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Existence of a Marginally Stable Intermediate during the Base-Catalyzed Methanolysis of Methylene Phosphate and ab Initio Studies of the Monohydration of the Pentacoordinated Oxyphosphorane Intermediate

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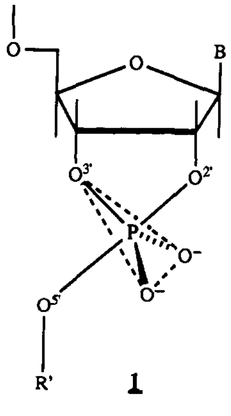
Contribution from the National Chemical Laboratory for Industry & Fermentation Research Institute, Agency of Industrial Science & Technology, MITI, Tsukuba Science City 305, Japan, and Department of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, California 90024-1569. *Received October 16, 1990*

Abstract: In the attack of OCH_3^- on ethylene phosphate monoanion, a dianionic pentacoordinate intermediate (**2a**) has been found by ab initio calculations at the 3-21G* level. Although only marginally stable, this contrasts with the results of Lim and Karplus (Nonexistence of Dianionic Pentacovalent Intermediates in the ab Initio Study of the Base-Catalyzed Hydrolysis of Ethylene Phosphate. *J. Am. Chem. Soc.* **1990**, *112*, 5872–5873) for attack by OH^- on ethylene phosphate monoanion where there is only a pentacoordinate transition state (**2b**). Together with the results of another paper,[8] it can be concluded that the cause of the discrepancy is attributable to the difference in axial substituents (OCH_3 vs OH). The dianionic species **2a** can better delocalize its charges over a larger space and thus exists, in gas phase, as a marginally stable intermediate. In contrast, Karplus' dianionic **2b** with a smaller substituent is too unstable in gas phase; thus, there is only one exocyclic $P-O_5$ bond-breaking/forming transition state (TS2 transition state: Taira, K.; et al. *Protein Eng.* **1990**, *3*, 691–701) and no intermediate. The identification of the intermediate **2a** enabled us to study monohydrations. The hydrations studied were those between the oxygen atoms of **2a**, representing the most significant interactions available and those most likely to have an influence on the solution-phase potential energy surface. As expected, bifurcating hydrations were more stabilizing than linear hydrations. However, unexpectedly, axial–equatorial interactions were found to be more stabilizing than equatorial–equatorial interactions.

Phosphorus dominates the living world: It plays a crucial role in genetic materials as well as in storage of biochemical energy.[1] We have been interested in the chemistry of the biologically important phosphate, including the tendency for phosphate to undergo nucleophilic attack to form a pentacoordinated intermediate. Such an intermediate has been shown to exist during acid-catalyzed hydrolysis of RNA[2,3] since (2′,5′)-UpU isomerizes to (3′,5′)-UpU via pseudorotation[4] of the intermediate. Recently, we carried out ab initio molecular orbital calculations on the model compound **2a** of the potential intermediate **1** using the STO-3G minimum basis set. We found a pentacoordinate oxyphosphorane that is intermediate to addition of 2′-oxygen and elimination of 5′-oxygen. The transition state for the exocyclic $P-O_5$ bond-breaking step is found to be higher in energy than the endocyclic $P-O_2$ bond-breaking step, consistent with there being a rapid equilibrium leading to formation of the cyclic oxyphosphorane.[5] Meanwhile, Lim and Karplus carried out similar calculations, utilizing the 3-21G* and 3-21+G* basis sets, on a simpler model compound (**2b**) and concluded that **2b** *does not* exist as an intermediate.[6] We now report that **2a**, which is closer in nature to the RNA backbone than **2b** *does exist* as an intermediate at the 3-21G* level of theory. Both, stereoelectronically favored and unfavored, transition states have been located,[7] in contrast to the acyclic system,[8] due to the unique cyclic nature of the RNA model intermediate. Moreover, the existence of the intermediate enables us to study interactions between the dianionic **2a** and water.



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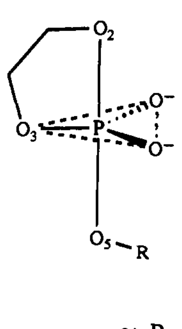

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a: $R = CH_3$

b: $R = H$

Our interests involve the effect of solvation on the entire potential energy surface[7] for the RNA cleaving mechanism, and we are currently utilizing Jorgensen's BOSS Monte Carlo program for this purpose.[9] In pursuit of the solution-phase potential energy surface, we have carried out ab initio molecular orbital calculations to determine the stabilization energies for interaction of a water monomer with the pentacoordinated oxyphosphorane intermediate. We present in this paper the structures of seven monohydrations bifurcating the oxygens of the pentacoordinate oxyphosphorane **2a**. The structure of water used for this study corresponds to the TIP4P model developed by Jorgensen to reproduce the thermodynamic properties of water within the confines of the Monte Carlo approach.[10]

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Table I. Stabilization Energies for the Hydrations Shown in the Figure

structure	RHF/3-21G* (hartrees)	stabilization (kcal/mol)	RHF/6-31G*[a] (hartrees)	stabilization (kcal/mol)	CP correction[a,b] (kcal/mol)	CP corrected[b] stabilization (kcal/mol)
TIP4P	-75.585 39		-76.010 53			
intermediate	-828.300 69		-832.602 69			
(1)	-903.950 02	-40.12	-908.657 87	-28.02	2.52	-25.50
(2)	-903.949 63	-39.88	-908.657 57	-27.84	2.78	-25.06
(3)	-903.947 68	-38.66	-908.655 86	-26.76	2.30	-24.46
(4)	-903.943 68	-36.14	-908.654 86	-26.13	2.35	-23.78
(5)	-903.943 52	-36.04	-908.653 15	-25.06	2.53	-22.53
(6)	-903.940 38	-34.07	-908.649 37	-22.68	1.85	-20.83
(7)	-903.938 01	-32.59	-908.648 68	-22.25	2.07	-20.18

[a] These are RHF/6-31G*//RHF/3-21G* energies. [b] The BSSE (basis set superposition error) was estimated with a counterpoise (CP) correction. This correction was made as implemented in GAUSSIAN 88. The order of stabilization does not change after CP correction, and the correction is roughly the same for each hydration.

Methods of Calculations

All calculations were carried out with GAUSSIAN 86[11] on FACOM M780/MSP or IBM 3090/MVS computers. The optimized geometry of dianionic **2a** was located at the RHF/3-21G* level of theory and verified by frequency analysis to have no vibrational modes immediately leading to a structure of lower energy. Then the oxyphosphorane intermediate was held frozen during the hydration studies. The frozen conformation (gs-G; with our earlier nomenclature[5] indicating that ground-state structure with axial methyl group gauche to the equatorial ring oxygen) is indeed the most stable conformer, also at the RHF/3-21G* level of theory, compared to the other conformers such as gs-T (methyl is *trans* to ring oxygen) and gs-G′ (methyl is gauche to ring oxygen, but it occupies opposite side of the ring envelope), all in agreement with our earlier calculations with STO-3G.[5] The TIP4P water monomer was used for all hydrations.[10] The internal structure of TIP4P water is held constant (O–H, 0.9572 Å; H–O–H, 104.52°), while its distance and orientation toward the constrained **2a** is fully optimized. Bifurcating hydrations were optimized at the RHF/3-21G* level. Energies were determined at the RHF/6-31G* level. The BSSE (basis set superposition error) was estimated with a counterpoise (CP) correction at the RHF/6-31G*//RHF/3-21G* level. This correction was made as implemented in GAUSSIAN 88.[12]

Results and Discussion

In contrast to the ab initio findings by Lim and Karplus,[6] suggesting the nonexistence of pentacoordinate intermediate **2b** in the base-catalyzed hydrolysis of ethylene phosphate, a marginally stable intermediate of a related cyclic species (**2a**) has been well characterized.[7] During the base-catalyzed methanolysis of ethylene phosphate, corresponding in the reversed direction to the base-catalyzed RNA hydrolysis,[5] a pentacoordinate oxyphosphorane intermediate (**2a**) *does exist* at the 3-21G* level of theory. Moreover, because of the unique cyclic nature of the RNA model intermediate **2a**, both stereoelectronically favored and unfavored transition states have been located. The first step of RNase catalysis involves the formation of a nucleoside 2′,3′-cylic phosphate ester. At the active site of RNase A, for example, the basic imidazole of the enzyme (His12) acts to remove the proton from the attacking 2′-hydroxyl group and the resulting more nucelophilic 2′-hydroxide then adds to phosphorus from the opposite side of the leaving 5′-OR group, leading to the "in-line" mechanism intermediate (structure **1**). The stereoelectronically favored endocyclic 2′-alkoxide attack on the phosphate moiety (TS1 transition state[5]) is ca. 14 kcal/mol lower in energy than the stereoelectronically unfavored elimination of exocyclic 5′-alkoxide (TS2 transition state[5]) at the level of 3-21G*.[7] These reactivity differences may be explained by the optimal orbital interactions between nonbonding lone pair orbitals on equatorial oxygen and the antibonding σ^* orbital of axial P–O bonds.[13] Although we call this reactivity dependence on the orientation of lone pair electrons a "stereoelectronic effect", we do not know the exact origin of the effect as to whether it is really orbital mixing or due to other factors, since the overlap populations and Mulliken charges calculated for oxyphosphorane species **2a** are not necessarily in accord with the orbital mixing interpretation. Nevertheless, the existence of the intermediate, which has the well depth on the order of k_BT and is unlikely to be kinetically significant for the gas-phase reaction, has enabled us to study interactions between the dianionic intermediate **2a** and a water molecule.

The solvent effect in chemical reaction can be dramatic. Rate changes of 10^{15} M^{-1} s^{-1} between gas-phase and aqueous-phase reactions have been observed.[14] These effects involve both enthalpic and entropic contributions due to differential solvation of reactants and transition states. Adequate theoretical treatment of these effects requires identification of reactants, intermediates, and the transition state and the simulation of the condensed phase. The application of statistical mechanics to the description of condensed-phase phenomena usually involves the Monte Carlo method developed by Metropolis.[15] The Metropolis algorithm generates a Boltzmann distribution of configurations that insufficiently represents high-energy, low-probability states that contribute to the free energy of the system.[16] Methods to improve the distribution have included umbrella sampling,[17] importance sampling,[18] and preferential sampling.[19] However, with these methods, simulations covering a range of energies greater than $4k_BT$ result in standard deviations similar in magnitude to the thermodynamic quantities of interest.[20] The statistical perturbation method by Zwanzig with the isothermal–isobaric ensemble successfully yields free energies with good precision.[21] Recent use of this method identifies its great utility and simplicity.[22] Examples include its use in calculating p*K*a's of weak organic acids in water, relative binding affinities for numerous ligand-receptor pairs, and free energies of hydration for protein side chains, hydrocarbons, and free ions in solution.[23] Several fundamental

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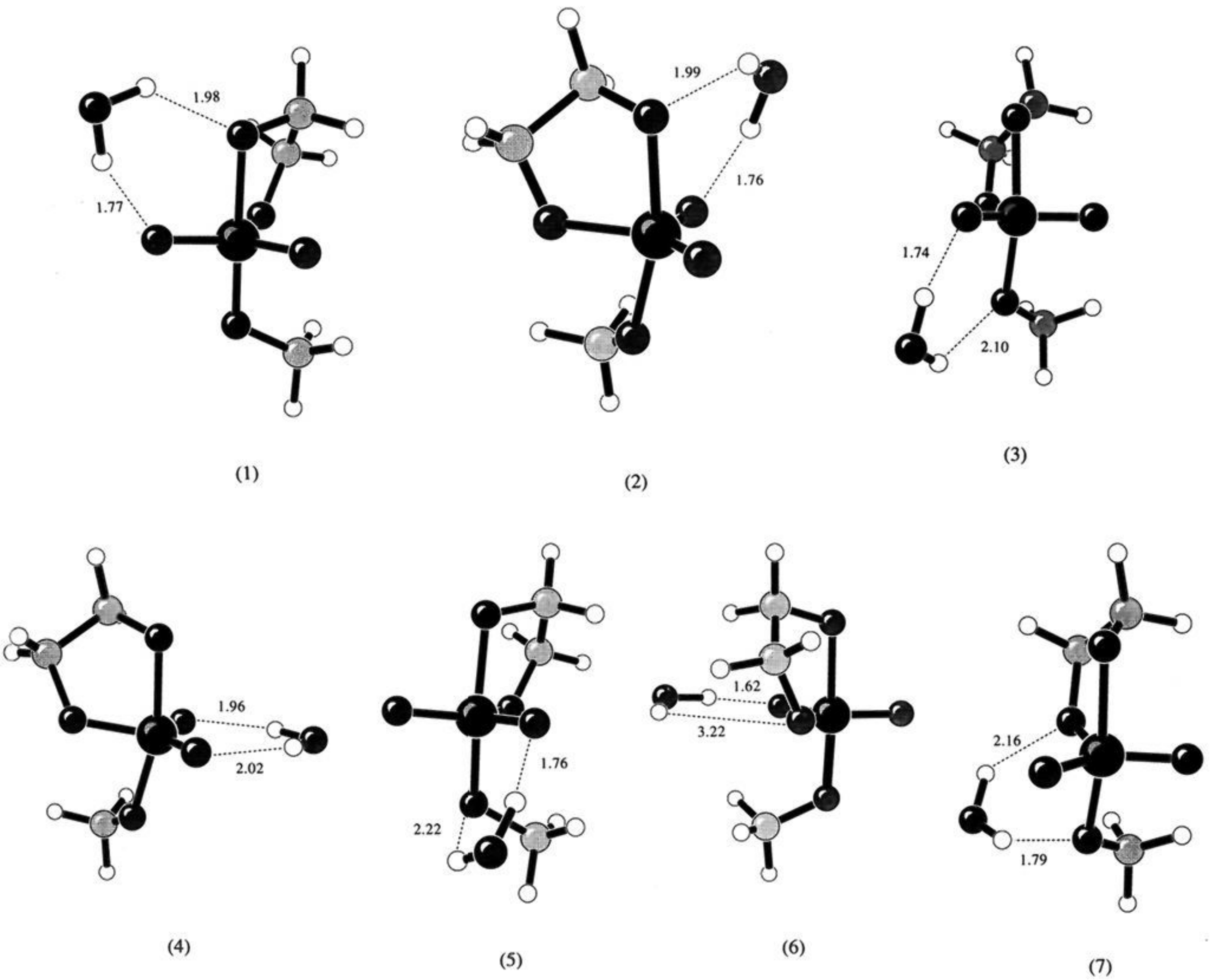

Figure 1. 3–21G*-optimized structures of pentacoordinated oxyphosphorane **2a** and seven monohydrations. The monohydrated molecules are arranged in order of decreasing stabilization from left to right and top to bottom.

examples of free energy perturbation have been presented, including thermodynamic cycle perturbation, as introduced by McCammon to calculate relative binding energies of Cl^- and Br^- with the macrocycles SC24. McCammon's calculations demonstrate the use of a creation/annihilation coordinate.[24] Additionally, the effect of solvation on conformational equilibria was reported with the prototype studies of butane by Jorgensen.[25] The analysis of differential solvation in the S_N2 reaction of Cl^- with CH_3Cl provided a well-known example of reaction coordinate simulation.[26]

Kollman has reported that a bifurcating hydration in the dimethyl phosphate and formate anions is more stabilizing than a linear hydration by 3–5 kcal/mol with RHF/4-31G geometries and RHF/6-31G* energies.[27] We also found bifurcating hydrations to be stabilized over structures with linear hydrogen bonds. Seven hydrations were found where hydrogen bonding occurred between five equatorial–axial combinations and two bifurcating equatorial–equatorial combinations. The third equatorial–equatorial hydration was found to decay to the equatorial–axial hydration of structure (3). These can be readily identified in Figure 1, where the numbering corresponds to that in Table I and the molecules are arranged in order of descending stabilization from left to right and top to bottom. The CP correction is roughly the same for each hydration, and the order of stabilization does not change after CP correction. The optimized hydrogen bond distances are reported in Figure 1. The hydrogen bond distance calculated for association with dianionic phosphoryl oxygen is ca. 1.75-Å, which is much shorter than the 2.10-Å hydrogen bond distance reported for the bifurcating hydration of the monoanion dimethyl phosphate.[27] The value of the overlap population for the 1.75-Å hydrogen bond found in this study is one-tenth that of a normal O–H bond.

The order of stabilization presented in Table I arises from several factors. The largest stabilization energy is found for structure (1). Though structure (2) is very similar to structure (1), it is destabilized by repulsion from the nearby methylene unit of the five-membered ring. Interestingly, compared to the axi-

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al–equatorial interactions ((1)–(3)), the equatorial–equatorial interaction ((4)) is less favored in energy than expected on the basis of electrostatic attraction (more negative charge is localized on the equatorial phosphoryl oxygens) as well as the linearity of the O–H···O$^-$ interactions;[27] the bond angles of O–H···O_{axial} and O–H···$O_{equatorial}$ are 131.8° and 153.8°, respectively, in structure (1); on the other hand, the corresponding bond angles O–H···$O_{equatorial}$ in structure (4) are 143.5° and 146.4°. The water molecule in structure (4) could have come closer to the phosphoryl oxygens to achieve more linear hydrogen bonds. This, however, did not occur despite the more spherical electron distribution about the anionic oxygens as compared to the electrons of a lone pair. As a result, axial attack and/or axial departure is further stabilized by the preferred axial–equatorial hydrations. Overall there is nearly a 6.0 kcal/mol range in stabilization energies reported in this study.

In summary, we have identified seven predominant monohydrations of a newly identified pentacoordinated oxyphosphorane intermediate (**2a**) found in the reaction of methoxide with tetracovalent ethylene phosphate monoanion. These results together with ongoing calculations[7] support our earlier conclusion[5] that the pentacoordinated intermediate is formed in a very rapid equilibrium and only a small fraction of 2′-alkoxide attack on the phosphate backbone results in productive 5′ cleavage under basic conditions.[28] The recent report by Lim and Karplus[6] suggesting the nonexistence of the dianionic intermediate of cyclic oxyphosphorane system **2b** is in contrast to our oxyphosphorane **2a** presented here. The cause of this discrepancy can be reconciled by the ability of the axial OMe group in **2a** to better delocalize the dianionic charges than OH in **2b**. In strong alkaline solution, in fact, **2a** does exist as an intermediate since the hydrolysis of methyl ethylene phosphate yields 2–4% exocyclic products, which can only be formed after pseudorotation of the intermediate **2a**.[29,30] Nevertheless, the overall transition-state structure is independent of the mechanism (stepwise vs concerted), and it has an extended P–O(5′) bond-breaking character (TS2 structure in ref 5). Location of the mechanistically relevant pentacoordinated oxyphosphorane intermediate together with the dominant monohydrations will now be applied to a theoretical evaluation of the effect of solvent on this potential energy surface.

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Singlet Nitrene Insertion into H_2O, H_2S, HF, and HCl

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Abstract: The insertion of singlet nitrene, ^{1}NH, into the O–H bond of water, the S–H bond of H_2S, and the F–H and Cl–H bonds has been studied by means of ab initio molecular orbital theory including electron correlation and zero-point corrections. Nitrene forms initial donor–acceptor complexes, with the exception of HF, after which hydrogen migration leads to the more stable tautomers H_2NX (X = OH, SH, F, Cl). Bader's charge density analysis has been used to delineate bonding properties. The ^{1}NH complexes with the second-row hydrides have very short N–S and N–Cl bonds. Correlation effects are important in the description of the complexes.

Diradicals are reactive, electron-deficient intermediates that lend themselves to addition and insertion reactions. They have been the subject of numerous studies that focus on the mechanistic pathways of their reactions.[1] In contrast to the wealth of experimental and theoretical information on carbene and silylene insertion reactions, relatively little is known about the corresponding nitrene reaction.[1–3] Theoretical studies concerning the insertion of carbenes[3h] and silylenes[3d,f] have suggested the formation of intermediate complexes. These are generally unstable in the case of carbenes with little or no barrier for hydrogen migration or fragmentation, but silylene complexes are thought to be spectroscopically observable.[3f] The objective of the present study is (a) to shed more light on the related singlet nitrene insertions into X–H bonds (X = O, S, F, Cl) by means of theoretical analyses and (b) to analyze possible intermediate complexes along the reaction pathway.

Nitrene (NH) has a triplet ground state that is an estimated 36 kcal/mol more stable than the singlet form;[4] a value of 41 kcal/mol was reported in a study using a large CI calculation.[5] Triplet nitrenes are well-known experimentally,[1a–d,6] and excited nitrene radicals have been implicated in the two-photon dissociation of ammonia.[7] However, the nitrenes generated from azides and isocyanates[1a–d,6,8] are in most instances singlets. This is also the case in many organic rearrangements involving nitrene centers as well as in the photochemistry of aroylnitrenes.[9] Even the

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