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Ab Initio Models for Metalation and Hydrogenolysis Reactions Involving Organolithium Compounds

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Abstract: The model lithiation reactions of methane (R = CH_3) and acetylene (R = C_2H) with lithium hydride, RH + LiH → RLi + H_2, have been calculated ab initio including electron correlation and zero-point energy (ZPE) corrections. The theoretical levels used were MP2/6-31++G**//6-31++G** + ZPE (R = CH_3) and MP2/6-31++G**//6-31G* + ZPE (R = C_2H). The initially formed complexes between the reactants are bound by 3.6 and 9.8 kcal/mol, respectively. The reactions proceed through highly ionic (charges on lithium >0.9) four-membered ring transition structures with almost linear C-H-H bridges. The activation energies, relative to the isolated educts, are 25.5 (R = CH_3) and 0.4 (R = C_2H) kcal/mol. The lithiation of acetylene with LiH is 23.4 kcal/mol exothermic, but the reverse process (the hydrogenolysis of methyllithium, $CH_3Li + H_2 \rightarrow CH_4 + LiH$) is favored by 8.8 kcal/mol with methane. The transition structures for metalation and addition reactions of acetylene with LiH, both of which commence from the acetylene-LiH complex, are compared. The less exothermic metalation reaction ($\Delta E = -23.4$ kcal/mol) is favored kinetically over addition ($\Delta E = -38.1$ kcal/mol) by 2.7 kcal/mol.

Metalation of carbon acids by organolithium compounds is one of the most useful reactions in synthetic organic chemistry.[1,2] Despite its widespread application for derivatization, C-C bond formation, etc., mechanistic details are not well established. Experimental studies[3a] led to the suggestion of a four-membered ring transition state with high ionic character for this reaction (eq 1). The significantly lower deuterium isotope effect in an

$$RH + R'Li \rightarrow RLi + R'H \qquad (1)$$

$$\text{(a) } R = CH_3 \qquad \text{(b) } R = C{\equiv}CH;\ R' = H$$

$$RLi + H_2 \rightarrow RH + LiH \qquad (2)$$

$$\text{(a) } R = CH_3 \qquad \text{(b) } R = C{\equiv}CH$$

intramolecular metalation involving hydrogen transfer has been attributed very recently[4] to the more highly bent character of the transition state. However, the degree to which bending occurs in corresponding intermolecular exchanges could not be established from the evidence available. In a previous paper[5] we examined lithium-hydrogen exchange processes by means of ab initio calculations for degenerate cases (i.e., R = R′ in eq 1). The reverse reaction with R′ = H (eq 2) is the also well-known hydrogenolysis of alkyllithiums.[6a,7] The related reaction of lithium with hydrogen ($Li_2 + H_2$, R = Li in eq 2) has been studied at high ab initio levels.[8] However, in the experimental work, four-membered ring transition states with an idealized geometry involving significantly nonlinear hydrogen transfer were assumed.[3a,6] This assumption, although appearing to be reasonable, is *not* supported by our calculations as we will show. Indeed, it has been stated that the kinetic parameters of the hydrogenolysis process[6a] (and also for β-hydride elimination from alkyllithiums)[6b] are not significantly different from those associated with processes that proceed through a linear (or near-linear) three-center hydrogen transfer.[6]

In the present study we use lithium hydride as the simplest model for a lithiating agent for methane and acetylene. Experimentally, if prepared in a finely divided state (e.g., by reaction of hydrogen gas with an alkyllithium),[6a,7] LiH is quite reactive as a metalating agent.[7] In our calculational studies, LiH has been shown to model the behavior of alkyllithiums and their aggregates in organolithium reactions quite well.[9] Methane (eq 1a) and acetylene (eq 1b) were chosen as substrates since they represent extremes in the pK_a scale of carbon acids (in the gas phase, C_2H_2 is more acidic than CH_4 by 41.4 kcal/mol, corresponding to 30.3 pK_a units).[10] The hydrogenolysis reaction (eq 2) also should be modeled well by this approach. However, it should be recognized that the reaction appears to take place experimentally within the aggregate without prior dissociation into monomeric lithium species.[6a] In previous work[5,9b] we have shown that the conclusions concerning organolithium reactions involving dimers are not significantly different from those deduced from monomeric models.

Calculational Methods

The procedures applied are analogous to those employed before.[5] Geometries were fully optimized within the designated symmetry constraints at the restricted Hartree-Fock (HF)[11] level using gradient optimization techniques[12] and the standard basis sets (3-21G, 6-31G*, 6-31+G*, and 6-31++G**)[13] incorporated in the GAUSSIAN 76 and

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Table I. Total (au) and Zero-Point Vibrational (kcal/mol) Energies

species		point group	3-21G// 3-21G	6-31G*// 6-31G*	MP2/6-31G*// 6-31G*	6-31+G*// 6-31G*	MP2/6-31+G*// 6-31G*
H_2		$D_{\infty h}$	−1.122 96^b	−1.126 83^b	−1.144 10^b	−1.126 83	−1.144 10
LiH		$C_{\infty v}$	−7.929 84^b	−7.980 87^b	−7.995 96	−7.981 01	−7.996 15
CH_4		T_d	−39.976 88^b	−40.195 17^b	−40.332 44^b	−40.195 67	−40.333 94
CH_3Li		C_{3v}	−46.752 48^b	−47.015 54^b	−47.162 01^b	−47.017 60	−47.166 65
CH_4/LiH, TS	**2**	C_s	−47.844 00	−48.108 90	−48.278 03	−48.110 40	−48.281 78
				−48.108 78^c	−48.278 14^c	−48.110 27^c	−48.281 87^c
CH_4·LiH	**1**	C_{3v}	−47.914 00	−48.181 75	−48.337 38	−48.182 18	−48.338 41
C_2H_2		$D_{\infty h}$	−76.395 96^b	−76.817 83^b	−77.064 64^b	−76.823 05	−77.070 76
C_2HLi		$C_{\infty v}$	−83.227 84	−83.692 06	−83.946 44	−83.701 46	−83.956 42
C_2H_2/LiH, TS	**5**	C_s	−84.315 20^f	−84.787 05^f	−85.058 09^f	−84.790 09	−85.063 06
C_2H_2/LiH, TS	**4**	C_s	−84.302 02	−84.774 28	−85.054 05	−84.778 72	−85.060 75
C_2H_2·LiH	**3**	C_{2v}	−84.344 47	−84.816 22	−85.081 08	−84.818 63	−85.084 69
C_2H_3Li		C_s	−84.386 63^b	−84.861 39	−85.124 59	−84.867 11	−85.132 34

species		point group	6-31++G**// 6-31G*	MP2/6-31++G**// 6-31G*	6-31++G**// 6-31++G**	MP2/6-31++G**// 6-31++G**	ZPE^a
H_2		$D_{\infty h}$	−1.131 40^b	−1.157 76^b	−1.131 40	−1.157 77	6.66 (0)
LiH		$C_{\infty v}$	−7.982 62	−8.002 83	−7.982 62	−8.002 83	2.04 (0)
CH_4		T_d	−40.202 17	−40.366 10	−40.202 17	−40.366 10	30.12 (0)
CH_3Li		C_{3v}	−47.023 17	−47.192 58	−47.023 18	−47.192 62	22.42 (0)
CH_4/LiH, TS	**2**	C_s	−48.123 17	−48.326 65	−48.123 20	−48.326 67	31.06 (1)
			−48.123 03^c	−48.326 61^c	−48.123 10^d	−48.326 71^d	
CH_4·LiH	**1**	C_{3v}	−48.189 91	−48.376 48	−48.189 92	−48.376 49	33.38 (0)
C_2H_2		$D_{\infty h}$	−76.827 26	−77.085 70			18.86 (0)
C_2HLi		$C_{\infty v}$	−83.703 67	*e*			12.33 (0)
C_2H_2/LiH, TS	**5**	C_s	−84.795 88	−85.085 96			22.52 (1)^f
C_2H_2/LiH, TS	**4**	C_s	−84.788 33	−85.087 09			20.39 (1)
C_2H_2·LiH	**3**	C_{2v}	−84.823 72	−85.105 36			21.84 (0)
C_2H_3Li		C_s	−84.872 84	−85.158 03			27.03 (0)

[a] Zero-point energy at 3-21G, number of imaginary frequencies in parentheses. [b] Reference 17. [c] MP2-FU/6-31G* geometry. [d] MP2-FU/6-31++G** geometry. [e] Virtual MO coefficients too large for MP2 method. [f] Reference 9a.

Table II. Relative Energies (kcal/mol) of Complexes, Transition Structures, and Products in the Lithiation Reactions RH + LiH → RLi + H_2 (Educts: 0.0)

		3-21G// 3-21G	6-31G*// 6-31G*	MP2/6-31G*// 6-31G*	6-31+G*// 6-31G*	MP2/6-31+G*// 6-31G*
R = CH_3						
CH_4·LiH	**1**	−4.6	−3.6	−5.6	−3.5	−5.2
CH_4/LiH, TS	**2**	39.4	42.1	31.6	41.6	30.3
			42.2^c	31.5^c	41.7^c	30.3^c
CH_3Li + H_2		19.6	21.1	14.0	20.2	12.1
R = C_2H						
C_2H_2·LiH	**3**	−11.7	−11.0	−12.9	−9.1	−11.2
C_2H_2/LiH, TS	**4**	14.9	15.3	4.1	15.9	3.9
C_2HLi + H_2		−15.7	−12.7	−18.8	−15.2	−21.1
C_2H_2/LiH, TS	**5**	6.7^f	7.3^f	1.6^f	8.8	2.4
C_2H_3Li		−38.2	−39.3	−40.2	−39.6	−41.1

		6-31++G**// 6-31G*	MP2/6-31++G**// 6-31G*	6-31++G**// 6-31++G**	MP2/6-31++G**// 6-31++G**	Δ(ZPE)^a	final est^b
R = CH_3							
CH_4·LiH	**1**	−3.2	−4.7	−3.2	−4.7	+1.1	−3.6
CH_4/LiH, TS	**2**	38.7	26.5	38.6	26.5	−1.0	25.5
		38.8^c	26.6^c	38.7^d	26.5^d		
CH_3Li + H_2		19.0	11.7	19.0	11.6	−2.8	8.8
R = C_2H							
C_2H_2·LiH	**3**	−8.7	−10.6			+0.8	−9.8
C_2H_2/LiH, TS	4	13.5	0.9			−0.5	0.4
C_2HLi + H_2		−15.8	−21.7^e			−1.7	−23.4
C_2H_2/LiH, TS	**5**	8.8	1.6			+1.5	3.1
C_2H_3Li		−39.5	−43.6			+5.5	−38.1

[a] Difference in zero-point energies, scaled by 0.9.[16] [b] Final estimate evaluated with data from the highest level employed plus Δ(ZPE). [c] MP2-FU/6-31G* geometry. [d] MP2-FU/6-31++G** geometry. [e] Estimated from the MP2 − HF difference at 6-31+G*. [f] Reference 9a.

GAUSSIAN 82 program systems.[14] Electron correlation was estimated by Møller–Plesset theory carried out to second order (MP2),[15] keeping the core electrons frozen. The MP2 corrections for geometry optimization included the core electrons (MP2-FU). Frequency analyses were carried out with the 3-21G basis set to characterize stationary points and to obtain zero-point vibrational energies (ZPE), which were scaled by the empirical factor 0.9.[16] Final estimates of relative energies were then

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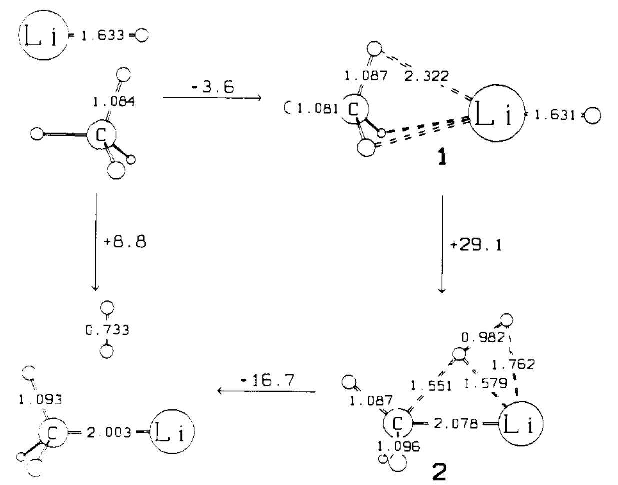

Figure 1. Lithiation reaction of methane with lithium hydride. The reverse reaction corresponds to the hydrogenolysis of methyllithium. Reaction energies (MP2/6-31++G**//6-31++G** + ZPE) are given in kilocalories per mole and geometrical parameters (6-31++G**) in angstroms.

obtained by adding the differences in zero-point energies and MP2 corrections to the HF results, at the highest levels employed. Table I lists the total energies at various levels and the ZPE's. Some of the energies were taken from the Carnegie-Mellon[17] Quantum Chemistry Archive. Relative energies are given in Table II. Charges and bond orders were obtained by the natural population analysis (NPA) of Reed et al.[18] Important geometrical parameters (at the highest levels employed for optimization) are given in the figures. Full geometry information in the form of archive entries[17] is available as supplementary material.

Results and Discussion

The courses of the lithiation reactions of methane (eq 1a) and acetylene (eq 1b) with lithium hydride together with reaction energies (in kcal/mol) are displayed in Figures 1 and 2, respectively. The transition structure **5** for the addition of LiH to acetylene[9a] is also shown for comparison. The usual first step in lithium reactions is a complexation between the lithium compound and the substrate.[5,9] The C_{3v} complex **1** between CH_4 and LiH, like that between CH_4 and $LiCH_3$,[5] is only bound by 3.6 kcal/mol. However, the complexation energy of lithium hydride with the π system of acetylene is much larger, 9.8 kcal/mol (Table II). The resulting C_{2v} complex **3** is similar to the complex of ethylene with lithium hydride (association energy of 12.9 kcal/mol at 3-21G).[9a,19] Complex **3** is characterized by almost unperturbed component geometries: the widening of the C–C and Li–H bond lengths is only 0.004 and 0.011 Å, respectively. The acetylenic hydrogens are bent 1.8° away from lithium (6-31G* data, Figure 2). The complexes between the products, RLi and H_2, are very weakly bound[5] and are not considered here.

Since the lithiation reactions involve hydridic hydrogens and the transition structures are characterized by hydrogen transfer, a proper description of the hydrogen atoms appeared to be necessary. Consequently, the largest basis set used was 6-31++G** with polarization and diffuse functions on both hydrogen and non-hydrogen atoms. To test for the influence of basis set on the geometries, the methane lithiation reaction (eq 1a) and the hydrogenolysis of methyllithium (eq 2a) also were optimized at this level. However, the geometries varied but little; e.g., a maximum change in bond lengths of 0.018 Å (for the "outer" Li–H; average 0.009 Å) occurred for the transition structure **2** on going from the 6-31G* to the 6-31++G** level (compare Table III). Thus, optimization at 6-31G* appeared to be adequate and was used for the acetylene lithiation reaction. Energies were somewhat more affected by the description of hydrogen: changes of up to 2.9 and 3.8 kcal/mol at the HF and MP2 levels, respectively, occurred when both diffuse and polarization functions were added to hydrogen (compare relative energies in Table II at the 6-31+G* and 6-31++G** levels). Electron correlation had a larger effect on relative energies; e.g., the transition structures were lowered in energy by up to 12.6 kcal/mol on going from HF to MP2. Therefore, the transition structure **2** also was optimized at MP2-FU/6-31G* and MP2-FU/6-31++G** to check for the influence of electron correlation on the geometry. The geometrical changes were not larger than those occurring with variation of

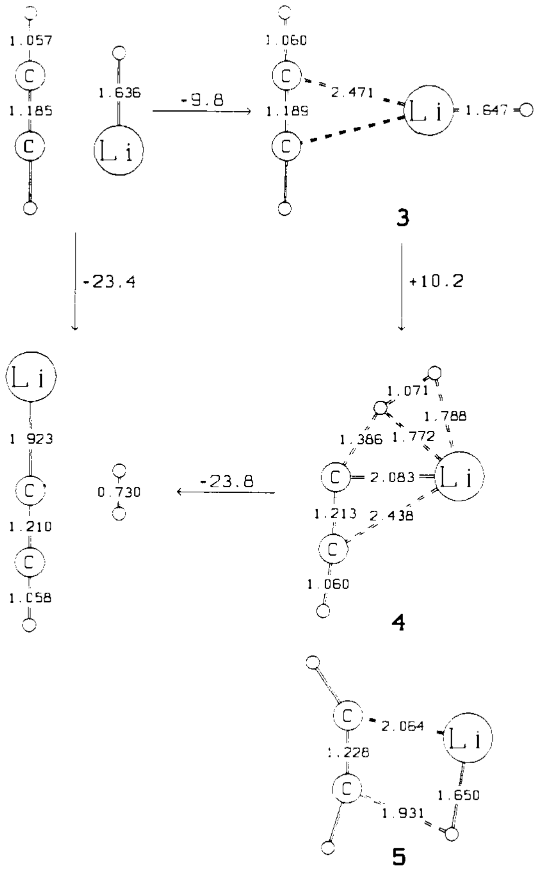

Figure 2. Lithiation reaction of acetylene with lithium hydride. The reverse reaction corresponds to the hydrogenolysis of lithioacetylene. Reaction energies (MP2/6-31++G**//6-31G* + ZPE) are given in kilocalories per mole and geometrical parameters (6-31G*) in angstroms. The transition structure **5** for the addition of LiH to acetylene (which leads to vinyllithium)[9a] is included for comparison.

Table III. Geometries of the Transition Structure **2** for the Metalation of Methane with Lithium Hydride at Various Levels[a]

param[b]	3-21G	6-31G*	6-31++G**	MP2-FU/ 6-31G*	MP2-FU/ 6-31++G**
C–Li	2.101	2.085	2.078	2.068	2.058
C–H_i	1.553	1.557	1.551	1.552	1.531
Li–H_i	1.606	1.590	1.579	1.591	1.573
Li–H_o	1.780	1.780	1.762	1.780	1.748
H_i–H_o	0.989	0.980	0.982	0.984	0.976
C–H(1)	1.088	1.088	1.087	1.094	1.089
C–H(2)	1.095	1.096	1.096	1.102	1.098
H(1)–C–Li	137.8	138.9	140.6	138.5	141.0
H(2)–C–Li	97.4	97.7	96.5	97.7	96.0
H(2)–C–Li–H(1)[c]	125.1	125.5	125.7	125.4	125.8
C–H_i–H_o	166.4	167.1	166.7	166.2	166.1

[a] Distancs in angstroms; angles in degrees. [b] H_i is the "inner" and H_o is the "outer" hydrogen within the four-membered ring. H(1) is the unique; H(2) are the symmetry equivalent hydrogens. [c] Dihedral angle.

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basis sets. The Li–H and H–H separations remained almost unchanged, whereas the C–Li and C–H bonds shortened by up to 0.02 Å (Table III). This is in contrast to the analogous transition structure for the reaction of Li_2 with H_2,[8] where larger changes occurred on optimization at correlated levels (e.g., a widening of 0.08 Å of the H–H separation). Thus, the HF level seems to be adequate for the geometrical description of this kind of reaction. The changes in relative energies for the MP2-FU-optimized transition structure **2** were negligible (less than 0.1 kcal/mol, compare Table II).

Transition Structures. The transition structures are characterized by four-center Li–C–H–H rings with the exchanging hydrogens forming *nearly linear* C–H–H bridges (angles of 166.7° and 154.9° in **2** and **4**, respectively; at the correlated MP2-FU/6-31G* and MP2-FU/6-31++G** levels, the angles in **2** are 166.2° and 166.1°, respectively). Similar results have been obtained for the transition structure in the model reaction $Li_2 + H_2$ (the hydrogenolysis of the lithium molecule): the Li–H–H angle is 178.2° at MP2-FU/6-31G**.[8] This is in contrast to previous experimental work[6a] where *significantly nonlinear* hydrogen transfer was assumed for the hydrogenolysis of *n*-octyllithium, which is the microscopic reverse reaction to our lithiation model (eq 2a). Our calculations show the hydrogen bridge part of the transition structures to approach linearity much more than anticipated. Indeed, the measurement of the kinetic isotope effect (H_2 vs D_2)[6a] revealed kinetic parameters that were not significantly different from those of linear, three-center hydrogen transfers. The authors concluded[6a] that "a temperature-independent kinetic isotope effect is not a necessary criterion for characterizing transition states involving a four-center cyclic hydrogen transfer". This is in line with our calculations because the C–H–H unit in the transition structure **2** deviates from linearity only by 13.3° (HF/6-31++G**) or by 13.9° (MP2-FU/6-31++G**). A larger deviation occurs in the acetylenic transition structure **4** (25.1°, 6-31G* data), but still this is not significantly nonlinear. The same is true for the model metalation reactions of methane with methyllithium annd methylsodium.[5] The deviations from linearity of the C–H–C bridges are only 5.5° and 0.5°, respectively, at 6-31G*. In a dimeric model[5] the deviation is 18.9° at 3-21G. Thus, we conclude that the hydrogen bridge part of the four-membered ring transition structures, involved in both the hydrogenolysis of alkyllithiums and the lithiation of carbon acids, is nearly linear.

Similar conclusions with regard to the nonlinearity of hydrogen transfer have been drawn for the β-hydride elimination from alkyllithiums.[6b] The transition structures involved *are* nonlinear,[9a] and the conclusion holds that four-center, cyclic hydrogen-transfer processes are not necessarily distinguished by kinetic isotope effect parameters, which are uniquely characteristic.

Table IV shows the four lowest vibrational modes of the transition structures of the hydrogenolysis and addition reactions. Only **2** has a very low lying frequency, at 98.9 cm^{-1}. This corresponds to a methyl rotation. Modes with vibrational components perpendicular to the reaction coordinates of **2** and **4** (i.e., perpendicular to the movement of the shifting hydrogen) have frequencies of at least 450 cm^{-1}. The out-of-plane (453.8 cm^{-1}) and in-plane (478.8 cm^{-1}) rocking motions of the methyl group in **2**, for example, are combined with out-of-plane and in-plane distortions, respectively, of the C–H–H bridge. Thus, the nearly linear arrangement of the latter is quite rigid and appears to be a significant structural feature.

The transition structures **2** and **4** are highly ionic species: the NPA charges (at 3-21G) of lithium are +0.920 and +0.906, respectively. These values are rather independent of basis set (e.g., the charge on lithium in **2** is +0.937 at 6-31G* and +0.945 at 6-31++G**). Therefore, we limit ourselves to the discussion of the 3-21G population data. In general, lithium compounds tend to become only slightly more ionic with the NPA method when larger basis sets are used.[18,20] The shifting hydrogens also are charged positively whereas the outer ones have hydridic character. The charge separation between the inner and outer hydrogens is much less in **2** (+0.127 and −0.405) than in the acetylenic transition structure **4** (+0.201 and −0.520), indicating an earlier transition state for the latter. The shifting hydrogens show a weak bonding interaction with lithium: the NPA bond orders are +0.093 and +0.079 at 3-21G for **2** and **4**, respectively. In **4**, the lithium bridges the acetylene moiety. The distances to the α- and β-carbons are 2.083 and 2.438 Å, respectively (6-31G* data). At 3-21G the bridging is less significant: the C–Li distances are 2.077 and 3.107 Å, respectively.

Table IV. Four Lowest Vibrational Modes (cm^{-1}) of the Hydrogenolysis (**2**, **4**) and Addition (**5**) Transition Structures at 3-21G

species and mode	description of mode
CH_4/LiH, TS **2**	
1500.7i[a]	hydrogen shift
98.9	CH_3 rotation
453.8	CH_3 out-of-plane wagging, puckering of the four-membered ring
478.8	CH_3 in-plane rocking, C–Li stretch
C_2H_2/LiH, TS **4**	
1762.3i[a]	hydrogen shift
176.1	C–C–Li in-plane bending
259.6	H–C–C out-of-plane bending
524.6	C–Li stretch
C_2H_2/LiH, TS **5**	
952.2i[a]	hydrogen addition, C–C–H in-plane bending
477.9	twisting of the four-membered ring
557.4	C–Li stretch
585.5	C–C–H in-plane bending, C–Li stretch, Li–H stretch

[a] Imaginary frequency corresponding to the reaction coordinate.

Our final overall activation energies (i.e., the energy difference between the isolated educts and the transition structures) are 25.5 and 0.4 kcal/mol for reactions 1a and 1b, respectively. There is essentially no barrier for the lithiation of acetylene. The overall reaction energies are +8.8 (the MP4SDTQ/6-311+G** + Δ(ZPE) value is +9.2 kcal/mol)[20] and −23.4 kcal/mol, respectively, also reflecting the easy metalation of acetylene in contrast to the saturated hydrocarbon methane. In the latter case, the reverse reaction (hydrogenolysis) is favored, as is found experimentally. There is a close relationship between relative carbanion energies and those of the corresponding lithium compounds; the attenuation factor due primarily to ion-pair formation is about 0.72.[21] Hence, the 32.2 kcal/mol difference in energies for the lithio-compound-forming reactions 1a and 1b should correspond to about 44.7 kcal/mol for the corresponding anion-forming reactions. The experimental gas-phase enthalpy difference, 41.2 ± 2.2 kcal/mol,[10] between CH_3^- and C_2H^- agrees reasonably well.

In accord with the Hammond postulate, the less exothermic lithiation reaction of methane (eq 1a) has the later transition state; e.g., the widening of the C–H bond and the H–H separation of the dihydrogen being formed are 0.467 and 0.249 Å, respectively, compared to the corresponding parameters for the acetylenic transition structure (eq 1b), 0.329 and 0.341 Å, respectively.

A comparison of **4**, the transition structure for the lithiation of acetylene with lithium hydride, and the transition structure **5** for the addition of LiH to C_2H_2[9a] is of interest. The latter (and also the corresponding product, vinyllithium) has been recalculated at the same (higher) levels used in this work. Both transition structures lie only slightly higher in energy than the reactants. Whereas **5** is favored by about 8 kcal/mol at lower levels, addition of both diffuse and polarization functions to hydrogen and inclusion of electron correlation reverse the relative energies of **4** and **5**. In addition, the zero-point energy of the addition transition

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structure **5** is 2.0 kcal/mol higher than that of **4**. Thus, our final estimates (Table II) indicate metalation to be favored kinetically over addition by 2.7 kcal/mol, in agreement with experiment. Despite the larger thermodynamic driving force for addition (ΔE = -38.1 kcal/mol), only metalation (ΔE = -23.4 kcal/mol) is observed.

The α-C-Li separations in **4** and **5** are very similar, 2.083 and 2.064 Å,[9a] respectively; these values are close to the C-Li bond in lithioacetylene (1.923 Å at 6-31G*, Figure 2) indicating the C-Li interaction to be dominant in both transition states. The Li-H separation in the transition structure for addition is smaller (1.650 Å)[9a] than that in the metalation transition structure **4** (1.788 Å).

Conclusions

The mechanism for metalation of carbon acids deduced calculationally in this work is consistent with the experimental findings: the reactions proceed through the highly ionic four-membered ring transition states that have been implicated in experimental work by kinetic measurements and Hammett relationships. The transition structures are characterized by more nearly linear C-H-H geometries than have been assumed in experimental studies.

Acetylene is metalated easily (very low activation energy) in an exothermic reaction, whereas the lithiation of methane is endothermic with a high activation barrier. The experimentally known reverse process, hydrogenolysis of methyllithium, is favored instead.

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Registry No. CH_4, 74-82-8; C_2H_2, 74-86-2; HLi, 7580-67-8; CH_3Li, 917-54-4; C_2HLi, 1111-64-4.

Supplementary Material Available: Full geometry information in the form of archive entries (3 pages). Ordering information is given on any current masthead page.

Solution Chemistry of the Cuboidal Mixed-Valence (3.25) Molybdenum/Sulfido Cluster $[Mo_4S_4(H_2O)_{12}]^{5+}$

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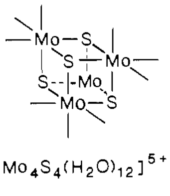
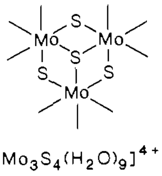
Abstract: The green aqua ion of cuboidal $Mo_4S_4^{5+}$, here designated as $[Mo_4S_4(H_2O)_{12}]^{5+}$, average oxidation state 3.25 (11 Mo valence electrons), exhibits remarkable stability in acidic solutions, *p*-toluenesulfonic acid (HPTS), and $HClO_4$, $[H^+]$ = 0.01-4.0 M. At 50 °C (pH <2) in air (1 M acid), slow oxidation of $Mo_4S_4^{5+}$ ($t_{1/2} \sim 4$ days) occurs, giving 1:1 amounts of the incomplete cuboidal Mo^{IV}_3 ion, $[Mo_3S_4(H_2O)_9]^{4+}$. In 1 M HCl ($t_{1/2} \sim 10$ h at 50 °C) the reaction is used as a preparative procedure (~90 °C) for $Mo_3S_4^{4+}$. No large variations in UV-vis spectrum are observed for $Mo_4S_4^{5+}$ at pH < 2. At pH > 2, however, a purple hydrolysis product is generated, complete formation of which is observed at, e.g., pH 6.2 and 8.4. This product is stable for at least 1 h (but subsequently decomposes), and on acidification (2 M $HClO_4$) it reforms overnight $Mo_4S_4^{5+}$ (86%) along with $Mo_3S_4^{4+}$ (10%). Cyclic voltammetry of $Mo_4S_4^{5+}$ in 2 M HPTS gives two one-electron waves, and reduction potentials for $Mo_4S_4^{5+/4+}$ and $Mo_4S_4^{6+/5+}$ of 0.21 and 0.86 V, respectively (vs NHE). The orange $Mo_4S_4^{4+}$ ion obtained on constant potential reduction (-0.12V vs SCE) rapidly reoxidizes in air. At 25 °C under N_2, I = 2.0 M ($LiClO_4$), reduction of $Mo_4S_4^{5+}$ to $Mo_4S_4^{4+}$ with Cr^{2+} (0.61×10^3 M^{-1} s^{-1}) and V^{2+} (24.5×10^3 M^{-1} s^{-1}) occurs by outer-sphere processes, with no dependence on $[H^+]$ (0.5-1.9 M). From the Marcus equations the self-exchange rate constant for $[Mo_4S_4(H_2O)_{12}]^{4+/5+}$ is 760 M^{-1} s^{-1}. On constant potential oxidation of $Mo_4S_4^{5+}$ (+0.70 V vs SCE) for ~40 min, chromatographically separated products are $Mo_3S_4^{4+}$ (15% of Mo), the di-μ-sulfido Mo^V_2 ion (30%), unreacted $Mo_4S_4^{5+}$ (25%), and Mo^{VI}, with no evidence for $Mo_4S_4^{6+}$. With a large excess of $V(O)_2^+$ (1.0 V) as oxidant the reaction $Mo_4S_4^{5+} + 5V^V \rightarrow Mo_3S_4^{4+} + Mo^{VI} + 5V^{IV}$ occurs via a red purple intermediate. With a 2:1 molar excess of $V(O)_2$, red-purple $Mo_4S_4^{6+}$ (or a closely related hydrolyzed product) can be separated chromatographically and is stable under N_2 at 4 °C. It oxidized in air within ~12 h to give $Mo_3S_4^{4+}$. On complexing $Mo_4S_4^{5+}$ with NCS^- (~0.10 M) air oxidation gives the thiocyanato complex of $Mo_4S_4^{6+}$ overnight. The same product is formed rapidly on addition of NCS^- to $Mo_4S_4^{6+}$.

Procedures for the preparation of the aqua ion of the cuboidal mixed-valence $Mo_4S_4^{5+}$ core have been described.[1] An X-ray crystallographic study of the edta (ethylenediamine-N,N′-tetraacetate) complex, $Ca_3[Mo_4S_4(edta)_2]\cdot 28H_2O$,[2] is the basis for designating the aqua ion as $[Mo_4S_4(H_2O)_{12}]^{5+}$ The incomplete cuboidal ion $[Mo_3S_4(H_2O)_9]^{4+}$ is also known.[1] Also from crystallographic studies the $Mo_4S_4^{6+}$ core has been characterized as red $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$,[3] and structures of the edta complexes of $Mo_4S_4^{6+}$ and $Mo_4S_4^{4+}$ have been reported.[4] In contrast there have as yet been no studies on the solution chemistry of the 5+ aqua ion, including investigations as to the accessibility and stability of the corresponding 4+ and 6+ states. In view of the wide ranging occurrence of cuboidal structures in metalloproteins,[5-8] through organometallic (cyclopentadienyl) chemistry,



$[Mo_4S_4(H_2O)_{12}]^{5+}$



$[Mo_3S_4(H_2O)_9]^{4+}$

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