

in different matrix cages with  $\text{MnH}_2$  possibly immobilized with slightly different structures.<sup>10,11</sup>

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**Registry No.**  $\text{MnH}_2$ , 13767-07-2;  $\text{MnHD}$ , 88392-37-4;  $\text{MnD}_2$ , 88392-36-3;  $\text{Mn}$ , 7439-96-5;  $\text{H}_2$ , 1333-74-0;  $\text{HD}$ , 13983-20-5;  $\text{D}_2$ , 7782-39-0;  $\text{Xe}$ , 7440-63-3;  $\text{Ar}$ , 7440-37-1.

(10) It is not possible from the IR data to make a definitive statement at this time concerning the structure of  $\text{MnH}_2$  in  $\text{Xe}$ . All that one can say, is that the two slightly different forms of  $\text{MnH}_2$  in  $\text{Xe}$  (multiple-site effect or geometrical isomers) display no evidence for a symmetrical IR active  $\nu(\text{MnH}_2)$  stretching mode. This could be taken to indicate linearity for both forms. However, caution must be exercised here, as the sym  $\nu(\text{MnH}_2)$  mode of a bent  $\text{MnH}_2$ , B molecule could be overlapped by the asym  $\nu(\text{MnH}_2)$  mode of the A form, and/or A and B might be only slightly bent yielding an IR sym  $\nu(\text{MnH}_2)$  band that remains below the detection limit of our experiment. Raman data will help clarify this important point.

(11)  $\text{MnH}_2$  can also be generated in solid  $\text{Ar}$  by using similar experimental techniques.

### Displacement, Proton Transfer, or Hydrolysis? Mechanistic Control of Acetonitrile Reactivity by Stepwise Solvation of Reactants

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The absence of solvation can drastically alter many ionic reaction mechanisms from that which occurs in solution. There are several recent reports of mechanistic changeovers from solution to gas phase occurring on detachment of the last molecule of solvent from the reactive ion.<sup>1</sup> We report here what is to our knowledge the first case where three distinct reactivity pathways occur upon stepwise solvation: bare, monosolvated, and bulk-solvated hydroxide ion react with acetonitrile to give three different sets of products.

As part of a general study of the formation, thermochemistry, and reactivity of monosolvated anions,<sup>2</sup> we have examined the reactions of a number of carbon acids with species such as  $\text{RO}^- \cdot \text{HOR}$  in our ICR spectrometer.<sup>3</sup> Ketones, aldehydes, and acetylenes readily exchange into such alcohol-alkoxide species to give ions corresponding in mass to the deprotonated carbon acid solvated by the alcohol.<sup>1b,c</sup> Further reactions of such species are consistent with such a structure: either the solvent alcohol or the carbon acid can undergo further switching reactions with other alcohols, and the threshold for the carbon acid switching into the monosolvated ion is consistent with its acidity.<sup>4</sup>

When acetonitrile, water, and dimethylformamide are present in the ICR spectrometer, monosolvated hydroxide produced by the reaction sequence (1)–(4) reacts to form an ion of mass 58,

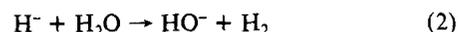
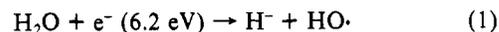
(1) (a) Asubiojo, O. I.; Blair, L. K.; Brauman, J. I. *J. Am. Chem. Soc.* **1975**, *97*, 6685. (b) Comisarow, M. *Can. J. Chem.* **1977**, *55*, 171. (c) Fukuda, E. K.; McIver, R. T., Jr. *Ibid.* **1979**, *101*, 2498. (d) Bartmess, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 2483.

(2) Caldwell, G.; Bartmess, J. E. *J. Am. Chem. Soc.*, submitted.

(3) McIver, R. T., Jr. *Rev. Sci. Instrum.* **1970**, *41*, 555; **1978**, *49*, 111. McIver, R. T., Jr.; Hunter, R. L.; Ledford, E. B., Jr.; Locke, M. J.; Francl, T. *J. Int. J. Mass Spectrom. Ion Phys.* **1981**, *39*, 65. Bartmess, J. E.; Caldwell, G. *Ibid.* **1981**, *41*, 125.

(4) Bartmess, J. E.; Scott, J. A.; McIver, R. T., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 6046; **1979**, *101*, 6056. Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979, Chapter 11, *The Gas Phase Acidity Scale*.

(5) Kebarle, P. *Ann. Rev. Phys. Chem.* **1977**, *28*, 445.

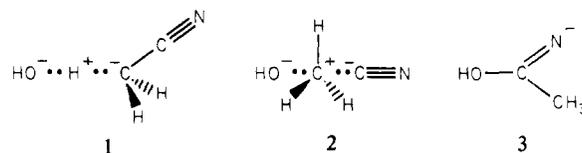


corresponding to  $\text{CH}_2\text{CN}^- \cdot \text{HOH}$ . No such product is observed when acetonitrile is absent or when  $\text{MeO}^- \cdot \text{HOME}$ , formed by the Riveros reaction of  $\text{MeO}^-$  with  $\text{HCO}_2\text{Me}$ , analogously to (3), reacts with acetonitrile. The differing reactivity of the ions  $\text{HO}^- \cdot \text{HOH}$  and  $\text{MeO}^- \cdot \text{HOME}$  would seem to denote a thermochemical threshold. However, acetonitrile reacting with  $\text{MeO}^- \cdot \text{HOH}$  (from  $\text{HO}^-$  and  $\text{HCO}_2\text{Me}$ ) gives a product of mass 58, corresponding to  $\text{CH}_2\text{CN}^- \cdot \text{HOH}$ , but no 72. This latter ion would be the methanol-solvated product  $\text{CH}_2=\text{C}=\text{N}^- \cdot \text{HOME}$  and should be preferred thermochemically, methanol being more acidic than water and therefore a better hydrogen bond donor. We believe that reaction 5 has occurred, involving an internal  $\text{S}_{\text{N}}2$



reaction, rather than a simple proton transfer and solvent switching, based on the following facts: (1) The pattern of reaction, with  $\text{HO}^- \cdot \text{HOH}$  but not with  $\text{MeO}^- \cdot \text{HOME}$ , is observed only for the carbon acid with a reasonably good leaving group,  $\text{CN}^-$ , and not for those carbon acids, such as acetone or acetophenone, of comparable acidity but with poor leaving groups. (2) The displacement mechanism explains the lack of the 72<sup>-</sup> ion on reaction with  $\text{MeO}^- \cdot \text{HOH}$ ; if methoxide is the nucleophile, the product would be dimethyl ether, which cannot hydrogen bond to cyanide like methanol can. (3) If various alcohols such as ethanol are present with the 58<sup>-</sup> species, signals corresponding in mass to  $\text{MeOH}^- \cdot \text{OR}$  and  $\text{ROH}^- \cdot \text{CN}$  are observed, but none for  $\text{CH}_2\text{CN}^- \cdot \text{HOR}$ , though all these reaction products should be formed exothermically. (4) Addition of  $\text{CO}_2$  to 58<sup>-</sup> results in a product at the mass of  $\text{MeOCO}_2^-$ , but none for  $\text{HOCO}_2^-$  or  $\text{NCCH}_2\text{CO}_2^-$ . We thus conclude that the methyl cation transfer, rather than proton transfer, is the principal mode of reaction.

The trifold pathways can be rationalized on the basis of the nature of the solvation. In general, transition states with diffuse charge are most favored in the absence of solvent, while charge localization results in better solvation and more stabilization in condensed protic media. For bare hydroxide reacting with the nitrile, deprotonation (-18.7 kcal/mol) and displacement of cyanide (-14.6 kcal/mol) are both exothermic. The preference for proton transfer must therefore reflect a rate phenomenon. The transition state for deprotonation should involve a looser complex, **1**, than the transition state for displacement, **2**, since the bonding



is centered about an s rather than a p orbital on the transferred cation.<sup>6</sup> While the thermochemistry of simple addition of hydroxide to form the imide **3** is not known, the fact that it is an addition, with no fragment to bear away any excess energy, makes its observation unlikely under the conditions in the ICR spectrometer.<sup>1d</sup>

For the solution-phase counterparts of these processes, in protic solvents a slow hydrolysis ( $k = 3 \times 10^{-6} \text{ M}^{-1} \text{ s}^{-1}$  at 35 °C) is observed.<sup>7</sup> Deuterium exchange catalyzed by  $\text{DO}^-$  occurs at "30–40 times" the hydrolysis rate.<sup>8</sup> In the solution phase, the attacking hydroxide should be well solvated by a protic solvent, while the transition states **1** and **2**, where the charge is more

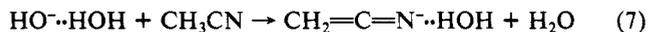
(6) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891. Pellerite, M. J.; Brauman, J. I. *Ibid.* **1980**, *102*, 5993.

(7) Reitz, O. *Z. Phys. Chem., Abt. A* **1939**, *183*, 371. Rabinovitch, B. S.; Winkler, C. A. *Can. J. Res.* **1942**, *20B*, 185. Wideqvist, S. *Ark. Kemi* **1956**, *10*, 265. Schaefer, F. C.; Peters, G. A. *J. Org. Chem.* **1961**, *26*, 412.

(8) Bonhoeffer, K. F.; Geib, K. H.; Reitz, O. *J. Chem. Phys.* **1939**, *7*, 664.

diffuse, should be less favorably solvated. The reaction involving **1** should also be considerably endothermic. Structure **3** is the first intermediate for hydrolysis; the charge, localized on the imide nitrogen, should be a better hydrogen bond acceptor than that of **1** or **2**. The net effect of solvation is to slow all reactions due to reactant solvation, but to stabilize **3** the most.

Why does HO<sup>-</sup>·HOH not deprotonate acetonitrile in the gas phase? The basicity of the monosolvated hydroxide is lower than that of the bare hydroxide by the hydrogen bond strength of 25 kcal/mol,<sup>5</sup> making reaction 6 endothermic by 6.3 kcal/mol.<sup>1d</sup>



Deprotonation with solvation of the product, as in reaction 7, is about 7 kcal/mol exothermic, if a estimate of ca. 13 kcal/mol for the hydrogen bond strength in the product is made.<sup>2</sup> The observed process (5) is likewise ca. 7 kcal/mol exothermic, based on the 13.8 kcal/mol bond strength of HOH<sup>-</sup>·CN.<sup>5</sup> We speculate that the controlling factor is the amount of charge developed on the potential solvation site in the transition state. The cyano group stabilizes adjacent anions primarily by polar effects, with little charge developed on the nitrogen due to resonance delocalization.<sup>9</sup> Cyanide, however, involves a localized charge more suitable for solvation. To the extent that localized charge is developed on the product anion in the transition state, solvation should favor that transition state, all other things such as total exothermicity being equal. We do not observe "hidden" proton transfer in the gas phase, since HO<sup>-</sup>·HOH does not incorporate any deuterium when in the presence of CD<sub>3</sub>CN in the ICR spectrometer.

**Acknowledgment.** We thank the National Institutes of Health, Grant GM 22743-03, for support of this work.

(9) Bordwell, F. G.; Van Der Puy, M.; Vanier, N. R. *J. Org. Chem.* **1976**, *41*, 1853. Fujio, M.; McIver, R. T., Jr.; Taft, R. W. *J. Am. Chem. Soc.* **1981**, *103*, 4017.

### Search for Oxygen Scrambling during Ethanolsis of [ether-<sup>17</sup>O]-endo-2-Norbornyl Mesylate. The True Exo/Endo Rate Ratio and the Nature of the Rate-Controlling Steps

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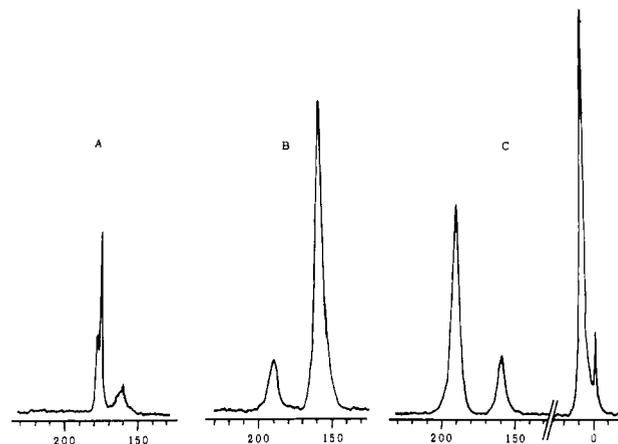
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Few facts in organic chemistry have inspired so much research as the large ratio of solvolysis rates of the epimeric 2-norbornyl pair of substrates. Oddly enough, in spite of all that has been written about the topic,<sup>1</sup> the magnitude of this ratio is subject to a possibly major uncertainty in the rate constant of one of the isomers. Thus, while the ratio of solvolysis rates was originally described<sup>2</sup> to be 350, it was later raised<sup>3</sup> several fold when racemization of the exo substrate was found to be several times faster than solvolysis; this process is of course a more sensitive indicator of ionization than the appearance of solvolysis products. The reason is that the endo isomer cannot racemize as a consequence

(1) Much of the literature on this subject is quoted by: Brown, H. C. "The Non-Classical Ion Problem"; Plenum Press: New York, 1977; with comments by Schleyer, P. v. R. For recent summaries, see the December issue of *Acc. Chem. Res.* **1983**.

(2) Winstein, S.; Trifan, D. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154.

(3) Winstein, S.; Clippinger, E.; Howe, R.; Vogelfanger, E. *J. Am. Chem. Soc.* **1965**, *87*, 376.



**Figure 1.** <sup>17</sup>O NMR spectra of *endo*-2-norbornyl mesylate in ethanol, with external water reference: (A) Natural abundance 20% solution in ethanol, showing base-line separation of the broad ether signal and sharp sulfone signal, a small amount of methanesulfonic acid is visible just upfield of the latter (600 000 transients, 500-μs delay time). (B) Ether-labeled ester 3 h after dissolution in ethanol at 75 °C, with some Pr(NO<sub>3</sub>)<sub>3</sub> added to shift the acid liberated (100 000 transients). (C) The same solution after 64 h, with additional shift reagent and with solvent and reference shown. The sharp sulfonyl signal at 173.5 is clearly not detectable.

of heterolysis to an ion pair and return. Should there nevertheless be substantial endo return, we would have an exaggerated notion of how large the rate ratio really is.

Other means of searching for return are available. As is known from Goering's painstaking researches,<sup>4</sup> the only general one is oxygen scrambling when the leaving group is an oxy anion such as a sulfonate. This requires that the anion within the pair be able to undergo rotation about the C-S bond at a rate not very much slower than the pair collapse. In all of the known cases of return in which a search for such scrambling has been made, it has been found and always at a rate equal to or only moderately less than return. Thus, oxygen scrambling is clearly a very useful cue. Until recently, its use was based on sampling, isolation, degradation, the use of <sup>18</sup>O and mass spectrometry;<sup>5</sup> however, we recently showed that the process can easily be followed in situ by means of NMR if <sup>17</sup>O is used.<sup>6</sup> Return in the *exo*-brosylate during ethanolsis was confirmed. We have now applied the same tool to the *endo*-mesylate during ethanolsis at 75 °C; we were forced to the change in anion because the two oxygen atoms in the *endo*-brosylate were found to have virtually identical chemical shifts (both within 0.1 of 161.5 ppm in ethanol at 75 °C; ethanol itself is at 7.3 ppm relative to external water at that temperature).<sup>7a,b</sup>

The natural-abundance spectrum of the mesylate in ethanol at 75 °C shows signals at 158.3 and 173.5 ppm; ether-labeled material<sup>8</sup> confirms our assumption on the basis of line widths that

(4) For some pertinent examples, see: Goering, H. L.; Anderson, R. P. *J. Am. Chem. Soc.* **1978**, *100*, 6469. Goering, H. L.; Humski, K. *J. Org. Chem.* **1975**, *40*, 920. Goering, H. L.; Thies, R. W. *J. Am. Chem. Soc.* **1968**, *90*, 2967, 2968. Goering, H. L.; Levy, J. F. *J. Am. Chem. Soc.* **1964**, *86*, 120. Goering, H. L. *Rec. Chem. Prog.* **1960**, *21*, 109.

(5) One major experimental advance had been the introduction of whole molecule mass spectrometry to analyze the reisolated substrate: Paradisi, C.; Bunnnett, J. F. *J. Am. Chem. Soc.* **1981**, *103*, 946. Their experiment led to the unexpected finding that 2-adamantyl tosylate, the arch example of a secondary substrate ionizing by a purely *k<sub>c</sub>* process, is subject to major return during solvolysis.

(6) Chang, S.; le Noble, W. J. *J. Am. Chem. Soc.* **1983**, *105*, 3708. For another NMR method potentially applicable in this field, see: Risley, J. M.; Van Etten, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 252. It rests on the <sup>18</sup>O isotope shift of <sup>13</sup>C resonances.

(7) (a) We confirm that this is slightly different from the 25 °C value of 6 ppm; Crandall, J. K.; Centeno, M. A. *J. Org. Chem.* **1979**, *44*, 1183. (b) The change from brosylate to mesylate has little effect on the exo and endo ethanolsis rates and virtually none on the ratio of the two: Brown, H. C.; Ravindranathan, M.; Chloupek, F. J.; Rothberg, I. *J. Am. Chem. Soc.* **1978**, *100*, 3143. (c) For another extensive search for possible solvent assistance, see: Harris, J. M.; Mount, D. L.; Raber, D. J. *Ibid.* **1978**, *100*, 3139.