Foundation Regional Instrumentation Facility (Grant No. CHE 8211164).

Supplementary Material Available: Experimental details and spectral and analytical data for the formation of π-allyl complexes **5** (3 pages). Ordering information is given on any current masthead page.

Cs^+-Induced Dehydration Reaction in $Cs[methanol]_N^+$ Cluster Ions

Jeffrey A. Draves and James M. Lisy*,†

Department of Chemistry, University of Illinois
Urbana, Illinois 61801

Received June 2, 1990
Revised Manuscript Received October 3, 1990

We report the observation of an alkali ion induced dehydration reaction in cluster ions $Cs[CH_3OH]_N^+$ and $Cs[CD_3OD]_N^+$. This gas-phase reaction differs in two respects from similar reactions reported in protonated methanol clusters.[1,2] First, the energy needed for the reaction is obtained via collision–solvation of a Cs^+ with methanol, and second, Cs^+ acts as the charge center. The observation of this reaction suggests the possibility of a catalytic effect.

The ion clusters are formed by merging Cs^+ from a thermionic filament with neutral methanol clusters from a molecular beam expansion in an apparatus described elsewhere.[3] The mass spectrum of the clusters is shown in Figure 1A. Two progressions are observed; the first is due to $Cs[CH_3OH]_N^+$, and the second which occurs 18 amu higher has the form $Cs[CH_3OH]_N[H_2O]^+$. These cluster ions bearing water may be formed (I) in the expansion, requiring the presence of water in the methanol, (II) as a result of reaction 1 where the water is coming from background water vapor

$$Cs[CH_3OH]_N^+ + H_2O \rightarrow Cs[CH_3OH]_{N-M}[H_2O]^+ + M(CH_3OH) \quad (1)$$

and (III) as the result of reaction 2, an intracluster reaction.

$$Cs[CH_3OH]_N^+ \rightarrow Cs[CH_3OH]_{N-M}[H_2O]^+ + CH_3OCH_3 + (M-2)(CH_3OH) \quad (2)$$

We believe that mechanism III is the most likely for the following reasons. The methanol used contains only trace amounts (0.05%) of H_2O. The cluster distribution of $Cs[CH_3OH]_N[H_2O]^+$ from expansions of methanol solution with 20% water was observed to have a maximum intensity for $N = 6$ and decreased for higher mixed clusters. This is consistent with the results of Stace,[4] who found that 1% solutions of methanol in water exhibited their most intense methanol–water peak for the subunit ratio 1:1 followed by decreasing intensities of the 1:2, 1:3, etc. ratios. Thus, a small percentage of water in methanol would be expected to have its most intense mixed cluster peak at a small cluster size and larger mixed cluster peaks would be found with decreasing intensity. This is *not* observed, as Figure 1A clearly shows the intensity of the mixed cluster peak increasing with cluster size. We may therefore discount mechanism I.

We may confirm mechanism III by using CD_3OD to solvate the Cs^+. Products of reaction 2 occurring in clusters of the form $Cs[CD_3OD]_N^+$ will be $Cs[CD_3OD]_{N-2}[D_2O]^+$ and CD_3OCD_3. Figure 1B shows the results of this test. The peak between $Cs[CD_3OD]_{19}^+$ and $Cs[CD_3OD]_{20}^+$ is now 20 amu higher than that for $Cs[CD_3OD]_{19}^+$ and is due to $Cs[CD_3OD]_{19}[D_2O]^+$. Thus, it appears clear that the reaction is indeed occurring as a result of mechanism III. Mechanism II is also eliminated by this test since it is highly unlikely that D_2O is being picked up from background vapor. The value of M in reaction 2 cannot be determined with our current apparatus. For protonated methanol clusters, a value of $M = 3$ was observed.[1]

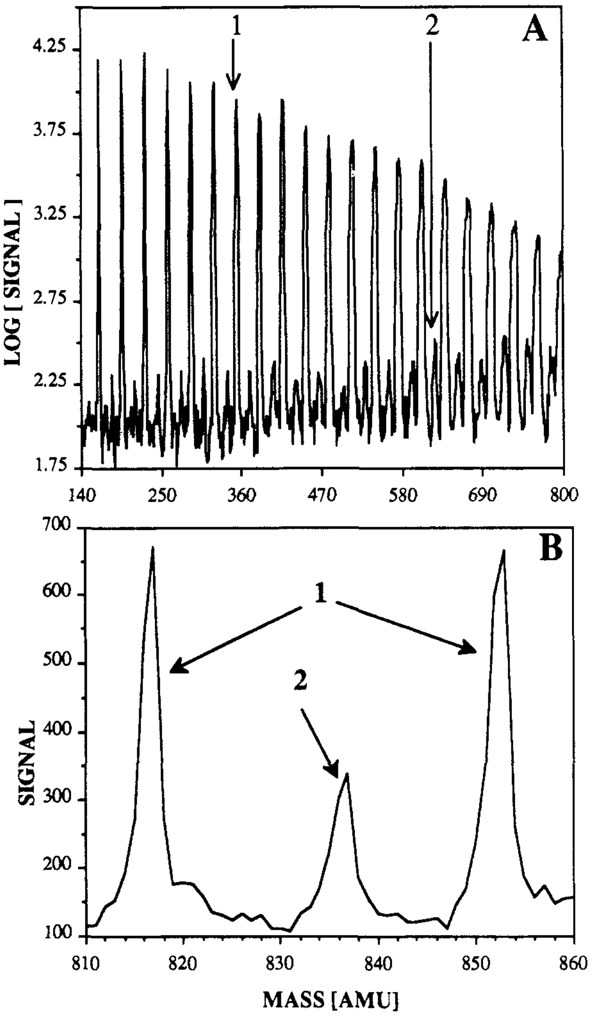

Figure 1. Mass spectrum of $Cs[CH_3OH]_N^+$ (A) and $Cs[CD_3OD]_N^+$ (B). Part A shows the mass spectrum of $Cs[CH_3OH]_N^+$, progression 1, for $N = 1$ to 21. Progression 2 indicates a cluster of the form $Cs[CH_3OH]_N[H_2O]^+$. Part B shows the mass spectrum of $Cs[CD_3OD]_N^+$. The peaks labeled 1 are the clusters $Cs[CD_3OD]_N^+$, $N = 19, 20$. The peak labeled 2 is the cluster $Cs[CD_3OD]_{19}[D_2O]^+$.

The gas-phase reaction between $CH_3OH_2^+$ and CH_3OH to produce $(CH_3)_2OH^+$ and H_2O is exoergic ($\Delta G° = -13.26$ kcal/mol[5]) but has a considerable activation energy of 26.5 kcal/mol.[6] The gas-phase reaction of two methanols to form dimethyl ether and water is slightly exoergic ($\Delta G° = -4.56$ kcal/mol[5]) but with an activation barrier that is comparable if not larger than the protonated case. The energy to overcome this barrier is apparently supplied from the collision and solvation of the Cs^+ ion. All of the Cs^+ produced via thermionic emission are in the ground ($^1S_0$) electronic state since the lowest lying excited state (^3P) is 13.4 eV above ground.[7] Thus electronic excitation

---

* Author to whom correspondence should be addressed.

† Alfred P. Sloan Fellow.

(1) Morgan, S.; Keesee, R. G.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1989**, *111*, 3841. Morgan, S.; Castleman, A. W., Jr. *J. Am. Chem. Soc.* **1987**, *109*, 2867.

(2) Huisken, F.; Stemmler, M. *Chem. Phys. Lett.* **1988**, *144*, 391.

(3) Draves, J. A.; Schulten, Z. L.; Liu, W-L.; Lisy, J. M. *J. Chem. Phys.* **1990**, *93*, 4589. Liu, W.-L.; Lisy, J. M. *J. Chem. Phys.* **1988**, *89*, 605.

(4) Stace, A. J.; Shukla, A. K. *J. Chem. Soc.* **1982**, *104*, 5314.

(5) Based on free energies of formation for neutrals from: Rossini, F. D.; Wagman, D. D.; Evans, W. H.; Levine, S.; Jaffe, I. Selected Values of Chemical Thermodynamic Properties. *Circ. Natl. Bur. Stand.* **1952**, *500*. Gas-phase basicities are from: Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York 1979, Vol. 2, Chapter 9.

(6) Bass, L. M.; Cates, R. D.; Jarrold, M. F.; Kirchner, N. J.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 7024.

(7) Olthoff, J.; Sawyer, R. A. *Phys. Rev.* **1932**, *42*, 766.

0002-7863/90/1512-9006$02.50/0

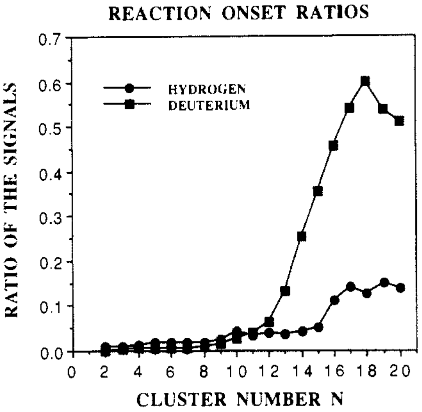

Figure 2. The ratio of the signals $Cs[CH_3OH]_{N-2}[H_2O]^+$:$Cs[CH_3OH]_N^+$ and $Cs[CD_3OD]_{N-2}[D_2O]^+$:$Cs[CD_3OD]_N^+$ are plotted vs cluster number N. These ratios were chosen because two methanols are consumed in reaction 2.

of the Cs^+ does not play a role in the intracluster chemistry.

We do not observe any signals in the mass spectrum due to clusters of the form $Cs[CH_3OH]_N[CH_3OCH_3]^+$. This is somewhat surprising in view of the high-pressure mass spectrometry data for the enthalpy of formation of Li^+ with H_2O (34 kcal/mol), CH_3OH (38.1 kcal/mol), and CH_3OCH_3 (39.5 kcal/mol).[8] If the same trend were present for Cs^+, one would expect to see preferential loss of H_2O over CH_3OCH_3 given comparable ion-neutral distances. However, in large protonated clusters containing one molecule of $(CH_3)_2O$ in CH_3OH[1,9] or H_2O,[9] elimination of $(CH_3)_2O$ appears to be the most favored evaporative process. One interpretation of these results is that the CH_3 groups disrupt the hydrogen bonding within large clusters and lead to looser structures.[10] The possibility of the reaction occurring and neither the H_2O or the CH_3OCH_3 leaving has been investigated by depletion spectroscopy.[3,11] Clusters of the form $Cs[CH_3OH]_{N-2}[H_2O][CH_3OCH_3]^+$ have the same mass-to-charge ratio as $Cs[CH_3OH]_N^+$. Laser scans in the region of 938 cm^{-1}, where CH_3OCH_3 has a monomer absorption,[12] detected no depletion.

The size dependence for reaction 2 may be seen in the reaction onset curves in Figure 2, which remain flat until a cluster size of $N = 10$. At this point a sharp increase in the curve is observed, which levels off in the region of $N = 17$–18. These cluster sizes are significant in that 10 methanols fill the first solvation shell of the Cs^+ and the 17th methanol is the last to enter the second solvent shell.[3] Therefore the reaction seems to be occurring most frequently for clusters that have some methanols in the second solvent shell.[13]

This reaction is unique in that first the cluster ion is generated by impact of a Cs^+ into a cluster of methanols, not by electron impact[2] or multiphoton ionization[1] and second the Cs^+ is the center of charge, not a proton. The bonding properties of these two species are vastly different as seen by comparison of the enthalpy of association of the Cs^+ with methanol (~13 kcal/mol[14]) to the proton affinity of methanol (184.9 kcal/mol[15]). Clearly, the proton achieves a much greater degree of covalency than does the Cs^+. Furthermore, the difference in bonding properties of Cs^+ and H^+ suggests the possibility of a catalytic effect. Current research is underway to determine if such reactions are present when other alkali ions act as the charge center.

Acknowledgment. This work has been supported in part by the National Science Foundation (Grant CHE-8714735) and the University of Illinois Research Board. Achnowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

---

(8) Keesee, R. G.; Castleman, A. W., Jr. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1011.

(9) Hiraoka, K.; Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1974**, *96*, 3359.

(10) Grimsrud, E. P.; Kebarle, P. *J. Am. Chem. Soc.* **1973**, *95*, 7939.

(11) Michael, D. W.; Lisy, J. M. *J. Chem. Phys.* **1986**, *85*, 2528.

(12) Herzberg, G. *Infrared and Raman Spectra of Polyatomic Molecules*; Van Nostrand: New York, 1945.

(13) The apparent isotopic dependence on reaction extent may be due to the increased density of states for the deuterated species, since the solvent shell structure for the protonated and deuterated cluster ions is the same. Draves, J. A.; Lisy, J. M., unpublished results.

(14) Smith, S. F.; Chandrasekhar, J.; Jorgensen, W. L. *J. Phys. Chem.* **1982**, *86*, 3308.

(15) Wolf, J. W.; Staley, R. H.; Koppel, I.; Taagepera, M.; McIver, R. T.; Beauchamp, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 5417. Yamdagni, R.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 1320.

Ultraviolet Resonance Raman Spectroscopy of Bacteriorhodopsin: Evidence against Tyrosinate in the Photocycle

James B. Ames, Sarah R. Bolton, Madeline M. Netto, and Richard A. Mathies*

Department of Chemistry, University of California
Berkeley, California 94270

Received July 18, 1990

Ultraviolet resonance Raman (UVRR) spectroscopy is a powerful technique for probing the structure of proteins.[1,2] Vibrational scattering from different aromatic residues may be selectively enhanced by choosing appropriate excitation wavelengths. This raises the attractive possibility of using UVRR to study dynamic structural changes in proteins such as bacteriorhodopsin (BR), which functions as a light-driven proton pump.[3,4] Indeed, the feasibility of UVRR experiments on BR has recently been demonstrated.[5,6] It was previously proposed that light-adapted bacteriorhodopsin (BR_{568}) contains an ionized tyrosine (Tyr-185) which protonates upon light absorption and when the protein relaxes to its dark-adapted state (BR_{DA}).[7-10] The presence of tyrosinate in BR_{568} has also been suggested by recent UVRR experiments.[6] In this communication, we present UVRR spectra of BR_{568} and BR_{DA} which indicate that tyrosinate does *not* play a role in the photocycle.

Figure 1 presents UVRR spectra of BR_{568} and BR_{DA} excited at 253 and 240 nm. Lines at 1618, 1578, 1554, 1460, 1360, and 1340 cm^{-1} are due to tryptophan whereas tyrosine contributes scattering at ~1615 cm^{-1}.[11,12] No vibrational bands from tyrosyl radicals at 1393, 1502, and 1552 cm^{-1} or photoproducts of Trp at 1522, 1593, and 1646 cm^{-1} were detected.[13] The Raman signals were linear in laser power from 1.5 to 15 mJ/cm^2 per pulse. Using

---

*To whom correspondence should be addressed.

(1) Spiro, T. G.; Grygon, C. A. *J. Mol. Struct.* **1988**, *173*, 79-90.

(2) Asher, S. A. *Annu. Rev. Phys. Chem.* **1988**, *39*, 537-588.

(3) Birge, R. R. *Biochim. Biophys. Acta* **1990**, *1016*, 293-327.

(4) Khorana, H. G. *J. Biol. Chem.* **1988**, *263*, 7439-7442.

(5) Netto, M. M.; Fodor, S. P. A.; Mathies, R. A. *Photochem. Photobiol.* **1990**, *52*, 605-607.

(6) Harada, I.; Yamagishi, T.; Uchida, K.; Takeuchi, H. *J. Am. Chem. Soc.* **1990**, *112*, 2443-2445.

(7) Rothschild, K. J.; Roepe, P.; Ahl, P. L.; Earnest, T. N.; Bogomolni, R. A.; Das Gupta, S. K.; Mulliken, C. M.; Herzfeld, J. *Proc. Natl. Acad. Sci. U.S.A.* **1986**, *83*, 347-351.

(8) Roepe, P. D.; Ahl, P. L.; Herzfeld, J.; Lugtenburg, J.; Rothschild, K. J. *J. Biol. Chem.* **1988**, *263*, 5110-5117.

(9) Dollinger, G.; Eisenstein, L.; Lin, S.-L.; Nakanishi, K.; Termini, J. *Biochemistry* **1986**, *25*, 6524-6533.

(10) Braiman, M. S.; Mogi, T.; Stern, L. J.; Hackett, N. R.; Chao, B. H.; Khorana, H. G.; Rothschild, K. J. *Proteins: Struct., Funct. Genet.* **1988**, *3*, 219-229.

(11) Fodor, S. P. A.; Copeland, R. A.; Grygon, C. A.; Spiro, T. G. *J. Am. Chem. Soc.* **1989**, *111*, 5509-5518.

(12) Asher, S. A.; Ludwig, M.; Johnson, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 3186-3197.

(13) Johnson, C. R.; Ludwig, M.; Asher, S. A. *J. Am. Chem. Soc.* **1986**, *108*, 905-912.

0002-7863/90/1512-9007$02.50/0