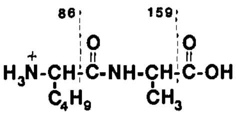


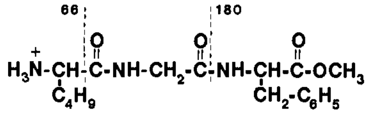
$$H_3\overset{+}{N}\text{-}\underset{C_4H_9}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}\underset{CH_3}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OH$$

The dominant photofragmentation process is loss of CO_2 to give m/z 159. A smaller peak at m/z 86 results from cleavage of the α-C–C bond in leucine with transfer of a hydrogen and charge retention on the N-terminus. These are the A_2 and A_1 sequence ions, respectively. Weber and Levson have reported the CAD spectra of several protonated oligopeptides made by field desorption.[20] For protonated Leu-Ala they report a base peak at m/z 87, and in none of the spectra is loss of CO_2 apparent. Comparison can also be made with the electron impact mass spectrum of Leu-Ala, which has m/z 86 as the major fragment.[21] Thus, the loss of CO_2 seen in the FT-MS laser photodissociation spectrum is an unusual fragmentation that may be indicative of absorption of the photon energy specifically by the carboxyl chromophore.

We have observed that the extend of photofragmentation of protonated Leu-Ala depends strongly on the wavelength of the laser radiation. Protonated Leu-Ala readily photodissociates at 193 nm and to a smaller extent at 249 nm, but photofragment ions were not observed at 350 nm. For comparison we recorded the absorption spectrum of Leu-Ala in methanol (0.44 g/L) using a Cary 219 UV–visible spectrophotometer. The absorbance was negligible between 400 and 260 nm but increased sharply below 250 nm, in parallel with the photodissociation yields of the gaseous positive ions. A number of previous studies have shows a close correlation between solution absorption spectra and gas-phase photodissociation spectra.[6,7,22]

Loss of CO_2 from protonated Leu-Ala is not particularly desirable. One way we have circumvented this is to make the methyl ester derivative by treating the peptide with a stock solution of 0.5 N HCl in methanol for 1 h at room temperature. Photodissociation of the protonated *O*-methyl ester of Leu-Ala at 193 nm produces only m/z 86.

Photodissociation of the protonated *O*-methyl ester tripeptide Leu-Gly-Phe also proceeds efficiently at 193 nm. The fragmentation pattern is



$$H_3\overset{+}{N}\text{-}\underset{C_4H_9}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}NH\text{-}\underset{CH_2\text{-}C_6H_5}{CH}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3$$

The major photofragment peak is m/z 180, which corresponds to the Z_1 sequence ion $^+NH_3CH(CH_2C_6H_5)COOCH_3$. A small amount of the A_1 sequence ion m/z 86, $^+NH_2{=}CH(C_4H_9)$, is also seen, and its relative abundance increases as the laser power is increased. In order to confirm the structure of the m/z 180 photofragment, the C-terminus was labeled 50/50 with acidic CH_3OH/CD_3OH, so that fragment ions containing the C-terminus appear in the mass spectrum as doublets three mass units apart. From 193-nm radiation, photodissociation of protonated Leu-Gly-Phe-OCH_3/OCD_3 produces the doublet m/z 180/183, confirming that it is the C-terminus Z_1 sequence ion.

We plan to investigate the photodissociation of other oligopeptides, but their low volatility will probably limit these studies to molecular weights less than about 800 u. For high molecular weight biomolecules, we plan to utilize a tandem quadrupole–Fourier transform mass spectrometer (QFT-MS) where ions made by fast atom bombardment in the source of a quadrupole mass spectrometer are stored and mass analyzed in a separate ICR analyzer cell.[23,24] It should also be possible to use several laser pulses to sequentially fragment ions, in a manner similar to the consecutive CAD experiments (MS/MS/MS) done by FT-MS.[25,26]

Acknowledgment. Our first ion photodissociation experiments were performed with lasers loaned by the San Francisco Laser Center, and currently we are using an excimer laser on loan from F. S. Rowland. This work was supported by the National Science Foundation and a grant from the Chevron Research Co. S.S.D is grateful to the University of California for a Regents Fellowship.

---

(20) Weber, R.; Levson, K. *Biomed. Mass Spectrom.* **1980**, *7*, 314–316.

(21) Svec, H. J.; Junk, G. A. *J. Am. Chem. Soc.* **1964**, *86*, 2278.

(22) Freiser, B. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1977**, *99*, 3214.

(23) McIver, R. T., Jr.; Hunter, R. L.; Bowers, W. D. *Int. J. Mass Spectrom. Ion Processes*, in press.

(24) Hunt, D. F.; Shabanowitz, J.; McIver, R. T., Jr.; Hunter, R. L.; Syka, J. E. P. *Anal. Chem.*, submitted for publication.

(25) McIver, R. T., Jr.; Bowers, W. D. "Tandem Mass Spectrometry"; McLafferty, F. W., Ed.; Wiley: New York, 1983; pp 287–301.

(26) Cody, R. B.; Burnier, R. C.; Cassady, C. J.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 2225.

A New Environment for Water. The First Authenticated Example of Water Molecules Engaged in Twin, Three-Center Hydrogen Bonds: The Crystal and Molecular Structure of $\{[(CH_3)_2SnCl_2\cdot H_2O]_2\cdot 18\text{-crown-6}\}_n$

M. M. Amini,[†] A. L. Rheingold,*[‡] R. W. Taylor,*[†] and J. J. Zuckerman*[†]

Department of Chemistry, University of Oklahoma
Norman, Oklahoma 73019
Department of Chemistry, University of Delaware
Newark, Delaware 19716

Received June 19, 1984

A uniquely situated water molecule is found in the lattice of $\{[(CH_3)_2SnCl_2\cdot H_2O]_2\cdot 18\text{-crown-6}\}_n$. While no stable binary complexes of water with 18-crown-6 have been isolated,[1,2] enhanced dipole and acidity can be brought about in water by complexation to a metal.[1] The water molecules, which are coordinated to tin in the title compound, engage in twin, three-center (bifurcated) hydrogen bonding to the crown ethers. The protons, which have been located in two X-ray structure determinations on the same data crystal, one at 23 and one at -120 °C,[3] each participate in a short contact to two oxygen atoms in two crown molecules. Thus each water molecule is five-coordinated with the geometries depicted in Figure 1 [O(5) and O(6) lie on mirror planes, so the environments of each pair of attached hydrogens are identical]. There is no authenticated precedent for such an

---

[†] University of Oklahoma.

[‡] University of Delaware.

(1) Elbasyouny, A.; Brügge, H. J.; von Deuten, K.; Dickel, M.; Knöchel, A.; Koch, K. U.; Kopf, J.; Melzer, D.; Rudolf, G. *J. Am. Chem. Soc.* **1983**, *105*, 6568.

(2) Newcombe, G. R.; Taylor, H. C. R.; Fronczek, F. R.; Delord, T. J.; Kohli, D. K.; Vögtle, F. *J. Am. Chem. Soc.* **1981**, *103*, 7376.

(3) Dimethyltin(IV) dichloride crystallizes with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) as a hydrated dimer, mp 132–138 °C, $\{[(CH_3)_2SnCl_2\cdot H_2O]_2\cdot 18\text{-crown-6}\}_n$, $C_{16}H_{40}Cl_4O_8Sn_2$, fw 739.683 daltons, in the monoclinic space group $C2/m$ with $a = 16.348$ (3) Å, $b = 11.668$ (2) Å, $c = 15.063$ (4) Å, $\beta = 93.22$ (2)°, $V = 2868$ (1) Å^3, $Z = 4$ at 23 °C. The structure was studied at 23 °C ($\rho_{calcd} = 1.713$ g cm^{-3}) and −120 °C ($\rho_{calcd} = 1.769$ g cm^{-3}) and solved by direct methods (SHELXTL-SOLV) using 2951 unique reflections (3σ cutoff) from 3459 collected (3341 unique) on an R3 Nicolet automated diffractometer (Mo K_α, $\mu = 21.48$ cm^{-1}, $4° \leq 2\theta \leq 55°$; scan speed 3°/min) to a final, conventional R value of 0.0331 and R_w of 0.0371 at 23 °C and 0.0282 and 0.0269, respectively, at −120 °C. Corrections for absorption (empirical) and secondary extinction were applied. The final refinement utilized anisotropic thermal parameters for all non-hydrogen atoms and isotropic parameters for the two hydrogen atoms of interest; the remaining hydrogen atoms were treated as fixed, idealized isotropic contributions. The water molecule hydrogen atoms were not found at 23 °C but were positioned so as to minimize the hydrogen-bonded distances to the ether oxygen atoms. At −120 °C, the two independent water hydrogen atoms were located at conventional hydrogen-bonded distances in positions indistinguishable from those assigned at 23 °C. Their inclusion lowered R from 0.0291 to 0.0282. Crown C(7) and C(8) atoms are disordered in equal occupancy locations, viz., C(7′) and C(8′) about the crystallographically imposed mirror plane. No peaks on the final difference map were greater than a diffuse background (0.66 e$^-$ Å^{-3} at 23 °C; 0.87 e$^-$ Å^{-3} at −120 °C) at convergence.

0002-7863/84/1506-7289$01.50/0

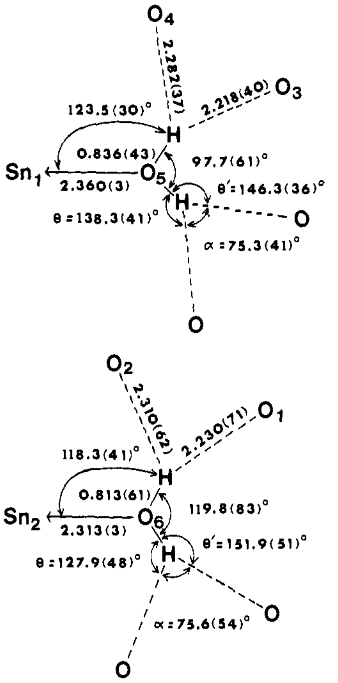


Figure 1. Geometry about the two independent water molecules. The oxygen–oxygen distances at 23 and -120 °C, respectively: d[O(5)–O(3)] = 2.976 (6), 2.950 (4); d(O(5)–O(4)] = 3.023 (7), 2.959 (4); d[O(6)–O(1)] = 3.011 (6), 2.971 (3); d[O(6)–O(2)] = 2.921 (6), 2.881 (4) Å.

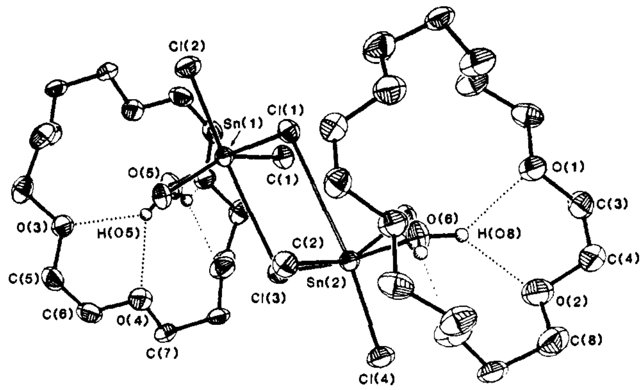


Figure 2. Molecule structure and labeling scheme for $\{[(CH_3)_2SnCl_2 \cdot H_2O]_2 \cdot 18\text{-crown-}6\}_n$. Hydrogen-bonded interactions with 18-crown-6 molecules are indicated by broken lines. Selected bond distances and angles at -120 °C: Sn(1)–Cl(1), 2.524 (1); Sn(1)–Cl(2), 2.419 (1); Sn(1)–Cl(3), 3.050 (1); Sn(1)–C(1), 2.104 (3); Sn(1)–O(5), 2.360 (3); Sn(2)–Cl(3), 2.536 (1); Sn(2)–Cl(4), 2.393 (1); Sn(2)–Cl(1), 3.311 (1); Sn(2)–C(2), 2.112 (3); Sn(2)–O(6), 2.313 (3); H(O5)–(3), 2.22 (1); H(O5)–O(4), 2.28 (1); H(O6)–O(1), 2.23 (1); H(O6)–O(2), 2.31 (1) Å; Cl(1)–Sn(1)–Cl(2), 93.4 (0)°; Cl(1)–Sn(1)–C(1), 95.8 (1)°; Cl(1)–Sn(1)–O(5), 176.2 (1)°; Cl(1)–Sn(1)–Cl(3), 81.0 (1)°; Cl(2)–Sn(1)–Cl(3), 175.4 (1)°; Cl(2)–Sn(1)–O(5), 90.5 (1)°; Cl(2)–Sn(1)–C(1), 101.0 (1)°; C(1)–Sn(1)–O(5), 83.4 (1)°; Cl(3)–Sn(2)–Cl(4), 93.3 (0)°; Cl(3)–Sn(2)–C(2), 93.6 (1)°; Cl(3)–Sn(2)–O(6), 172.5 (1)°; Cl(3)–Sn(2)–Cl(1), 76.7 (1)°; Cl(1)–Sn(2)–Cl(4), 170.5 (1)°; Cl(4)–Sn(2)–C(2), 102.6 (1)°; Cl(4)–Sn(2)–O(6), 94.2 (1)°; C(2)–Sn(2)–O(6), 84.7 (1)°; Sn(1)–Cl(1)–Sn(2), 103.9 (1)°; Sn(1)–Cl(3)–Sn(2), 98.4 (1)°.

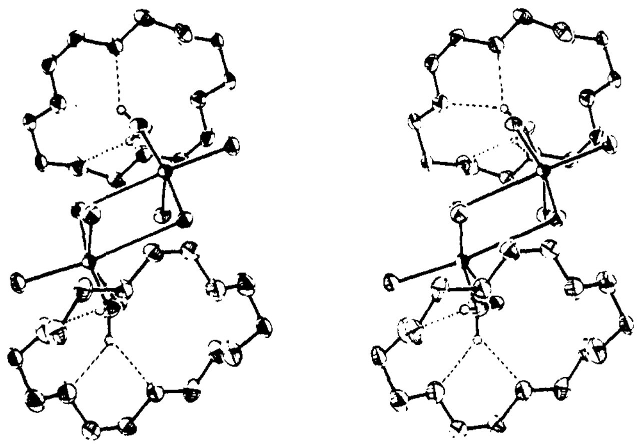


Figure 3. Stereoview of $\{[(CH_3)_2SnCl_2 \cdot H_2O]_2 \cdot 18\text{-crown-}6\}_n$.

arrangement in any form of ice or in biological, geological, or mineralogical systems known to us.[4-17]

One of the coordinated water molecules in $Gd(NO_3)_3 \cdot 3H_2O \cdot 18$-crown-6 apparently makes contacts of 3.01–3.14 Å to four crown ether oxygen atoms, but the hydrogen atoms have not been located, and there seems to be some question of whether the structure was solved in the correct space group ($Pn2_1a$ vs. disordered $Pnma$) despite $R = 2.9\%$.[18] There are also some suggestive short O···O contacts to the water molecule in 5,6-dihydroisocystidine monohydrate, but the authors do not comment on this aspect of the structure.[19]

The range of known three-center $O\text{–}H \cdots O_2$ hydrogen bonds[15] is from symmetrical with r and r' equal to 2.085 and 2.140 Å, respectively, $\theta + \theta' + \alpha = 358°$ to unsymmetrical with r and r' equal to 1.836 and 2.814 Å, respectively, and $\theta + \theta' + \alpha = 352°$ (Figure 2). In a quantum-mechanical treatment at the SCF·HF/4-31G level of approximation, binding energies of 10.3 and 10.9 kcal/mol were calculated, respectively, for water trimers with a symmetrical bond ($r = r' = 2.15$ Å, $\theta = \theta' = 135°$, $\alpha = 90°$) and with an unsymmetrical bond [$r = 1.94$, $r' = 2.50$ Å, $\theta = 150°$, $\theta' = 110°$, $\alpha = 100°$). These bonds were calculated to be 1–2 kcal/mol more stable than an equilibrium linear dimer with H···O = 1.882 Å and $\alpha = 180°$.[13] In the title compound the hydrogens attached to O(5) and O(6) make bonds to the crown oxygens which differ by only 0.064 and 0.080 Å with angle sums of 360.2° and 355.4°, respectively. The average O···O distances are 2.983 (9) Å at 23 °C and 2.940 (6) Å at -120 °C.

The two crystallographically independent 18-crown-6 molecules have an unusual ring conformation, with the sequence of torsional angles [(anti-gauche-anti)$_2$ gauche-gauche-anti]$_2$. This conformation, found previously in complexes with organic amines,[20-24]

---

(4) Hadzi, D., Ed. "Hydrogen Bonding"; Pergamon Press: Oxford, England, 1959.

(5) Pimentel, G. C.; McClelland, A. L. "The Hydrogen Bond"; Freeman: San Francisco, 1960.

(6) Donohue, J. In "Structural Chemistry and Molecular Biology"; Rich, A., Davidson, N., Eds.; Freeman: San Francisco, 1968; p 443.

(7) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968.

(8) Vinogradov, S. N.; Linnell, R. H. "Hydrogen Bonding"; Van Nostrand Reinhold: New York, 1971.

(9) Pimentel, G. C.; McClellan, A. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 347.

(10) Baur, W. H. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1456.

(11) Pedersen, B. *Acta Crystallogr., Sect. B* **1974**, *B30*, 289.

(12) Olovsson, I.; Jönsson, P.-G. In "The Hydrogen Bond"; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland Publishing Co.: Amsterdam, 1976; Vol. 2, p 408.

(13) Newton, M. D.; Jeffrey, G. A.; Takagi, S. *J. Am. Chem. Soc.* **1979**, *101*, 1997.

(14) Kuleshova, L. N.; Zorkii, P. M. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1363.

(15) Ceccarelli, C.; Jeffrey, G. A.; Taylor, R. *J. Mol. Struct.* **1981**, *70*, 255.

(16) Schuster, P., Ed. *Top. Curr. Chem.* **1984**, *120*.

(17) Jeffrey, G. A.; Mitra, J. *J. Am. Chem. Soc.* **1984**, *106*, 5546.

(18) Backer-Dirks, J. D. J.; Cooke, J. E.; Galas, A. M. R.; Ghotra, J. S.; Gray, C. J.; Hart, F. A.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1980**, 2191.

(19) Kojic-Prodic, B.; Ruzic-Toros, Z.; Coffou, E. *Acta Crystallogr., Sect. B* **1976**, *B32*, 1103.

(20) Knochel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *J. Chem. Soc., Chem. Commun.* **1978**, 595.

(21) Harkema, S.; van Hummel, G. J.; Daasvatn, K.; Reinhoudt, D. N. *J. Chem. Soc., Chem. Commun.* **1981**, 368.

(22) Bandy, J. A.; Truter, M. R.; Wingfield, J. N.; Lamb, J. D. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1025.

(23) Weber, G.; Sheldrick, G. M. *Acta Crystallogr., Sect B* **1981**, *B37*, 2108.

(24) Weber, G. *Acta Crystallogr., Sect. B* **1982**, *B38*, 629.

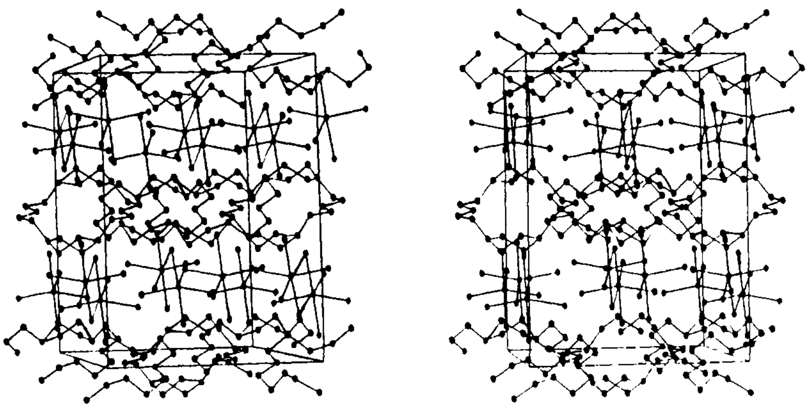


Figure 4. Unit cell packing as viewed along the *b* axis.

UCl_3^+ cations,[25] and hydrated $UO_2(NO_3)_2$,[26] differs from those usually encountered with metal cations (e.g., K^+),[27] hydrogen-bonded molecules (e.g., malononitrile),[28] or cation-coordinated water (e.g., $Mn(NO_3)_2{\cdot}6H_2O$)[29] in that two aga units are replaced with gga units which allows two $Sn{-}OH_2$ groups to approach opposite sides of the ring to interact each with four ether oxygens (see stereoview in Figure 3).

Each of the two crystallographically independent tin atoms lying at a badly distorted O_h site [∠C–Sn–C = 154.4 (2)°, 153.2 (2)°] is coordinated to a water molecule *trans* to a μ-Cl atom of the central Sn_2Cl_2 ring. Such Cl-bridged Sn_2Cl_2 systems are found in $[C_9H_8]^+[(CH_3)_2SnCl_3]^-$ (∠C–Sn–C = 152.2°),[30] bis(dimethyltin dichloride–2,6-dimethylpyridine *N*-oxide) (145.3°),[31] $[(CH_3)_2SnCl_2{\cdot}O{=}CC_2(C_6H_5)_2]_2$ (142.2°),[32] and $(CH_3)_2SnCl_2$ itself (123.5°).[33,34] Of the five known examples, our μ-Cl- -Sn distance is shortest.

Although crown ether complexes of tin(II) salts,[35,36] triphenyltin(II) alkali-metal derivatives,[37] and inorganic[38,39] and organotin(IV) halides and pseudohalides[40,41] have been prepared, the only structural determination available shows O_h, *cis*-$(H_2O)_2SnCl_4$ units hydrogen bonded to uncoordinated water and ether oxygen atoms in $Sn(OH_2)_2Cl_4{\cdot}18\text{-crown-}6{\cdot}2H_2O{\cdot}CHCl_3$.[41] Preparations of the title compound from methanol (mp 119–123 °C)[40] and isopropyl ether (mp 98–101 °C)[42] give different melting points from our product (mp 132–138 °C) from chloroform, recrystallized from methylene chloride. From the tin-119m Mössbauer [isomer shift = 1.59 ± 0.03; quadrupole splitting (QS) = 3.93 ± 0.06 mm s^{-1}] QS value, an ∠C–Sn–C angle of 160° can be calculated.[43]

Acknowledgment. Our work is supported by the Office of Naval Research (to J.J.Z.). We thank M&T Chemicals, Inc., for the donation of organotin starting materials. Purchase of the University of Delaware X-ray diffractometer was supported by a grant from the National Science Foundation. We thank Dr. R. Harlow at the E. I. du Pont de Nemours and Co. for help with recording the low-temperature data set.

Supplementary Material Available: A listing of atomic coordinates and temperature factors (Table 1S), bond lengths (Table 2S), bond angles (Table 3S), anisotropic temperature factors (Table 4S), hydrogen coordinates (Table 5S), and observed and calculated structure factors (Table 7S) (18 pages). Ordering information is given on any current masthead page.

---

(25) Bombieri, G.; DePaoli, G.; Immirzi, A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 1889.

(26) Bombieri, G.; DePaoli, G.; Immirzi, A. *J. Inorg. Nucl. Chem.* **1978**, *40*, 799.

(27) Dunitz, J. D.; Dobler, M.; Seiler, P.; Phizackerley, R. P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2733.

(28) Kaufmann, R.; Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *Chem. Ber.* **1977**, *110*, 2249.

(29) Vance, T. B.; Holt, E. M.; Varie, D. L.; Holt, S. L. *Acta Crystallogr., Sect. B* **1980**, *B36*, 153.

(30) Buttenshaw, A. J.; Duchene, M.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2230.

(31) Ng, S.-W.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *Organometallics* **1983**, *2*, 600.

(32) Ng, S.-W.; Barnes, C. L.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Kumar Das, V. G. *J. Am. Chem. Soc.* **1982**, *104*, 5359.

(33) Davies, A. G.; Milledge, H. J.; Puxley, D. C.; Smith, P. J. *J. Chem. Soc. A* **1970**, 2862.

(34) The two central, six-coordinated diphenyltin(IV) dichloride molecules in that tetrameric chain structure form a Cl-bridged Sn_2Cl_2 system (Bokii, N. G.; Struchkov, Yu. T.; Prokof'ev, A. K. *J. Struct. Chem.* (*Engl. Transl.*) **1972**, *13*, 619) with ∠C–Sn–C = 125.5° (Greene, T.; Bryan, R. F. *J. Chem. Soc. A* **1971**, 2549).

(35) Herber, R. H.; Smelkinson, A. E. *Inorg. Chem.* **1978**, *17*, 1023.

(36) Herber, R. H.; Carrasquillo, G. *Inorg. Chem.* **1981**, *20*, 3693.

(37) Bullard, W. R.; Taylor, M. J. *Aust. J. Chem.* **1981**, *34*, 1337.

(38) Gur'yanova, E. N.; Ganyushin, L. A.; Romm, I. P.; Shcherbakova, E. S.; Movsumzade, M. *J. Gen. Chem. USSR* (*Engl. Transl.*) **1981**, *51*, 356.

(39) Cusak, P. A.; Patel, B. N.; Smith, P. J. *Inorg. Chim. Acta* **1983**, *76*, L21.

(40) Smith, P. J.; Patel, B. N. *J. Organomet. Chem.* **1983**, *243*, C73.

(41) Cusack, P. A.; Patel, B. N.; Smith, P. J.; Allen, D. W., Nowell, I. W. *J. Chem. Soc., Dalton Trans.* **1984**, 1239.

(42) Russo, U.; Cassol, A.; Silvestri, A. *J. Organomet. Chem.* **1984**, *260*, 69.

(43) Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281.

Rate-Determining General-Base Catalysis in an Obligate $1e^-$ Oxidation of a Dihydropyridine

Ashoke Sinha and Thomas C. Bruice*

Department of Chemistry, University of California
at Santa Barbara, Santa Barbara, California 93106

Received July 30, 1984

In the main, reduction reactions by dihydropyridines involve hydride transfer. Many proposals that the overall two-electron reductions of oxidants proceed by an initial electron transfer from dihydropyridine to oxidant have recently been shown to be faulted by the experimental methods employed to study these reactions.[1] There are, of course, examples of one-electron transfer from dihydropyridines.[2-5] Experimental evidence has been offered in support of the following mechanism (eq 1) for the ferricyanide reaction.[4] The rate-determining step, shown here in the ferricyanide oxidation of *N*-methylacridan (MH_2), is the general-base-catalyzed proton ionization (k_2).

---

(1) Powell, M. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 7139–7149. Powell, M. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1982**, *104*, 5834–5836.

(2) Schellenberg, K. A.; Hellerman, L. *J. Biol. Chem.* **1958**, *231*, 547.

(3) Carlson, B. W.; Miller, L. L. *J. Am. Chem. Soc.* **1983**, *105*, 7453–7454.

(4) Powell, M. F.; Wu, J. C.; Bruice, T. C. *J. Am. Chem. Soc.* **1984**, *106*, 3850.

(5) Okamoto, T.; Ohno, A.; Oka, S. *J. Chem. Soc., Chem. Commun.* **1977**, 181. Okamoto, T.; Ohno, A.; Oka, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 330.