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Density functional theory investigation of the deprotonation of oxete

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Abstract—The deprotonation of oxete by ether solvated methyl lithium was investigated by geometry optimization of reactants, transition states and products using the density functional theory (DFT) method (B3LYP/6-31++G(d,p)). The calculations suggest that allylic deprotonation is favored over the corresponding vinylic process by 1.5 kcal/mol in the transition structures and 1.7 kcal/mol in the products. This is in contrast to previous calculations of products (MP2/6-31++G(d,p)//HF/6-31++G(d,p)) that favored vinylic deprotonation. © 2002 Elsevier Science Ltd. All rights reserved.

There is widespread interest in the structures and reactions of organolithium reagents in general and in lithiated vinyl ethers in particular, primarily because of their synthetic applications. Deprotonation reactions of cyclic vinyl ethers have been of interest in our group in recent years. A major interest is the question of vinylic versus allylic deprotonation in these systems. We have experimentally[1] and computationally[2] examined allylic and vinylic deprotonation of some mid-sized (5-, 6-, and 7-membered rings) cyclic vinyl ethers with certain alkyllithium reagents. Previously, we have examined such deprotonation reactions in the gas phase and with water solvent by ab initio calculations (MP2/6-31++G(d,p)//HF/6-31++G(d,p)). We now wish to report on the inclusion of ether solvent using density functional theory (DFT) calculations. The DFT method, B3LYP, has been widely used and has proved to be significantly more efficient than ab initio methods of comparable accuracy, especially in optimizing transition structures. DFT has been successfully used in investigations of ether solvent effects involving lithium enolates, the results of which agree well with more expensive MP4 calculations.[3] Although many substituted oxetes are known, the parent oxete does not exist at room temperature.[4] Thus, its deprotonation in solution has not been experimentally examined. Herein we wish to report our recent computational work on the deprotonation of oxete by monoether solvated methyllithium by geometry optimization of reactants, transition states, and products using a DFT method—B3LYP/6-31++G(d,p).[5] The results presented here favor allylic deprotonation of oxete in contrast to previous computational results which predicted vinylic deprotonation and were based on less realistic models and less rigorous computational methods.

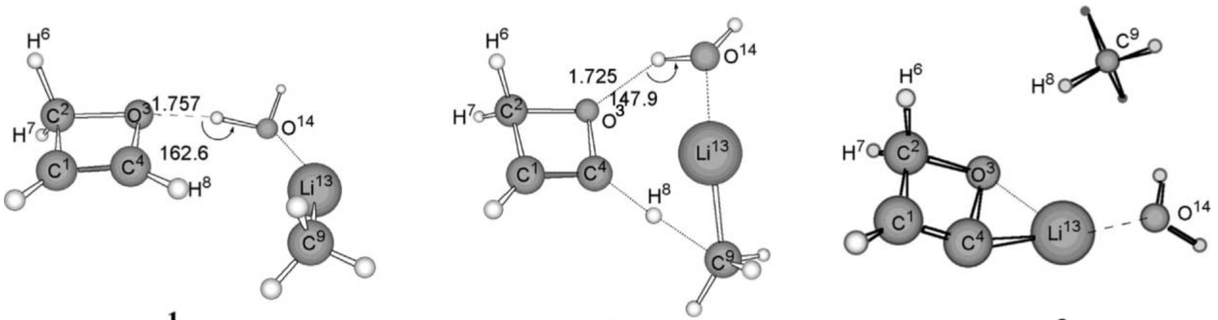

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Figure 1. DFT optimized water solvated system (bond lengths in Å, bond angles in °).

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In a few of our initial attempts at examining the water-solvated model of oxete using DFT theory (B3LYP/6-31++G(d,p)), the geometry optimization results suggested that there was a tendency for hydrogen bonding both in the reactant **1** and in the vinyl-deprotonation transition state **2** (Fig. 1). The basis set we use here contains polarization functions on hydrogen, which is particularly useful in dealing with systems where hydrogen could act as a bridging atom. The existence of hydrogen bonding could have some effect on the optimized geometries and thereby on the resulting energies, as previously pointed out by Schleyer.[3] Thus, water is not a suitable ether model and should be replaced by dimethyl ether.

We noticed that the optimized geometries of the water solvation system (Fig. 1) and those of the dimethyl ether solvated system are indeed quite different (Fig. 2). Limited by computational efficiency and cost, we used only one molecule of dimethyl ether as the 'microsolvent;' this should nevertheless show the trend of explicitly including solvent molecules.

The results of the DFT calculations suggest that methyl lithium, dimethyl ether and oxete tend to form a complex (**4** in Fig. 2), in which the lone pairs of electrons on the two oxygen atoms interact with lithium.

In the proton abstraction reaction, deprotonation at the allylic position of oxete is favored over that at the vinylic position (Fig. 3). The transition state barrier of allylic deprotonation is 1.47 kcal/mol lower in energy than the corresponding barrier of vinylic deprotonation, as predicted by both the synchronous transit-guided quasi-Newton method with three molecule specifications and the Berny algorithm. In the allylic deprotonation reaction, we used ab initio methods (RHF/6-31++G(d,p)) to show that the two allylic protons (H6 and H7) are equivalent—the energies of both optimized allylic deprotonation products are exactly the same. We assume that this is also true at the DFT level.

Not surprisingly, the configurations of the optimized allylic **5** and vinylic **6** deprotonation transition structures are very different. The heavy atoms in **6** are coplanar and seem to have a symmetry of C_s, and the lithium atom and C2, O3 are in a straight line (Table 1, ∠C2-O3-Li10). However, the oxete ring and the lithium cation in **5** form an angle of nearly 90° (Table 1, dihedral angle Li10-O3-C4-C1). Both the transition structures **5** and **6** were verified to be connecting the corresponding minima (reactant and product) by a proceeding IRC calculation[6] using the same basis set and theory level.

As we can see in Fig. 3, the allylic deprotonation product **7** is predicted to be about 1.67 kcal/mol more stable than **8**. This result is opposite to that of our previous work of single point calculation (MP2/6-31++G(d,p)//HF/6-31++G(d,p)) of a water solvated system, in which vinylic deprotonation is predicted to be preferred by 2.14 kcal/mol.[2] We believe that the present work is more reasonable because of the inclusion of electronic correlation in a full geometry optimization. The distances between Li10 and C1, C2, O3, C4, respectively (Table 1) in **7**, are comparable to the previous ab initio results (MP2/6-31G**) of water solvated allyllithium[10] and experimental results of solid state cyclopetadienyllithium.[11] In structure **7**, lithium sits right above the oxete molecule (but not in the center) and forms an asymmetric pyramid; while in the vinylic deprotonation product **8**, most of the heavy

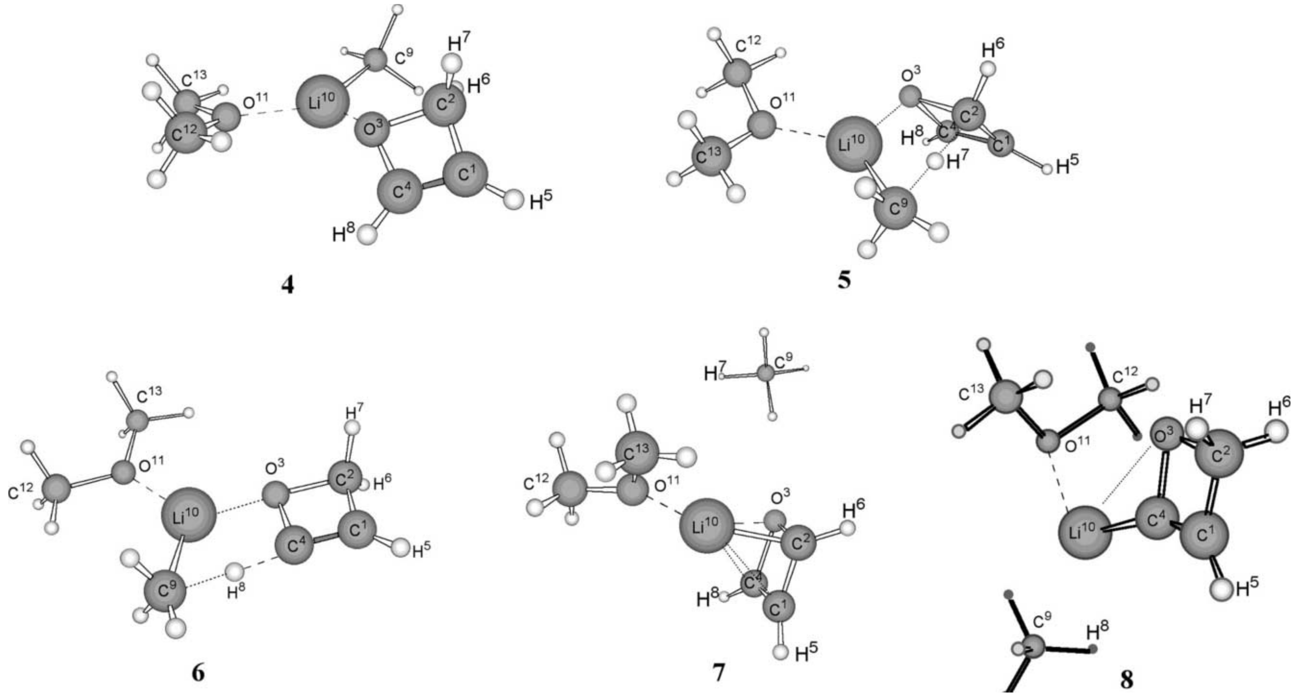

Figure 2. DFT optimized geometries of dimethyl ether solvated system.

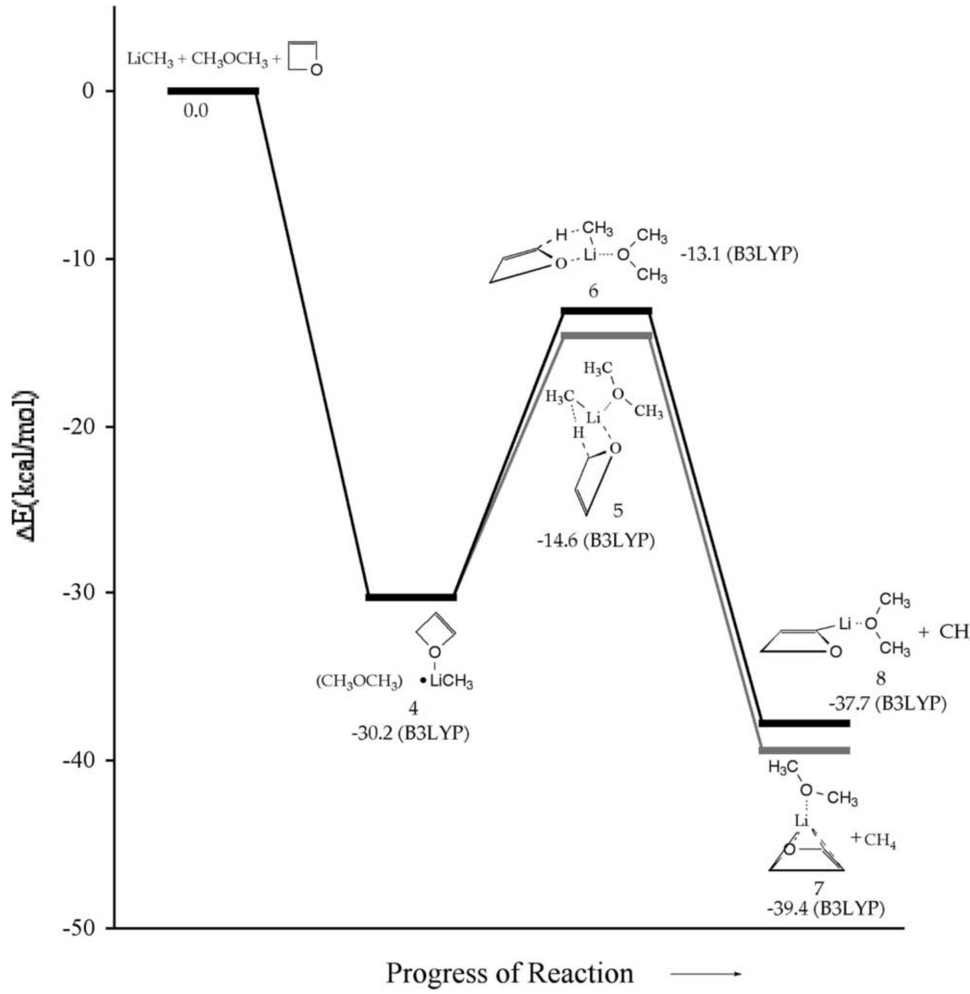

Figure 3. Progress of reaction diagram for deprotonation of oxete resulting from DFT geometry optimizations (B3LYP/6-31++G(d,p), relative energies are in kcal/mol).

Table 1. Selected structural parameters of species **4**–**8** from DFT calculations[7]

Species	Bond lengths (Å)		Bond angles (°)		Dihedral angles (°)	
4	–	–	C2-C1-C4	88.163	–	–
	–	–	C1-C4-O3	98.514	H5-C1-C4-H8	−0.316
	C2-H7	1.446	C2-C1-C4	90.649	Li10-O3-C4-C1	−89.352
5	H7-C9	1.460	C1-C4-O3	97.323	H5-C1-C4-H8	4.522
	–	–	C2-H7-C9	173.260	–	–
	–	–	C2-O3-Li10	87.818	–	–
	C4-H8	1.385	C2-C1-C4	91.651	Li10-O3-C4-C1	180.000
6	H8-C9	1.490	C1-C4-O3	92.863	–	–
	–	–	C4-H8-C9	167.588	–	–
	–	–	C2-O3-Li10	179.684	–	–
	C1-C4	1.375	C2-C1-C4	90.677	C4-C1-C2-O3	−3.609
	Li10-C1	2.305	C1-C4-O3	95.017	C1-C2-O3-C4	3.511
7	Li10-C2	1.966	–	–	H5-C1-C4-H8	8.316
	Li10-O3	1.939	–	–	C4-C1-C2-H6	−120.141
	Li10-C4	2.186	–	–	H6-C2-O3-C4	132.024
8	C1-C4	1.361	C2-C1-C4	91.364	C4-C1-C2-O3	0.000
	–	–	C1-C4-O3	92.567	C1-C2-O3-C4	0.000

atoms are still coplanar except for the two methyl carbons of the solvent (and methane). Compared to structure **8**, the double bond length (C1=C4) in **7** is slightly increased and the oxete ring becomes slightly distorted and is not perfectly planar (Table 1, dihedral angle H5-C1-C4-H8 and C4-C1-C2-O3). Without the lithium cation, the heavy atoms of the oxete anions in gas phase are coplanar (B3LYP/6-31++G(d,p)), which

Table 2. Relative energies (kcal/mol) obtained using Onsager model and PCM model

Models	Reactant	Vinylic transition state	Allylic transition state	Vinylic product	Allylic product	ΔE (TS)[a]	ΔE (products)[a]
Onsager model	0.00	9.04	8.40	−19.90	−20.06	0.64	0.16
PCM model	0.00	12.32	11.68	−16.63	−15.68	0.64	−0.95

[a] $\Delta E = E_{\text{vinylic}} - E_{\text{allylic}}$.

is consistent with our previous calculations (HF/6-31++G(d,p)).[2] In the present study (B3LYP/6-31++G(d,p)), the vinyl anion in the gas phase is 2.12 kcal/mol lower in energy than the allyl one. The allyl anion is potentially aromatic and when lithium is included, this π-system interacts with the lithium cation, via the oxygen and all three carbons. In the vinylic deprotonation, however, the lithium cation interacts directly with the vinyl carbon C4 in the ring plane.

Comparing the angle ∠C2-C1-C4 in the structures **4**, **5**, and **7**, we notice that the allyl angle expansion reported previously for allylic anions[2] is smaller (2.5°) here. In the vinyl lithiated product **8** and transition structure **6**, the angle (∠C1-C4-O3) compressions are 6.0° and 5.6°, respectively, somewhat smaller than reported previously.[2] Atomic charges were determined by Natural Population Analysis (NPA) at the same level of theory. The charges of the migrating hydrogens in both transition structures are low (0.22 for H7 in **5**; 0.24 for H8 in **6**), suggesting that the transition structures are multicenter processes.

In addition to explicitly modeling the solvent, an alternative way to calculate the solvent effect is to use self-consistent reaction field (SCRF) methods or continuum representations of the solvent, such as the Onsager model and polarized continuum models (PCM).[12] The reactant, vinylic and allylic transition states, and products were optimized using the Onsager model at the DFT (B3LYP/6-31++(d,p)) level, and then the obtained geometries were submitted to a proceeding PCM calculation.[13] The results are summarized in Table 2.

Although the optimized geometries of the SCRF calculations are similar to those of the monosolvated calculations, the energy differences between the deprotonation species including transition states and products are smaller (Table 2). Indeed the vinylic product of the PCM model is slightly favored in energy instead of the allylic product. However, it is likely that the solution deprotonation reactions of oxete are kinetically controlled rather than thermodynamically controlled and thus all three solvation models reported here favor the allylic deprotonation process, which is different from the previously reported computations. Further investigations including the deprotonation of other larger-sized cyclic vinyl ethers with the DFT method are in progress.

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5. The RHF calculations were performed using the GAUSSIAN 94 program package and all the DFT calculations were performed using the GAUSSIAN 98w program. All stationary points were characterized as minima or saddle points by harmonic vibrational frequency analysis at the same level. The transition states herein were optimized using both the synchronous transit-guided quasi-Newton method with three molecule specifications (QST3)[8] and the Berny algorithm (TS).[9]
6. In each of the IRC calculations, six points on each side of the transition structure along the reaction path with a step size of 0.1 a.u. were examined.
7. All the structural parameters were obtained with CS Chem 3D PRO version 6.0.
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13. The solvent used in the SCRF calculations is diethylether which is available in Gaussian 98w program package.