3.[19] The oxo-bridged triangular core associated with I and II is not retained, and significant structural reorganization is required to produce the "open" trinuclear structure of the anion of III. A notable feature of this structure is the presence of five-coordinate molybdenum centers, Mo(1) and Mo(3), with geometries intermediate between the idealized square-pyramidal and trigonal-bipyramidal limits.

We are currently pursuing studies of the solution properties of the pentamolybdate (I) and of its potential applications as a synthetic precursor.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE8514634).

Registry No. I, 120904-99-6; II, 120881-76-7; IIa, 120881-80-3; III, 120881-78-9; $[(n\text{-}C_4H_9)_4N]_2[Mo_2O_7]$, 64444-05-9; $C_6H_{10}NNHC(O)C(O)NHNC_6H_{10}$, 370-81-0.

Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, and thermal parameters for I, II, and III (18 pages); tables of observed and calculated structure factors (51 pages). Ordering information is given on any current masthead page.

(19) Pinacol (1.18 g, 1.0 mmol) was added to a solution of I (6.50 g, 0.5 mmol) in CH_2Cl_2 (75 mL), and the solution was stirred for 24 h at room temperature. After addition of ether and standing for 5 days, colorless translucent crystals of III were obtained in 30% yield. IR (KBr, cm^{-1}) 2930 (s), 2865 (m), 1475 (m, br), 1375 (vs), 1075 (m), 1010 (s), 910 (sh), 900 (vs), 780 (s, br). Anal. Calcd for $C_{44}H_{96}N_2O_{12}Mo_3$: C, 46.7; H, 8.48; N, 2.47. Found: C, 46.4; H, 8.29; N, 2.36.

(20) Crystal data for (III), $C_{44}H_{96}N_2O_{12}Mo_3$: monoclinic space group $P2_1/n$, a = 17.137 (5) Å, b = 17.513 (5) Å, c = 18.878 (5) Å, β = 91.01 (2)°, V = 5665.8 (25) Å^3, Z = 4, D_{calcd} = 1.33 g cm^{-3}. Structure solution and refinement based on 4056 reflections with $F_o \geq 6\sigma(F_o)$ (7861 collected, Mo Kα) converged at R = 0.064.

Observation of a Stepwise Double Proton Transfer in Oxalamidine Which Involves Matched Kinetic HH/HD/DD Isotope and Solvent Effects

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Received March 21, 1989

The determination of kinetic HH/HD/DD isotope effects[1-5] is an important tool in the elucidation of the mechanisms of double-proton-transfer reactions.[1-28] Depending on the molecular reaction systems, smaller or larger deviations from the so-called rule of the geometric mean (RGM),[17,19] which states that the isotopic rate constants are related by $k^{HH}/k^{HD} = k^{HD}/k^{DD}$, have been observed.[1-5] These deviations were particularly strong in the case of the symmetric double proton transfer in porphyrine (POR)[1] and azophenine (AP),[4] where $k^{HH} > k^{HD} \simeq k^{DD}$. This finding was first interpreted in terms of a synchronous tunneling process.[1] It can, however, also be explained by formal kinetics in terms of two consecutive single proton-transfer steps via a metastable intermediate.[1,4] The proton in flight contributes a primary kinetic isotope effect P and the bound proton a secondary isotope effect S to the reaction rates according to[1,4]

$$k^{HH}/k^{DD} = P{\cdot}S,\ k^{HD}/k^{DD} = 2/(S^{-1} + P^{-1}),\ P \gg S \simeq 1 \quad (1)$$

Evidence for a stepwise double proton transfer in POR and AP has been obtained by theoretical calculations[24-28] and in the case of POR also by simulation of the Arrhenius curves with use of various tunnel models.[10,24,25] However, eq 1 is not able to describe

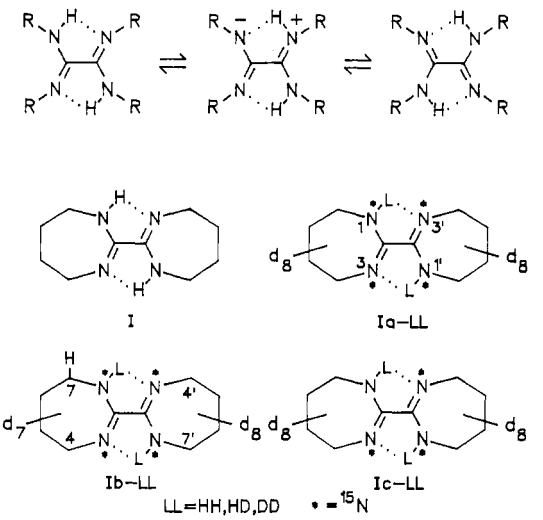

Figure 1. The stepwise double-proton-transfer in oxalamidine (OA, R = H), tetraphenyloxalamidine (TPOA, R = phenyl),[6] and I.[29]

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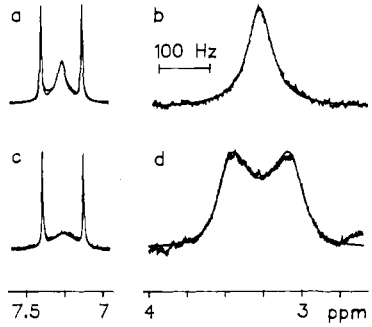

Figure 2. Superposed experimental and calculated 300.13 MHz ^1H NMR spectra of a 0.1 M solution of I in methylcyclohexane-d_{14} (MCY) at 362 K: (a) ^{15}N–^1H···^{15}N signal of Ia-HH and (b) 4,4′ and 7,7′ proton signal of Ib-HH at a deuterium fraction $D = 0$ in the mobile proton sites; (c) ^{15}N–^1H···^{15}N signal of Ia-HD, and (d) 4,4′ and 7,7′ proton signal of Ib-DD at a deuterium fraction $D = 0.94$ in the mobile proton sites (200–1800 scans on average, 60° pulses, 3s repetition time, 2500 Hz sweep width, 16 K spectra). The presence of a small amount of Ic was taken into account in the simulations; in addition, at $D = 0.94$ the presence of Ia-HH, Ib-HH, and Ib-HD was also taken into account. Simulation parameters: a, b, $k^{HH} = 635\ s^{-1}$; c, $k^{HD} = 260\ s^{-1}$, d, $k^{DD} = 215\ s^{-1}$. Further simulation parameters: $\nu_{^1H-^{15}N} = 7.26$ ppm, $^1J_{^1H-^{15}N} = 80.3$ Hz, $W_0 = 3.7$ Hz, and chemical shifts $\nu_4 = \nu_{4'} = 3.505$ ppm and $\nu_7 = \nu_{7'} = 3.03$ ppm. For further description see text.

the kinetic results of some degenerate intermolecular double-proton-transfer reactions where both proton sites contribute a primary kinetic isotope effect to the reaction rates.[1,2,5] Because of this uncertainty in the use of eq 1, we have tried to find a molecular system where eq 1 can be verified by an independent experimental method. We have succeeded in the case of oxalamidine (OA) tautomerism[6] (Figure 1). By using dynamic ^1H NMR spectroscopy, we find for OA "matched" kinetic solvent and isotope effects which indicate a stepwise reaction mechanism according to Figure 1.

Actual experiments were performed at 362 K on the isotopically labeled compound Ia (Figure 1) containing some Ib,[31] with use of methylcyclohexane-d_{14} (MCY) and acetonitrile-d_3 (AN) as solvents. The kinetic HH/HD isotope effects were determined by ^1H NMR line shape analysis of the ^{15}N–^1H···^{15}N signals of Ia-HH and Ia-HD, as shown in Figures 2a, 2c, 3a, and 3c. These signals constitute triplets with two sharp outer line components arising from the $^{15}N(\alpha)$–^1H···$^{15}N(\alpha)$ and $^{15}N(\beta)$–^1H···$^{15}N(\beta)$ spins, where α and β are the usual spin functions, and an exchange-broadened central line arising from the $^{15}N(\alpha)$–^1H···$^{15}N(\beta)$ spins. This signal pattern is expected for a moderately fast degenerate intramolecular proton transfer between two ^{15}N atoms; the rate constants k of the proton transfer are obtained by line shape analysis as described previously.[4] At a deuterium fraction of $D = 0$ in the labile proton sites the ^{15}N–^1H···^{15}N signal (Figure 2a and 3a) stems from the species Ia-HH; thus, the rate constant obtained by simulation corresponds to the rate constant k^{HH}. By contrast, at $D = 0.94$ (Figures 2c and 3c) the residual ^{15}N–^1H···^{15}N proton signal dominantly stems from the species Ia-HD, i.e., its line shape depends on k^{HD}. The observation that the center lines of the ^{15}N–^1H···^{15}N signals are larger for MCY as solvent than for AN and larger at $D = 0.94$ than at $D = 0$ indicates substantial kinetic HH/HD isotope and solvent effects on the reaction rates.

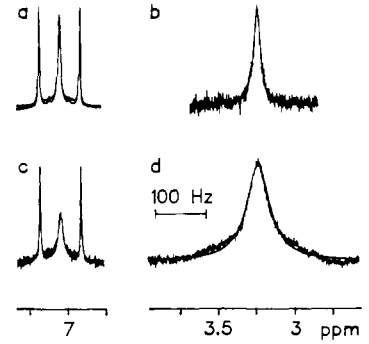

Figure 3. Superposed experimental and calculated 300.13 MHz ^1H NMR spectra of a 0.1 M solution of I in acetonitrile-d_3 (AN) at 362 K: (a) ^{15}N–^1H···^{15}N signal of Ia-HH and (b) 4,4′ and 7,7′ proton signal of Ib–HH at a deuterium fraction $D = 0$ in the mobile proton sites; (c) ^{15}N–^1H···^{15}N signal of Ia-HD, and (d) 4,4′ and 7,7′ proton signal of Ib-DD at a deuterium fraction $D = 0.94$ in the mobile proton sites. Simulation parameters: a, b, $k^{HH} = 2870\ s^{-1}$; c, $k^{HD} = 1090\ s^{-1}$; d, $k^{DD} = 830\ s^{-1}$. Further simulation parameters: $\nu_{^1H-^{15}N} = 7.05$ ppm, $^1J_{^1H-^{15}N} = 80.3$ Hz, $W_0 = 3$ Hz, and chemical shifts $\nu_4 = \nu_{4'} = 3.492$ ppm and $\nu_7 = \nu_{7'} = 2.965$ ppm. For further description see Figure 2 and text.

Actually, $k^{HH}_{MCY}/k^{HD}_{MCY} = 2.44$, $k^{HH}_{AN}/k^{HD}_{AN} = 2.63$, and $k^{HH}_{AN}/k^{HH}_{MCY} = 4.5$ at 362 K.

The kinetic HH/DD isotope effects were determined by line shape analysis of the 4 (4′) and 7 (7′) proton signals of Ib, as shown in Figures 2b, 2d, 3b, and 3d. Because of the deuteration at the carbon atoms these protons can be treated as one-spin systems for which the usual two-state exchange theory is valid. At $D = 0$ only exchange-broadened singlets are observed. Since the k^{HH} values are known, we obtain by line shape analysis the unknown chemical shifts of the 4 (4′) and of the 7 (7′) protons necessary to obtain the k^{DD} values from the spectra at $D = 0.94$. A comparison of Figure 2b with 2d and of Figure 3b with 3d shows substantial kinetic HH/DD isotope effects, i.e., $k^{HH}_{MCY}/k^{DD}_{MCY} = 3$, $k^{HD}_{MCY}/k^{DD}_{MCY} = 1.2$, $k^{HH}_{AN}/k^{DD}_{AN} = 3.5$, and $k^{HD}_{AN}/k^{DD}_{AN} = 1.3$.

As in the case of POR and AP, these kinetic HH/HD/DD isotope effects can be explained quantitatively[4] in terms of eq 1 with a stepwise reaction mechanism involving an intermediate as shown in Figure 1. However, in contrast to POR and AP, this interpretation is independently supported here by the observation of the increase of the rate constants with the solvent polarity.[32] Preliminary experiments indicate that the activation energy of the tautomerism of I in AN is several kcal/mol smaller than in MCY, as expected for the formation of ion pairs.[33-37] Because of an enthalpy/entropy compensation the differences between the rate constants in the two solvents are, however, attenuated. The absence of kinetic solvent effects in the related AP might be explained either by reduced solute–solvent interactions because of the bulky phenyl groups in this compound or by the formation of an apolar singlet biradical intermediate.[4]

These results definitively establish eq 1 as a criterion for a stepwise reaction pathway of degenerate double-proton-transfer reactions via an intermediate. This criterion is especially useful when kinetic solvent effects are absent and when temperature-dependent experiments cannot be performed.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, Bonn-Bad Godesberg, the Fonds der Chemischen Industrie, Frankfurt, and the Wissenschaftliche Gesellschaft Freiburg for financial support.

(29) I ≡ 2,2′-bis[4,5,6,7-tetrahydro-1,3-diazepine] has been synthesized from dicyan and 1,4-diaminobutane by Matsuda, K. U.S. Patent **1957**, No. 2.819.262. We found that this procedure is unsuitable for the synthesis of isotopically labeled I. Therefore, we modified a procedure of Weidinger et al.[30] for the synthesis of bicyclic oxalamidines from ethane diimidic acid dimethyl ester and aliphatic diamines. The modification consisted in an initial reaction temperature of 273 K instead of 298 K and in the use of methanol as solvent. For the preparation of Ia only the precursor, 1,4-diaminobutane needed to be isotopically labeled. The latter was prepared from isotopically labeled adipic acid via the amide with use of literature procedures.

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(31) Since the precursor adipic acid amide was labeled to about 95% with the ^{15}N isotope and to about 96% with the ^2H isotope, minor quantities of Ic as well as other isotopic species are present.

(32) The dielectric constant is 2 for MCY and 37.5 for AN, see: *Landolt-Börnstein, Zahlenwerte und Funktionen*, 6th ed.; Springer: Berlin–Göttingen–Heidelberg, 1959; Vol. II/6, p 613ff.

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