iso} is the equilibrium isotope effect, δ is the observed relative shift of the new peak, and Δ is the difference in shift between the two sites when the rapid exchange process is slowed down. We have assumed that intrinsic isotope shifts (the shifts of proton frequencies caused by a neighboring deuterium in a single structure) are small relative to the observed shifts. Using the value 3.55 ppm reported[5] for Δ and the observed values for δ, we obtained values for K_{iso} between 1.66 and 2.14 (Table I). A plot of ln K vs. $1/T$ yielded a value for ΔH of 310 ± 20 cal/mol. This is an extremely large equilibrium isotope effect for exchange of one hydrogen with one deuterium. For example, the equilibrium isotope effect observed in the 1,2-dimethylcyclopentyl cation yields a ΔH of 67 cal/mol.[7]

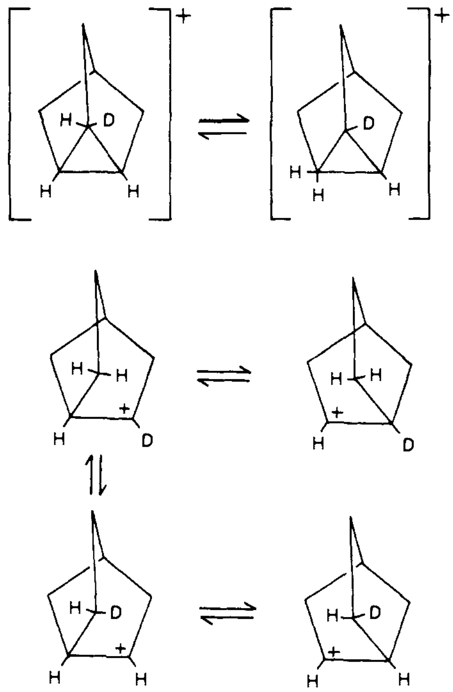
Table I

T, °C	δ	K_{iso}
−105	0.215	2.14
−100	0.206	2.07
−89	0.199	2.01
−76	0.185	1.91
−65	0.176	1.85
−55	0.159	1.73
−47	0.153	1.70
−43	0.146	1.66

Discussion

We will first discuss the experimental results using the nonclassical structure as the framework. Since there are not enough electrons to make five full single bonds to the pentacoordinated carbon of the nonclassical ion, it might be expected that all of these bonds would be significantly longer and looser than bonds to tetracoordinated carbons; thus the CH bending and stretching frequencies would be expected to be lower, lowering their zero-point energy in turn.

Deuterium *also* lowers vibrational frequencies and zero-point energies. Since the energy decrease is greatest when higher frequency protons are substituted by deuterium, the isotopomer with deuterium on the nonbridging carbon and hydrogens on the bridging carbons should be favored. In the analysis of the low-temperature proton spectrum the protons on the pentacoordinated carbon were assigned to the peak at higher field. Therefore, the observed upfield shift of the new peak in the deuterated ion is in the expected direction for the nonclassical structure, although we cannot predict the magnitude without first predicting the magnitude of the isotope effect.



To try to predict the effect that might be observed with the classical ion model, we need approximate values for the proton

---

[3] C. S. Yannoni, V. Macho, and P. C. Myhre, *J. Am. Chem. Soc.*, **104**, 907 (1982).

[4] M. Saunders, P. von R. Schleyer, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 5680 (1964).

[5] G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Am. Chem. Soc.*, **92**, 4627 (1970).

[6] M. Saunders, D. Cox, and J. R. Lloyd, *J. Am. Chem. Soc.*, **101**, 6656 (1979).

[7] M. Saunders, L. A. Telkowski, and M. R. Kates, *J. Am. Chem. Soc.*, **99**, 8071 (1977).

shifts and equilibrium isotope effects at each position. Taking the shift of the CH of isopropyl cation ($\delta \sim 11$) as our model for δ_2 and using the experimental shifts in the low-temperature spectrum of norbornyl[5] lead to $\delta_1 = 2$ ppm and the average of δ_{6exo} and $\delta_{6endo} = 3$ ppm. If, as is commonly assumed through applying the Hammond postulate, the transition state for solvolysis is close to the ion, it is reasonable to use the measured *kinetic* deuterium isotope effects for solvolysis to model equilibrium isotope effects on the ion. Equililibrium deuterium isotope effects in systems involving simple acyclic tertiary ions were found to be very similar in magnitude to the kinetic isotope effects in *tert*-butyl solvolysis,[8a-d] so this choice seems appropriate for the classical ion model.

Kinetic deuterium isotope effects for solvolysis of norbornyl brosylate of $C_2 = 1.124$, $C_1 = 1.081$, $C_{6exo} = 1.09$, and $C_{6endo} = 1.07$ (all at approximately 25 °C in acetic acid) have been reported.[9a-d] The proton shift of the peak due the 1, 2, 6_{exo}, and 6_{endo} protons is the average of the individual shifts. The shifted peak in the fraction of molecules containing the deuterium on carbons 1, 2, or 6 is the same average altered by the isotope effects. Assuming an exponential temperature dependence in order to extrapolate the kinetic isotope effects to −43 °C, we predict an isotopic shift of 0.059 ppm *downfield* on the basis of this classical model through the use of a computer program that calculates the average frequencies weighted by the above isotope effects. This is clearly incompatible with the observed shift of 0.146 ppm *upfield*.

If the transition state for solvolysis coincided exactly with the symmetrically bridged cation, it would be expected that the kinetic isotope effects for C_2 and C_1 would be the same as well as those for C_{6exo} and C_{endo}. Clearly it does not. The sign of the isotope shift, reported here, shows that the stable ion differs considerably from this transition state and must be bridged.

Acknowledgment. We acknowledge support of this work by a grant from the Chemical Dynamics division of the National Science Foundation. The high-field NMR spectra were obtained at the Northeast Regional NSF-NMR Facility.

Registry No. Norbornyl cation, 24321-81-1; deuterium, 7782-39-0; norbornanone, 497-38-1.

---

(8) (a) M. Saunders, M. H. Jaffe, and P. Vogel, *J. Am. Chem. Soc.*, **93**, 2558 (1971); (b) M. Saunders and P. Vogel, *ibid*, **93**, 2561 (1971); (c) J. C. Evans and G. Y.-S. Lo, *ibid.* **88**, 2118 (1966); (d) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *ibid.*, **85**, 2413 (1963).

(9) (a) H. Maskill, *J. Am. Chem. Soc.*, **98**, 8482 (1976); (b) J. M. Jerkunica, S. Borcic, and D. E. Sunko, *ibid.*, **89**, 1732 (1967); (c) B. L. Murr, A. Nickon, T. D. Swartz, and N. H. Werstiuk, *ibid.*, **89**, 1730 (1967); (d) B. L. Murr and J. A. Conkling, *ibid.*, **92**, 3462 (1970).

Cation–Anion Combination Reactions. 23. Solvent Effects on Rates and Equilibria of Reactions

Calvin D. Ritchie

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. *Received January 6, 1983*

Abstract: Rate and equilibrium constants for the reactions of 3,6-bis(dimethylamino)xanthylium cation with several amines and thiolates in dimethyl sulfoxide solution have been measured. Assumptions used in previous work to estimate equilibrium constants in dimethyl sulfoxide solution are found to be incorrect. Conclusions reached from those assumptions are not supported by the present data, and there are no examples in the present or past work where solvent effects on rates are appreciably greater than those on the corresponding equilibria for simple bond-forming reactions. Equilibrium constants have also been determined for the reactions of thiophenoxide and trifluoroethoxide ions with (*p*-(dimethylamino)phenyl)tropylium ion in water. The kinetic reactivities of trifluoroethoxide relative to hydroxide ion and of thiophenoxide relative to alkanethiolates are much greater than the corresponding equilibrium reactivities. In addition, an example of a slow, rate-determining, proton transfer in the reaction of morpholine with 3,6-bis(dimethylamino)xanthylium cation in dimethyl sulfoxide has been found.

In several papers of the present series,[1,2] we have suggested the possibility that solvent motion along the reaction coordinate could be an important contribution to the activation barriers of ionic reactions in solution. Any case of a change of solvent causing a larger change in rate constant than in corresponding equilibrium constant for a simple combination reaction would provide strong support for the suggestion. It has proved difficult, however, to find reactions for which both rate and equilibrium constants can be determined in two fundamentally different solvents, such as water and dimethyl sulfoxide. By the use of seemingly reasonable assumptions to estimate the solvent effect on either rate[1] or equilibrium[2] and the solvent effect on the other quantity determined experimentally, it has been concluded that the reactions of triarylmethyl cations with azide ion and with amines show behavior supporting the concept.

Pyronin cation (3,6-bis(dimethylamino)xanthylium cation) has provided an opportunity to check some of our assumptions and estimates. Rate and equilibrium constants for a number of reactions of this cation in water have already been reported.[3] The cation is reasonably stable in dimethyl sulfoxide solution, and rate and equilibrium constants for reactions with several amines and thiolates in that solvent have now been determined.

The reaction of pyronin with morpholine in dimethyl sulfoxide has been found to involve a slow, rate-determining, proton transfer. Details of that reaction are reported here.

In addition, it has been possible to determine equilibrium constants for reactions of thiophenoxide and trifluoroethoxide ions with (*p*-(dimethylamino)phenyl)tropylium ion in water to check whether or not the kinetic reactivities of these ions can be related to equilibrium reactivities.

Experimental Section

Materials. Dimethyl sulfoxide was purified by the procedure described by Bordwell[4] and was stored and handled under argon atmospheres.

---

(1) Ritchie, C. D.; Skinner, G. A.; Badding, V. G. *J. Am. Chem. Soc.* **1967**, *89*, 2063.

(2) Ritchie, C. D.; VanVerth, J. E.; Virtanen, P. O. I. *J. Am. Chem. Soc.* **1982**, *104*, 3491.

(3) Ritchie, C. D.; Kubisty, C.; Ting, G. Y. *J. Am. Chem. Soc.* **1983**, *105*, 279.

(4) Matthews, W. S.; Bares, J. E.; Bartmess, J. E.; Bordwell, F. G.; Cornforth, F. J.; Drucker, G. E.; Margolin, Z.; McCallum, R. J.; McCollum, G. J.; Vanier, N. R. *J. Am. Chem. Soc.* **1975**, *97*, 7006.

0002-7863/83/1505-3573$01.50/0