Theoretical Study of the Intrinsic Reactivities of Various Allylmetals toward Carbonyls and Water[⊥]

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Quantum mechanics MP2/6-31+G* calculations have been carried out for the reactions of a series of monomeric allylmetals with water and carbonyl compounds in the gas phase. Allyl complexes of groups IA and IIA and low-valent group IIIA and IVA metals are π-complexes or reactive σ-complexes. They show high reactivities toward hydrolysis. Group IIB, trivalent group IIIA, tetravalent group IVA, and both tri- and pentavalent group VA metals form σ-complexes with allyl. These allylmetals are less reactive toward hydrolysis than toward allylation. The calculated intrinsic kinetic preference of allylation over hydrolysis is found to correlate well with the reactivity of hydrolysis, the nucleophilicity of the allylmetals, and the lateness of hydrolysis transition structures. Both the nucleophilicity of the allylmetal complexes and the thermodynamic driving force are important to the reactivity of hydrolysis. Importantly, there is a large thermodynamic preference for allylation over hydrolysis for all allylmetals because the hydrolysis has to break a strong O−H bond. Thus, the kinetic preference for allylation is correlated with the degree of H−O bond breaking in the hydrolysis transition structure.

Introduction

Carbon−carbon bond formation by the reaction of organic halides with carbonyl compounds mediated by metals is a common and useful methodology in organic synthesis.[1] Traditionally, the Barbier−Grignard type reactions were carried out under anhydrous conditions, since the metals and organometallic intermediates generated in situ are very reactive toward water and oxygen. In recent years, significant progress has been made in using water as a solvent for organic synthesis,[2] especially for Barbier−Grignard allylation. In this connection, a number of metals, including beryllium,[3] magnesium,[4] manganese/copper,[5] iron,[6] zinc,[7] cadmium,[8] gallium,[9] indium,[10,11] tin,[11,12] lead,[13] antimony,[14] and bismuth,[15,16] have been found to mediate the reaction of allyl halides with carbonyl compounds in aqueous media. Water is considered safe, inexpensive, and environmentally benign. The amount of organic solvent disposal is often reduced. Moreover, for many water-soluble substrates, the need for derivatization and

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[⊥] This paper is dedicated to Professor Li-Xin Dai on the occasion of his 80th birthday.

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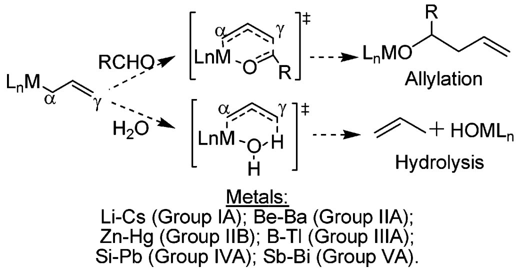
protection−deprotection often encountered in organic synthesis can be avoided, which increases the synthetic efficiency.[17]

Generally, organometallic compounds react with water readily. Initially, a radical mechanism was proposed, in which an allyl radical was derived from single-electron transfer (SET) from the metal followed by addition of the radical to the carbonyl group.[7] However, radical probe experiments did not detect any radical intermediate.[18] Later, a mechanism involving a radical anion coordinated onto the metal surface followed by carbonyl addition was proposed.[10b] In contrast, Whitesides[11] and others[19] demonstrated the probability of discrete organometallic indium and tin for allylation in the aqueous media. Experimentally, allylation with preformed discrete allylmetals in the presence of water, such as allylchromium(III),[20] allylmercury,[21] allylborane,[22] allylsilane,[23] allylgermane,[24] and allyltin,[25] have been reported. Recently, Fukuma et al. prepared several assumed Grignard-type allylating reagents for allylation in the aqueous media.[15] Chan et al. observed discrete allylindium, allyltin and allylantimony in water in a finite short time by ^{1}H NMR.[26] These experimental observations indicate that some discrete allylmetal intermediates are involved in the metal-mediated allylation in water. It is thus a fundamental question why do some allylmetals, even hydrolytically reactive ones, prefer to allylate carbonyl compounds?[10b]

Li rationalized the peculiar reactivity of discrete organometallic compounds in water by the hard−soft acid−base (HSAB) principle.[27] Water is considered to be “hard” and thus has less tendency to react with “soft” allylmetals.[28] The stability of organometallic compounds in water is alternatively attributed to the polarity of the carbon−metal bond.[29] A greater covalent character of the C−M bond corresponds to a higher stability in water. These two factors qualitatively explain the intrinsic reactivity of hydrolysis, *but they do not shed light on the intrinsic reactivity difference between allylation and hydrolysis, especially for the hydrolytically reactive organometallic compounds*![10b] Although many theoretical studies on the reaction of various allylmetals with aldehydes have been reported,[30] there has been no comparison between reactivities of allylmetals with water and aldehydes. Since some reactive intermediates are difficult to observe by experiments in a finite time in aqueous media prior to hydrolysis, we conducted theoretical calculations on the intrinsic reactivities of a series of monomeric allylmetals with water and carbonyl compounds (Scheme 1 and Table 1), in an effort to understand the origin of allylation mediated by some discrete allylmetals in aqueous media and to explore any possibility of other discrete allylmetals for allylation in aqueous media.

Scheme 1



Computational Method

Ab initio calculations were carried out with the Gaussian 98 and 03 programs.[31] The structures of various allylmetals and the corresponding allylmetal−water complexes and allylation and hydrolysis transition structures were first located by the HF/6-31+G* method and further optimized by the MP2/

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Table 1. Natural Charges of ML_n and $C_\gamma H_2$, Calculated Complexation Energies with One Water Molecule, Reaction Energies of Hydrolysis (ΔE_w) and Allylation ($\Delta E_{C=O}$), Thermodynamic Preferences toward Hydrolysis ($\Delta\Delta E = \Delta E_w - \Delta E_{C=O}$), Activation Energies of Hydrolysis ($\Delta E_w^\ddagger$) and Allylation ($\Delta E_{C=O}^\ddagger$), and Kinetic Preferences toward Hydrolysis ($\Delta\Delta E^\ddagger = \Delta E_w^\ddagger - \Delta E_{C=O}^\ddagger$) Obtained by the MP2 Method[a]

	ML_n	$C_\gamma H_2$	ΔE_{com}	ΔE_w[e]	$\Delta E_{C=O}$[e]	$\Delta\Delta E$[e]	$\Delta E_w^\ddagger$	$\Delta E_{C=O}^\ddagger$	$\Delta\Delta E^\ddagger$
Li	**0.91**	**−0.48**[b]	−16.5/−18.6[c]	−28.0	−40.6	12.6	0.9	3.2/3.0[g]	−2.3/−2.1[g]
Na	**0.94**	**−0.50**[b]	−17.5/−13.7[c]	−24.3	−37.2	12.9	−1.2[f]	4.1[g]	−5.3[g]
K	**0.97**	**−0.51**[b]	−16.1/−8.1[c]	−26.3	−37.0	10.7	−1.5[f]	8.7[g]	−10.2[g]
Rb	**0.98**	**−0.51**[b]	−15.8/−6.7[c]	−25.4	−36.6	11.2	−1.6[f]	9.1[g]	−10.7[g]
Cs	**0.99**	**−0.52**[b]	−15.5/−5.4[c]	−25.2	−36.9	11.7	N/D	9.7[g]	N/D
BeBr	0.75	−0.05	−22.2	−42.5	−52.0	9.5	4.6	4.1[g]	0.5[g]
MgBr	0.84	−0.21	−23.1	−34.1	−42.7	8.6	4.5	5.7[g]	−1.2[g]
CaBr	**0.94**	**−0.51**[b]	−20.6/−21.8[c]	−34.6	−43.7	9.1	1.0	9.3	−8.3
SrBr	**0.96**	**−0.52**[b]	−18.9/−21.2[c]	−33.4	−42.5	9.1	1.2	8.3	−7.1
BaBr	**0.98**	**−0.53**[b]	−18.8/−20.8[c]	−33.2	−42.6	9.4	0.7	7.8	−7.1
ZnBr	0.67	−0.05	−15.7	−16.2	−27.3	11.1	12.9	6.9	6.0
CdBr	0.63	−0.05	−11.7	−10.0	−21.2	11.2	15.2	9.0	6.2
HgBr	0.50	−0.03	−6.4	2.9	−9.1	12.0	27.6	16.9	10.7
BBr_2	0.32	0.03	−8.7	−28.2	−41.4	13.2	11.1	−0.2[f]	11.3
$AlBr_2$	0.57	0.01	−26.0	−31.8	−41.9	10.1	7.6	1.4	6.2
Ga(I)	**0.70**	**−0.35**[b]	−6.5	−40.1	−49.7	9.6	1.2	5.5/5.8[g]	−4.3/−4.6[g]
$GaBr_2$	0.53	0.01	−20.9	−19.6	−31.5	11.9	12.3	3.4	8.9
In(I)	**0.72**	**−0.37**[b]	−6.8/−4.1[c]	−36.9	−46.4	9.5	0.7	5.8[g]	−5.1[g]
$InBr_2$	0.52	0.00	−21.3	−16.7	−29.0	12.3	12.7	4.7	8.0
Tl(I)	**0.72**	**−0.37**[b]	−5.1	−23.2	−34.9	11.7	1.5	4.5/4.6[g]	−3.0/−3.1[g]
$TlBr_2$	0.36	0.03	−14.8	2.9	−11.8	14.7	23.0	10.6	12.4
Si(II)Br	0.56	0.00	−13.8	−34.4	−48.7	14.3	5.5	2.5	3.0
$SiBr_3$	0.43	0.04	*d*	−20.3	−34.7	14.4	35.9	20.6	15.3
Ge(II)Br	0.57	−0.01	−15.3	−29.7	−43.6	13.9	6.6	5.5	1.1
$GeBr_3$	0.39	0.06	−1.3	−6.8	−22.8	16.0	33.0	14.9	18.1
Sn(II)Br	**0.47**	**−0.25**[b]	−14.1	−30.6	−43.3	12.7	5.4	6.1	−0.7
$SnBr_3$	0.42	0.05	−7.5	−9.5	−24.3	14.8	25.0	8.8	16.2
Pb(II)Br	**0.47**	**−0.26**[b]	−11.2	−27.8	−40.1	12.3	5.3	7.0	−1.7
$PbBr_3$	0.26	0.09	−8.0	−0.8	−16.0	15.2	34.2	14.7	19.5
$SbBr_2$	0.41	0.02	−7.6	−10.1	−27.1	17.0	18.8	10.7	8.1
$SbBr_3Me$	0.22	0.10	−12.6	−1.0	−13.7	12.7	26.7	9.8	16.9
$BiBr_2$	0.41	0.01	−10.2	−10.7	−27.0	16.3	19.0	9.9	9.1
$BiBr_3Me$	0.08	0.14	−14.4	4.1	−10.6	14.7	32.1	12.8	19.3

[a] All energies are given in kcal/mol. [b] The charge of $C_\alpha H_2$ is same as that of $C_\gamma H_2$ in (π-allyl)metals (in boldface). [c] Model B (see Chart 2). [d] Water does not coordinate with the silicon but forms a van der Waals adduct with a complexation energy of −0.9 kcal/mol. [e] Reaction energies of ΔE_w and $\Delta E_{C=O}$ were approximated by the MP2/6-31+G*//HF/6-31+G* method. [f] The negative activation barriers are due to zero-point energy corrections. [g] Acetone was used for allylation.

6-31+G* method.[32] The effective core potentials (ECPs) of Hay and Wadt, Lanl2dz, with double-ζ valence basis sets were used for elements below the third row in the periodic table in all calculations.[33] Harmonic vibration frequencies were calculated with both methods to derive thermodynamic properties. To approximate the overall reaction energies, the allylation products with formaldehyde and hydrolysis products were fully optimized with the HF method, and their energies were evaluated with the MP2 method (thermal corrections were made with the HF frequency calculations). This simplified method of calculation does not seem to cause a significant problem for the current purpose.[34] Atomic charges were calculated by the natural population analysis (NPA) on the MP2 structures by the HF method.[35]

Acetaldehyde was generally used in the allylation transition structures. Regrettably, allylation transition structures for acetaldehyde with very reactive allyl−Na, −K, −Rb, −Cs, −Be, −Mg, and −In(I) could not be located, because the reactions are too reactive. Less reactive acetone was used instead in order to estimate the intrinsic reactivity of these allylmetals toward carbonyl compounds. Three examples, allyl−Li, −Ga(I) and −Tl(I), indicate that these very reactive allylmetals might have similar reactivities toward acetaldehyde and acetone (Table 1).[36] The transition structure for the hydrolysis of allylcesium could not be located by the MP2 method. All electronic energies listed were corrected with zero-point energy.

Results

Table 1 summarizes the calculated natural charges of allylmetals and energetics of water complexation, activation energies, and reaction energies of hydrolysis and allylation reactions. The calculated structures of various allylmetal complexes, the transition structures of hydrolysis, and allylation reactions of the allylmetal complexes by the MP2 method are shown in Figures 1−3.[37] Two types of allylmetal complexes are found (Chart 1): (1) Stable (π-allyl)metal complexes are found

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(34) When allylation and hydrolysis products for allyl−In(I), $-InMe_2$, and $-InBr_2$ were optimized, followed by frequency calculations by the MP2 method, the calculated reaction energies for allylation and hydrolysis and, especially, thermodynamic preference ($\Delta\Delta E$) are close to those values obtained by the MP2//HF method (in parentheses). allyl−In(I): ΔE_w, −33.2 (−36.9) kcal/mol; $\Delta E_{C=O}$, −42.2 (−46.4) kcal/mol; $\Delta\Delta E$, 9.0 (9.5) kcal/mol. Allyl−$InMe_2$: ΔE_w, −27.0 (−27.6) kcal/mol; $\Delta E_{C=O}$, −35.6 (−36.5) kcal/mol; $\Delta\Delta E$, 8.6 (8.9) kcal/mol. Allyl−$InBr_2$: ΔE_w, −16.4 (−16.7) kcal/mol; $\Delta E_{C=O}$, −28.4 (−29.0) kcal/mol; $\Delta\Delta E$, 12.0 (12.7) kcal/mol.

(35) (a) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(36) The allylation transition structure with acetone mediated by allyllithium, -gallium(I), and -thallium(I) were located by the MP2 method (Figure S1 (Supporting Information)). The calculated activation barriers and kinetic preferences toward acetone for these allylmetals are close to those of acetaldehyde (Table 1). Nevertheless, the activation barrier for acetone becomes less favorable than that of acetaldehyde by 1.1 (Li), 1.2 (Ga), and 1.2 kcal/mol (Tl) in terms of free energy.

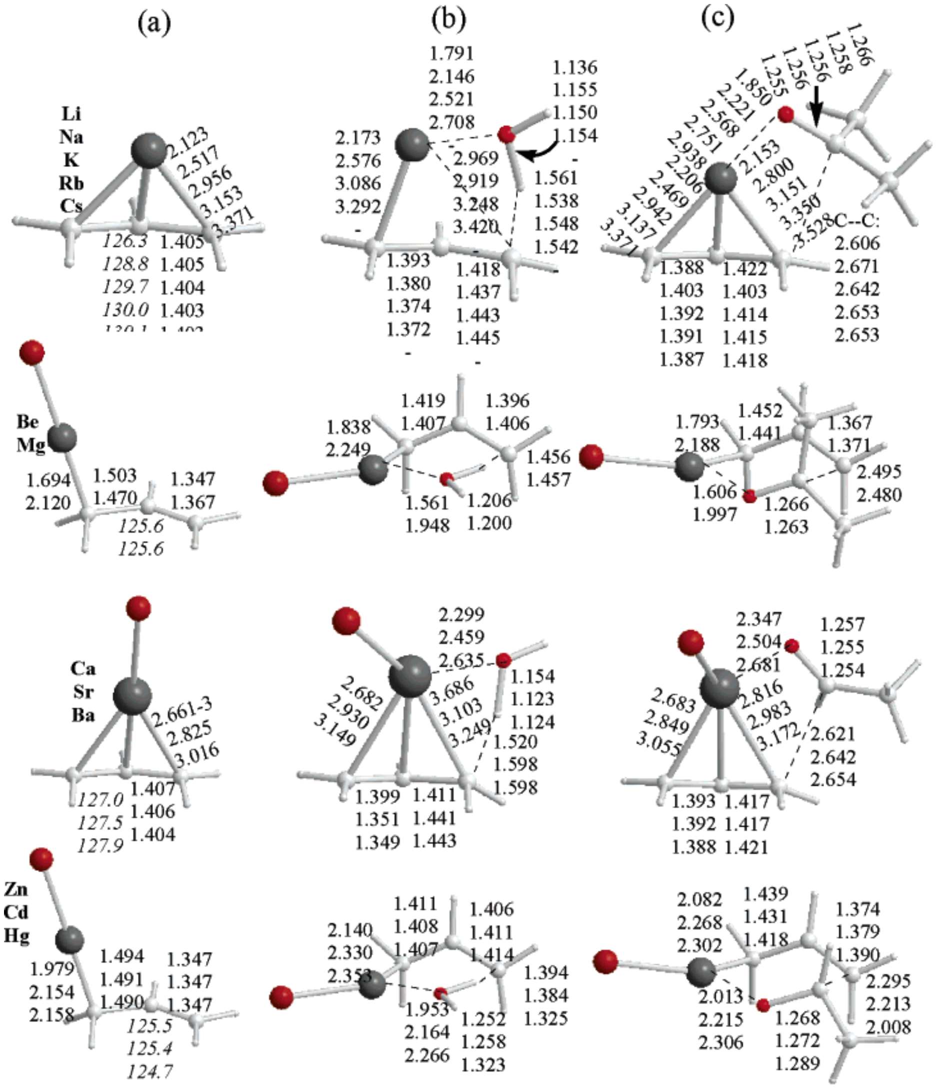

Figure 1. Calculated structures of (a) allyl−M(IA), −M(IIA), and −M(IIB) complexes, (b) transition structures of hydrolysis, and (c) transition structures of allylation by the MP2 method.

for highly electropositive metals, including alkali metals,[38] calcium, strontium, barium, and some hypovalent metals, such as gallium(I), indium(I), thallium(I), tin(II), and lead(II).[39] The rest of the allylmetal complexes are stable in σ-complexes. In general, carbonyl compounds feature higher-lying occupied and lower-lying unoccupied frontier molecular orbitals than does the water molecule, whereas the charge separation of the water molecule is larger than for carbonyl compounds (Table 2). As a result, the allylation reaction should be more orbital-controlled, while the hydrolysis reaction should be more charge-controlled.[40]

Allyl−Alkali-Metal Complexes (Group IA). All five alkali metals form π-allyl complexes. These complexes are highly ionic, according to the calculated natural charges. The calculated positive charge on the metal increases from Li (0.91) to Cs (0.99). In the meantime, $C_\alpha H_2$ and $C_\gamma H_2$ are highly negatively charged. The M−C_α and M−C_γ distances increase significantly from Li (2.123 Å) to Cs (3.371 Å). All these (π-allyl)-metal complexes form strong complexes (model A; see Chart 2 and Figure S3 (Supporting Information)) with one molecule of water (see ΔE_{com} in Table 1). The coordination of the water molecule partially breaks the M−C_γ bond (in the case of allyl−Li, the C_γ−Li bond becomes completely broken), so that one of the water O−H groups forms a hydrogen bond with the C_γ. The OH- - -C_γ distances in these complexes are very short (1.81−1.90 Å) (Figure S3), much shorter than those in the (σ-allyl)metal complexes. The calculated complexation energy, as expected, decreases from Na (−17.5 kcal/mol) to Cs (−15.5 kcal/mol). However, allyl−Li forms a more stable complex with water in model B with a binding energy of −18.6 kcal/mol. The model A complex of water−allyl−Li is less stable, with a binding energy of −16.5 kcal/mol, because it has to break the C_γ−Li bond. On the other hand, the model B complex for Na, K, Rb, and Cs is not stable because of the reduced acidity of these metals. All water−allylmetal complexes undergo hydrolysis reactions very readily.

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(37) Two conformations for allyl−$SbBr_2$ and −$BiBr_2$ and their adducts and transition structures were located (Figures 3 and S2 (Supporting Information)).

(38) Hommes, N. J. R. v. E.; Bühl, M.; Schleyer, P. v. R.; Wu, Y.-D. *J. Organomet. Chem.* **1991**, *409*, 307.

(39) Hypovalent allylgallium(I), -indium(I), -thallium(I), allyltin(II) bromide, and allyllead(II) bromide are found to be stable as σ-complexes by the HF method, but they are unstable and become π-allyl complexes when introducing the effects of electron correlation (MP2 method).

(40) Klopman, G. *J. Am. Chem. Soc.* **1968**, *90*, 223.

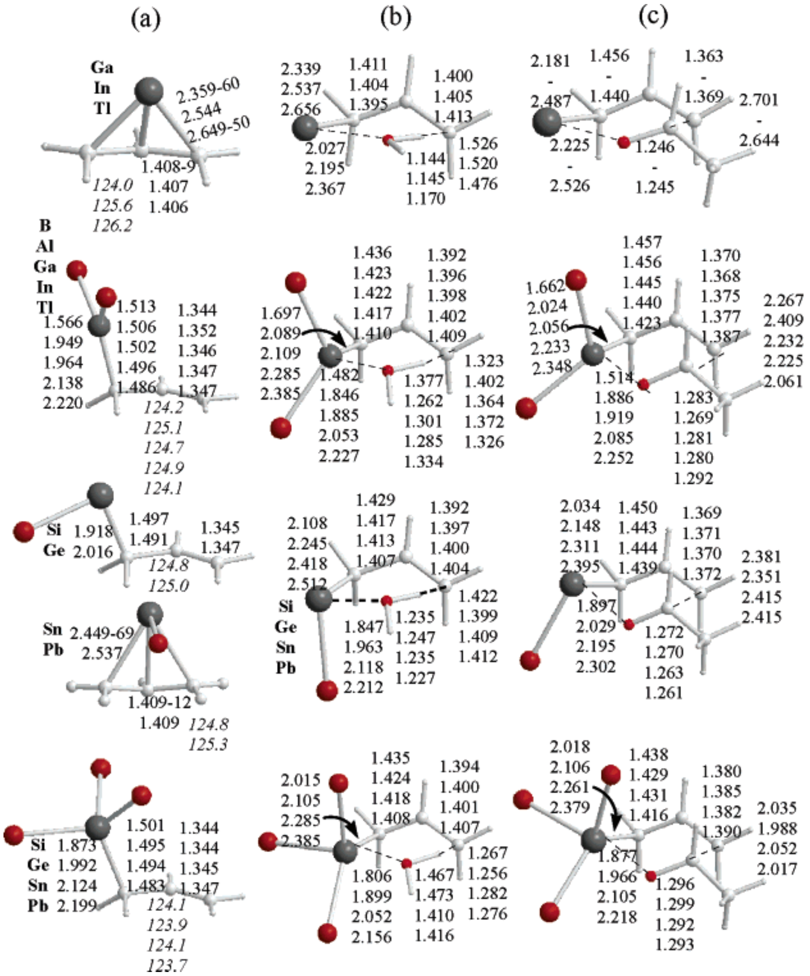

Figure 2. Calculated structures of (a) allyl−M(IIIA) and −M(IVA) complexes, (b) transition structures of hydrolysis, and (c) transition structures of allylation reactions by the MP2 method.

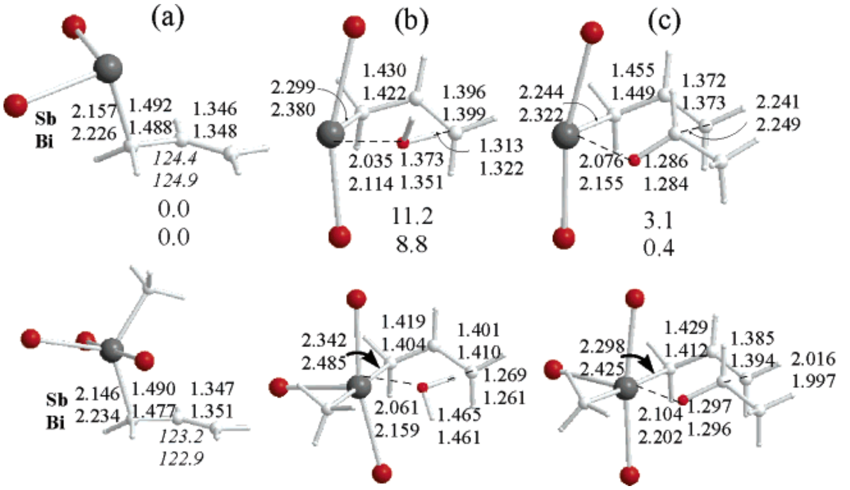

Figure 3. Calculated structures of (a) allyl−M(VA) complexes, (b) transition structures of hydrolysis, and (c) transition structures of allylation reactions by the MP2 method.

The transition structures are early with little O−H bond breaking (O−H = 1.14−1.16 Å). The forming C_γ- - -H distance is long (1.54−1.56 Å). As a matter of fact, the calculated activation energy ($\Delta E_w^\ddagger$ in Table 1) with zero-point energy correction for the complexes of Na−Cs is slightly negative.[41] The calculated reactivity of hydrolysis decreases from Li to Cs, which is in accord with the ionic character of the allylmetal complexes. These allylmetal complexes also have very high reactivities toward the addition of acetaldehyde, and no transition structure was located for these reactions, except for the reaction of allyl−Li. Allyl−Li reacts with acetaldehyde through a very early transition structure (the forming C−C bond distance is 3.055 Å) with an activation energy

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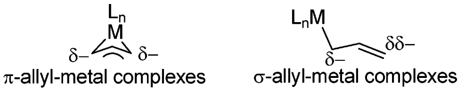
[41] The calculated negative activation barriers of hydrolysis mediated by allylsodium, -potassium, and -rubidium complexes and negative activation barriers of allylation mediated by allylborane are due to zero-point correction.

Chart 1. Classification of Allylmetals: (A) $\Delta\Delta E^{\ddagger} < -6$ kcal/mol; (B) $-6 < \Delta\Delta E^{\ddagger} < 6$ kcal/mol; (C) $\Delta\Delta E^{\ddagger} > 6$ kcal/mol



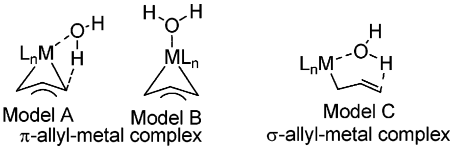
(B) Li, Na,
(A) K, Rb, Cs
(A) CaBr, SrBr, BaBr
(B) Ga, In, Tl, SnBr, PbBr

(B) BeBr, MgBr, SiBr, GeBr
(C) ZnBr, CdBr, HgBr
(C) BBr_2, $AlBr_2$, $GaBr_2$, $InBr_2$, $TlBr_2$
(C) $SiBr_3$, $GeBr_3$, $SnBr_3$, $PbBr_3$
(C) $SbBr_2$, $SbBr_3Me$, $BiBr_2$, $BiBr_3Me$

Table 2. Calculated Key Bond Lengths, Energies of Frontier Molecular Orbitals, and Natural Charges of Acetylaldehyde and Water by the MP2 Method

	MeCHO	H_2O
bond lengths (Å)	1.227 (C=O)	0.971 (H−O)
frontier molecular orbitals (eV)		6.0 (σ*) (LUMO + 1)
	2.7 (π*) (LUMO)	4.0 (p*) (LUMO)
	−11.7 (n) (HOMO)	−13.9 (p) (HOMO)
	−13.6 (π) (HOMO − 1)	−19.5 (σ) (HOMO − 2)
natural charges	0.50 (C)	0.50 (H)
	−0.63 (O)	−0.99 (O)

Chart 2. Three Modes of Water Complexation



of 3.2 kcal/mol (Table 1, $\Delta E_{C=O}{}^{\ddagger}$). Transition structures were located for the reaction of these allylmetal complexes with acetone. As shown in Figure 1, the forming C- - -C bond distances in these transition structures are quite similar: all around 2.6−2.7 Å. The M−C_γ bonds are only slightly elongated (by less than 0.3 Å) from those in the allylmetal complexes. They can be considered as [2 + 2] transition structures. The calculated activation energies with respect to the most stable water−allylmetal complexes increase from allyl−Li (3.0 kcal/mol) to allyl−Cs (9.7 kcal/mol). This order of reactivity is not in line with the nucleophilicity of the C_γ center but seems to be in parallel with the Lewis acidity of the metal center.

Allyl−Alkaline-Earth-Metal Complexes (Group IIA). BeBr and MgBr form σ-complexes while CaBr, SrBr, and BaBr form π-complexes with the allyl anion, as shown in Figure 1 and Table 1. On the basis of the calculated natural charges, the allyl−BeBr complex has the least ionic character with little negative charge at the $C_\gamma H_2$ center. The allyl−MgBr complex has more ionic character and the $C_\gamma H_2$ group has a negative charge of −0.21. While the complexes of water with (σ-allyl)metals are all in model C, in which one of the water hydrogens has a weak interaction with C_γ (H- - -C_γ = 2.14−2.16 Å). For the three (π-allyl)metal complexes (CaBr, SrBr, and BaBr), the coordination of water in both model A and model B is a stable minimum. However, model B is somewhat more stable than model A, resulting from a strong π-interaction between the metals and the allyl moiety and a hydrogen bond between water and the bromide in model B. The complexation energy of water to the five allylmetal complexes is very strong, and it decreases slightly down the periodic table (−23.1 to −20.8 kcal/mol). This again reflects the Lewis acidities of the metals. Interestingly, allyl−BeBr and allyl−MgBr have similar reactivities toward hydrolysis, with an activation energy of about 4.5 kcal/mol. The O−H bond (1.20 Å) is more elongated in these hydrolysis transition structures. No transition structure could be located for the polar addition reaction between these two complexes and acetaldehyde.[42] However, transition structures could be located for the reaction with acetone, which have activation energies similar to those of hydrolysis reactions. The three (π-allyl)metal (CaBr, SrBr, BaBr) complexes react with water very readily with activation energies of 0.7−1.2 kcal/mol. However, they react with acetaldehyde with a larger barrier. This barrier decreases from 9.3 for allyl−CaBr to 7.8 kcal/mol for allyl−BaBr.

Allyl−Group IIB Metal Complexes. The three complexes are all in σ-complexes. While there is little negative charge at the $C_\gamma H_2$ center, the polarity of the C_α−M bond decreases from Zn to Hg, as indicated by the charges on the metal centers. The energy for water complexation is −15.7 kcal/mol for allyl−ZnBr but drops to −6.4 kcal/mol for allyl−HgBr. Interestingly, these three allylmetal complexes have larger reaction barriers to hydrolysis, 12.9 (ZnBr), 15.2 (CaBr), and 27.6 kcal/mol (HgBr), respectively, compared with those of group IA and IIA metal complexes. A comparison of water complexation energy (ΔE_{com}) and reaction energy (ΔE_{w}) indicates that the hydrolysis products are either as stable as (ZnBr and CdBr) or less stable than (HgBr) the water complex. On the other hand, these allylmetal complexes react with acetaldehyde with smaller barriers, 6.9 (ZnBr), 9.0 (CaBr), and 16.9 kcal/mol (HgBr), respectively. These suggest that all three complexes have an intrinsic kinetic preference for allylation over hydrolysis, in accord with available experimental observation.[21]

Allyl−Group IIIA Metal Complexes. The three monovalent metal complexes allyl−Ga, −In, and −Tl, are all π-complexes. These monovalent metals only have a weak binding with water with complexation energies of −5.1 to −6.5 kcal/mol, due to the low Lewis acidities of these monovalent metals. The binding of water completely breaks the M−C_γ bond so that the water complexes are in the model C, indicating that the M−C_γ interaction is not very strong. These π-complexes only have moderate ionic character with a positive charge of about 0.72 on the metals and a negative charge of −0.36 on $C_\gamma H_2$. They are predicted to have high reactivities toward hydrolysis with activation energies of 0.7−1.5 kcal/mol. These complexes appear to also have high reactivities toward allylation with acetaldehyde and acetone, although the barriers of allylation are slightly higher than those of the corresponding hydrolysis. All of the trivalent metal complexes allyl−BBr_2, −$AlBr_2$, −$GaBr_2$, −$InBr_2$, and −$TlBr_2$ are σ-complexes. Except for the BBr_2 complex, these metal species display a strong affinity for water binding. However, they have moderate to high activation energies for hydrolysis reactions. As shown in Figure 2, the five hydrolysis transition structures are all six-membered rings and

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[42] Experimental mechanistic studies on allyllithium and -magnesium bromides showed a stepwise SET mechanism: Gajewski, J. J.; Bocian, W.; Harris, N. J.; Olson, L. P.; Gajewski, J. P. *J. Am. Chem. Soc.* **1999**, *121*, 326.

there is considerable C- - -H bond formation. On the other hand, these complexes display high reactivities toward allylation. Allyl−BBr_2 and −$AlBr_2$ are predicted to have very low barriers for allylation (−0.2 and 1.4 kcal/mol, respectively).[41] The barrier of allylation is increased slightly for allyl−$GaBr_2$ (3.4 kcal/mol) and allyl−$InBr_2$ (4.7 kcal/mol). Even for allyl−$TlBr_2$, the barrier for allylation is only about 10.6 kcal/mol. Experiments and theoretical calculations show that the reactivity of allylation is associated with the Lewis acidities of the metals (especially for BBr_2 and $AlBr_2$).[43] Thus, the calculations indicate that these allyl complexes may undergo allylation reactions in aqueous media.

Allyl−Group IVA-Metal Complexes. Allyl−SiBr, −GeBr, −SnBr, and −PbBr contain formally divalent metals. Allyl−SiBr and −GeBr are σ-complexes, while allyl−SnBr and −PbBr are π-complexes. The two σ-complexes have more polar C−M bonds than do the two π-complexes. All four complexes have considerable binding affinities with water, and the ΔE_{com} values are in the range of −11.2 to −15.3 kcal/mol. The four complexes also have similar reactivities toward hydrolysis with activation energies ($\Delta E_{\mathrm{w}}^{\ddagger}$) in the range of 5.3−6.6 kcal/mol. Interestingly, these complexes are also quite reactive toward allylation, with activation energies increasing from 2.5 kcal/mol for allyl−SiBr to 7.0 kcal/mol for allyl−PbBr. Thus, these complexes have similar reactivities toward hydrolysis and allylation. The situation is very different for the four allyl complexes of tetravalent metals allyl−$SiBr_3$, −$GeBr_3$, −$SnBr_3$, and −$PbBr_3$. All these species are σ-complexes with less polarization than their corresponding divalent counterparts. While allyl−$SiBr_3$ and −$GeBr_3$ have essentially no binding affinity to water, allyl−$SnBr_3$ and −$PbBr_3$ have moderate binding affinities to water: −7.5 and −8.0 kcal/mol, respectively. This is because the metal centers are coordination “saturated”. All four complexes have very high activation energies toward hydrolysis: 35.9, 33.0, 25.0, and 34.2 kcal/mol, respectively. However, they are much more reactive toward allylation, with activation energies of 20.6, 14.9, 8.8, and 14.7 kcal/mol, respectively, indicating that they are suitable for allylation in aqueous media.[23−25]

Allyl−Group VA Metal Complexes. Both trivalent (allyl−$SbBr_2$ and −$BiBr_2$) and pentavalent (allyl−$SbBr_3Me$ and −$BiBr_3Me$) complexes are σ-complexes; the former have higher polarities than the latter. In contrast with the allyl−group IVA metal complexes, the trivalent species have lower affinities to water than the pentavalent species. All four allylmetal complexes have moderate to high activation energies toward hydrolysis, but they are much more reactive toward allylation. Thus, they should be suitable for allylation in aqueous media.

Discussion

Reactivity and Intrinsic Kinetic Preference. Our calculations reveal that allylmetals that are in a stable π-complex display high reactivities toward hydrolysis. This is especially the case for highly electropositive metals. Although they are also quite reactive toward allylation, overall, they display an intrinsic kinetic preference for hydrolysis over allylation in the gas phase. Although allyl−BeBr, −MgBr, −SiBr, and −GeBr are σ-complexes, they are also quite reactive toward both hydrolysis and allylation. Thus, we can qualitatively conclude that the allyl complexes of group IA, group IIA, monovalent group IIIA, and divalent IVA metals are reactive toward both water and carbonyl compounds. Group IIB metals, high-valent group IIIA and group IVA metals, and both low- and high-valent group VA metals form σ-complexes with the allyl moiety. These complexes show moderate to low reactivities toward hydrolysis but higher reactivities toward allylation.

The intrinsic kinetic preference ($\Delta\Delta E^{\ddagger} = \Delta E_{\mathrm{w}}^{\ddagger} - \Delta E_{\mathrm{C=O}}^{\ddagger}$) is introduced to measure the relative kinetic preference of the allylmetals toward hydrolysis versus allylation. A positive value of calculated $\Delta\Delta E^{\ddagger}$ indicates a kinetic preference for the allylmetal to undergo allylation over hydrolysis, while a negative $\Delta\Delta E^{\ddagger}$ indicates a kinetic preference for hydrolysis. From the results in Table 1, the allylmetals can be divided into three classes (Chart 1). (A) Very reactive (π-allyl)metal complexes (M = K, Rb, CaBr, SrBr, and BaBr) are highly ionic and definitely hydrolyze more quickly than they allylate ($\Delta\Delta E^{\ddagger} < -6$ kcal/mol); (B) π-Complexes of Li, Na, Ga(I), In(I), Tl(I), $Sn^{II}Br$ and $Pb^{II}Br$ and polarized σ-complexes of BeBr, MgBr, $Si^{II}Br$, and $Ge^{II}Br$ are less polarized than the group A complexes. The calculated intrinsic kinetic preferences ($\Delta\Delta E^{\ddagger}$) are in the range of $-6 < \Delta\Delta E^{\ddagger} < 6$ kcal/mol. These allylmetals may hydrolyze or may allylate preferentially, depending on the experimental conditions. (C) The rest of the (σ-allyl)metal complexes, group IIB metals, high-valent group IIIA and group IVA metals, and both low-valent and high-valent group VA metals have $\Delta\Delta E^{\ddagger} > 6$ kcal/mol and likely prefer to allylate. Although some reactive allylmetals have negative $\Delta\Delta E^{\ddagger}$ values, the above calculations, which are based on a polar addition mechanism, cannot rule out a very facile single-electron-transfer mechanism (SET) on the metal surface or on the allylmetal surface[42] or allylation inside a hydrophobic core,[44] as proposed for the magnesium case.[4]

Figure 4 (top) shows a plot of calculated intrinsic kinetic preferences ($\Delta\Delta E^{\ddagger}$) against calculated activation energies for hydrolysis and allylation reactions. The calculated activation energies of hydrolysis vary over a span of about 38 kcal/mol, while the calculated activation energies of allylation span only about 21 kcal/mol. A good linear correlation is found between $\Delta\Delta E^{\ddagger}$ and the activation energy of hydrolysis. That is, a higher activation energy of hydrolysis corresponds to a higher kinetic preference toward allylation. On the other hand,

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[43] The Lewis acidity of allylborane, allylsilane, and enolate−tin was shown to play an important role carbonyl addition. See ref 30b,h and: (a) Brown, H. C.; Racherla, U. S.; Pellechia, P. J. *J. Org. Chem.* **1990**, *55*, 1868. (b) Yasuda, M.; Chiba, K.; Baba, A. *J. Am. Chem. Soc.* **2000**, *122*, 7549.

[44] Hydrophobic effects on reactions in water: (a) Breslow, R. *Acc. Chem. Res.* **2004**, *37*, 471. (b) Breslow, R. *Acc. Chem. Res.* **1991**, *24*, 159. (c) Gajewski, J. J. *Acc. Chem. Res.* **1997**, *30*, 219. (d) Pirrung, M. C.; Sarma, K. D.; *J. Am. Chem. Soc.* **2004**, *126*, 444. (e) Biscoe, M. R.; Breslow, R. *J. Am. Chem. Soc.* **2003**, *125*, 12718. (f) Wurz, R. P.; Charette, A. B. *Org. Lett.* **2002**, *4*, 4531. (g) Kita, Y.; Nambu, H.; Ramesh, N. G.; Anilkumar, G.; Matsugi, M. *Org. Lett.* **2001**, *3*, 1157. (h) Meijer, A.; Otto, S.; Engberts, J. B. F. N. *J. Org. Chem.* **1998**, *63*, 8989.

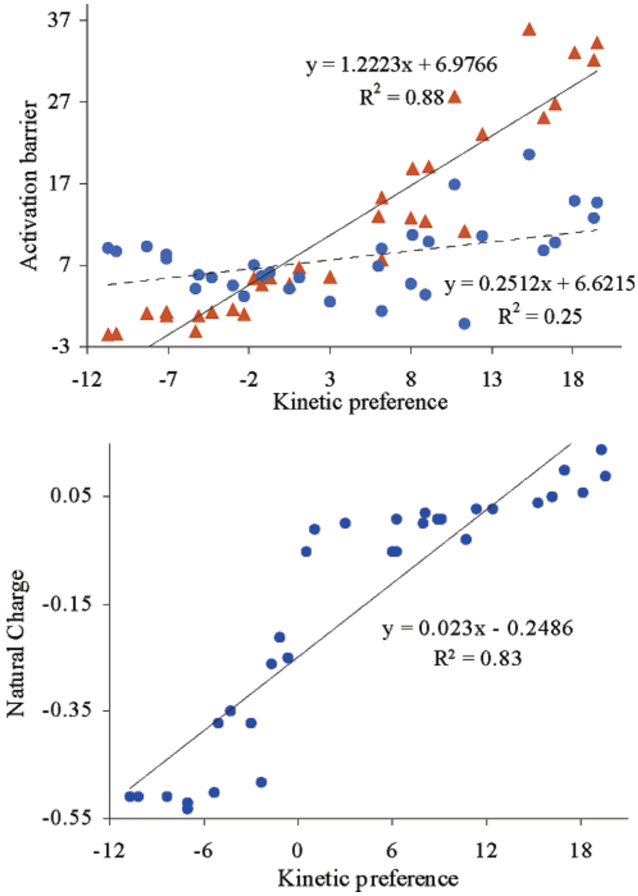

Figure 4. Plots of correlations of the calculated kinetic preference ($\Delta\Delta E^{\ddagger}$) against the activation barriers for hydrolysis (orange triangles) and allylation (blue circles) (top) and against calculated natural charges of $C_{\gamma}H_2$ of allylmetals (bottom).

the correlation between $\Delta\Delta E^{\ddagger}$ and the activation energy of allylation is not good. It should be pointed out that the activation energies for the allylation reactions are calculated with respect to the water-complexed allylmetals; that is, the carbonyl compound has to replace water in the water complex before allylation. Thus, the calculated activation energies of allylation for the (π-allyl)metal complexes are overestimated. Nevertheless, it can be concluded that the sharper variation in the reactivity of hydrolysis is the key determinant for the intrinsic kinetic preference of allylmetals. A fairly good linear correlation (R^2= 0.83) between the calculated intrinsic kinetic preference ($\Delta\Delta E^{\ddagger}$) and the nucleophilicity (in terms of natural charges at the $C_{\gamma}H_2$) is also found (Figure 4b).[45] Therefore, in the following analysis we will mainly focus on the activation energies of hydrolysis by allylmetals.

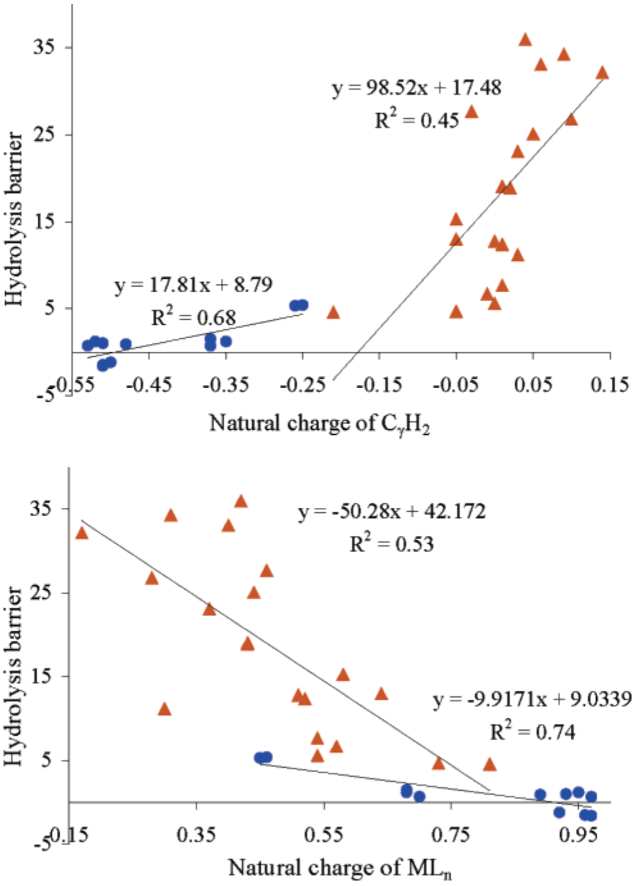

Figure 5. Plots of correlation between the calculated activation energy of hydrolysis against calculated natural charge of $C_{\gamma}H_2$ of allylmetals (top) and against the calculated natural charge of ML_n of allylmetals (bottom). Blue circles indicate (π-allyl)metals, and orange triangles denote (σ-allyl)metals.

Correlation between Reactivity and Nucleophilicity or C−M Bond Polarity. As pointed out earlier, the trend of reactivity of hydrolysis of allylmetals was qualitatively rationalized by the HSAB principle[28] or the C−M bond polarities of the allylmetals.[29] Figure 5 (top) shows the plot of the calculated activation energies for hydrolysis against the calculated natural charges at the $C_{\gamma}H_2$. The π-complexes and σ-complexes apparently display very different properties. For the π-complexes, the reactivities of hydrolysis and allylation roughly fall on a line with a small slope. That is, the reactivities of these π-complexes are related to but not very sensitive to the charges on the $C_{\gamma}H_2$ center or the nucleophilicity of these allylmetals. For the σ-complexes, the variation of charge on $C_{\gamma}H_2$ is less significant (−0.21 to +0.14) but the variation in the activation energy of hydrolysis is significant. The points are more spread, so that there is not a good correlation between the calculated reactivities and the calculated charge on the C_{γ} center (or nucleophilicity).

The polarity of the C−M bond can be approximately represented by the positive charge on the metal center (ML_n). Figure 5 (bottom) is the plot of the calculated activation energy of hydrolysis against the charge on ML_n. Again, the reactivity of hydrolysis of π-complexes is not very sensitive to the charge on ML_n, while the reactivity of σ-complexes does not correlate well with the charge on ML_n. Therefore, polarity of the C−M bond does not fully account for the reactivity of hydrolysis. For example, allyl−BeBr and −MgBr are much more polar than allyl−Ga, −In, and −Tl. However, the former are less reactive than the latter. Allyl−ZnBr and −CaBr are also much more polarized than allyl−SiBr, −GeBr, −SnBr, and −PbBr. Again, the former are much less reactive than the latter. Allyl−BBr_2 is much less polar

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[45] A fairly good correlation (R^2 = 0.80) between the calculated intrinsic kinetic preference and the polarity of the C−M bond (in terms of natural charge at ML_n) of the allylmetals is also found (see Figure S4 (Supporting Information)).

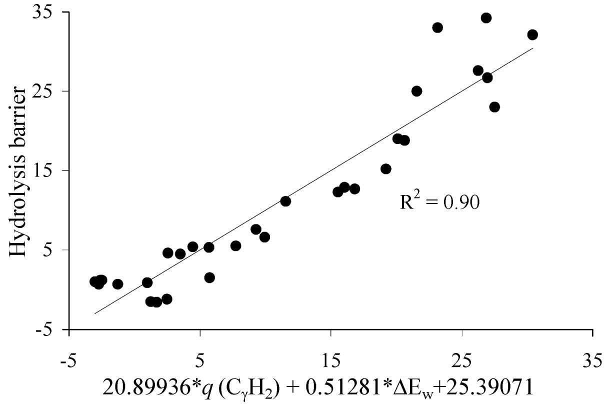

Figure 6. Plot of the correlation between the activation energy of hydrolysis and a combination of the calculated natural charge of $C_\gamma H_2$ and hydrolysis reaction energy for all allylmetals except allyl−$SiBr_3$.

than allyl−$GaBr_2$ and −$InBr_2$, but it is more reactive than the latter.

It is noted that the calculated reaction energies (ΔE_w) of these hydrolysis reactions vary significantly (Table 1). Those reactive allylmetals have large negative reaction energies, while those less reactive allylmetals have much smaller negative reaction energies. Some reaction products are even less stable than the water complexes (e.g. HgBr, $InBr_2$, $TlBr_2$, $PbBr_3$, $SbBr_3Me$, $BiBr_3Me$). It is thus expected that thermodynamic driving forces also play an important role in determining the reactivity of hydrolysis. Indeed, when the calculated activation energy of hydrolysis is plotted against a linear combination of calculated negative charge on the $C_\gamma H_2$ center and the hydrolysis reaction energy, a good correlation ($R^2 = 0.90$) is obtained, as shown in Figure 6. A similarly good correlation ($R^2 = 0.89$) is also found if the charge on the $C_\gamma H_2$ is replaced by the charge on ML_n (see Figure S6a in the Supporting Information). Although it is difficult to apply the Marcus theory in the current study, these analyses do provide a qualitative understanding of the reactivity of hydrolysis of allylmetals. That is, the nucleophilicity (or polarity) of the allylmetals and the reaction driving force of the hydrolysis both contribute significantly to the barrier of hydrolysis.[46]

Origin of the Intrinsic Kinetic Preference. Shown in Figure 7 are plots of calculated activation energies of hydrolysis and intrinsic kinetic preference against the distance of the forming H- - -C bond in the hydrolysis transition structure. Both plots display good linear correlations. Thus, the later the hydrolysis transition structure (the shorter the H- - -C bond distance), the higher the activation energy of hydrolysis and the greater the kinetic preference for allylation over hydrolysis. On the other hand, very early transition structures of hydrolysis correspond to a faster hydrolysis over allylation.[46]

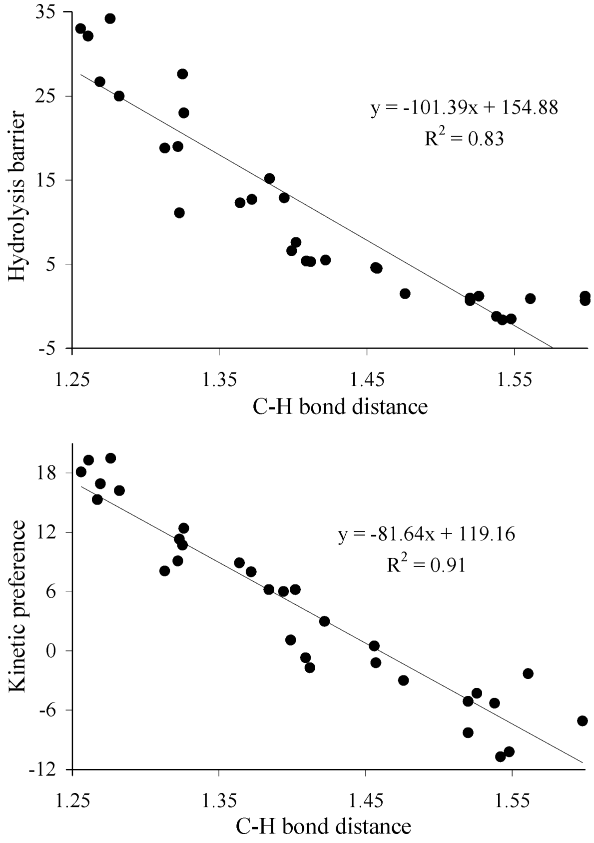

Figure 7. Plots of correlations between the hydrolysis barrier and the forming C- -H bond distances in the hydrolysis transition structures (top) and calculated intrinsic kinetic preferences and the forming C- -H bond distances in the hydrolysis transition structures (bottom).

It is important to note that the allylation process is thermodynamically more favorable than the hydrolysis process. A rough estimation based on bond energies gives a 17 kcal/mol thermodynamic preference for allylation of formaldehyde over hydrolysis of allylmetal, assuming that M−OH and M−OC_{allyl} bonds have similar bond energies.[47] The calculation results shown in Table 1 indicate that the calculated $\Delta\Delta E = \Delta E_w - \Delta E_{C=O}$ values are in the range 9−17 kcal/mol (Table 1). The thermodynamic preference for allylation over hydrolysis is somewhat independent of the polarity of the C−M bond. The hydrolysis has to break a very strong H−O bond (119 kcal/mol), while allylation breaks a weaker C=O π-bond (90 kcal/mol). According to the Hammond postulate,[48] allylation with a larger driving force has an earlier transition structure than hydrolysis (Scheme 2). This is in line with our calculations for all metals, except for the case of calcium (Figures 1−3). For very reactive allylmetals, mainly π-complexes, they have very early allylation and hydrolysis transition structures (i.e. insignificant π(C=O) and σ(O−H) bond breaking) and both reactions are quite exothermic (Scheme 2a). The effect of nucleophilicity of allylmetals overwhelms the thermodynamic preference. Thus, charge-controlled hydrolysis becomes more favorable over allylation for the (π-allyl)metals (more negative $\Delta\Delta E^\ddagger$), because of a favorable electrostatic interaction between the electron-rich $C_\gamma H_2$ center and the highly polarized water O−H bond. As the reactions become progressively

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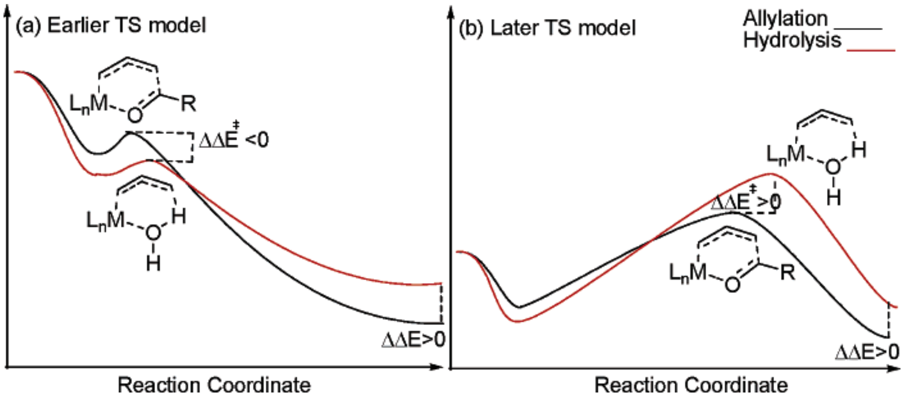
(46) The calculated reactivity of allylation does not correlate well with the linear combination of the charge on the $C_\gamma H_2$ and reaction energy. The reactivity is also influenced by the acidity of the metal. When the three factors are considered, a much better correlation is found for allylations of (σ-allyl)metals. For details see Figures S5 and S6 in the Supporting Information.

(47) $\Delta\Delta H = \Delta H_{H_2O} - \Delta H_{H_2CO} \approx \Delta H_{\sigma(HO-H)} - \Delta H_{\sigma(H-Call)} - \Delta H_{\pi(C=O)} + \Delta H_{\sigma(C-Call)} = 119 - 86 - 90 + 74$ kcal/mol = 17 kcal/mol. Bond energies are taken from: Laudon, G. M. *Organic Chemistry,* 3rd ed.; Benjamin/Cummings: New York.

(48) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, 77, 334.

Scheme 2. Energetic Diagram for Hydrolysis and Allylation Reactions



later (Scheme 2b), the large O−H bond breaking significantly increases the activation energy of hydrolysis, and the influence of thermodynamic preference on the transition structures become more pronounced. Thus, allylation becomes more kinetically favorable than hydrolysis (more positive $\Delta\Delta E^{\ddagger}$).

Low Valence vs High Valence. One interesting finding of this study is that monovalent group IIIA and divalent group IVA metals are all quite reactive for both hydrolysis and allylation. On the other hand, their corresponding high-valent allyl complexes display much lower reactivities toward hydrolysis but show moderate reactivities toward allylation. Thus, the latter are potential candidates as allylation agents in aqueous media. The calculations indicate that the low-valent species are more polarized and the allyl is more nucleophilic. A more important fact is that the reactions of allyl complexes of low-valent metals are significantly more exothermic than those of corresponding high-valent metal complexes by over 20 kcal/mol (except for Si). Both factors make the high-valent metal complexes much less reactive toward hydrolysis. Nevertheless, we cannot rule out the existence of the low-valent allylmetal complexes in metal-mediated allylations in aqueous media, because of the absence of the solvent effect in the calculations (hydrophobic effect). In addition, a single-electron-transfer mechanism might operate in these low-valent allylmetals.

Summary

In conclusion, the current simple model calculations provide a qualitative explanation and semiquantitative trend of the intrinsic kinetic preference of 32 discrete allylmetals. Allyl complexes of groups IA and IIA and low-valent group IIIA and IVA metals are in π-complexes or reactive σ-complexes. They show high reactivities toward hydrolysis. Group IIB, trivalent group IIIA, tetravalent group IVA, and both tri- and pentavalent group VA metals form σ-complexes with the allyl anion. These allylmetals are less reactive with water than with carbonyl compounds. The calculated kinetic preference is generally consistent with the experimental observations on various metal-mediated allylation reactions in aqueous media. The calculations also suggest that more allylmetal complexes may prefer allylation of carbonyl compounds and more discrete allylmetals may be intermediates responsible for metal-mediated allylation in water than have been observed experimentally thus far. The calculated intrinsic kinetic preference of allylation over hydrolysis is found to correlate well with the reactivity of hydrolysis. We found that, besides the nucleophilicity of the allylmetal complexes, the thermodynamic driving force is also an important factor for the reactivity of hydrolysis. In addition, there is a large thermodynamic preference for allylation over hydrolysis for all the allylmetals, because the hydrolysis has to break a strong O−H bond. Thus, the preference for allylation is parallel to the degree of strong H−O bond breaking in the hydrolysis transition structure. It is noted that the organometallic reaction in the aqueous solution is more complicated. The effects of ligand, explicit water solvent, and aggregation on the intrinsic kinetic preference have not been included in the current study. These effects will be addressed in our further investigation.

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Supporting Information Available: Figures S1−S7 and listings of Cartesian coordinates for allylmetals, allylmetal water complexes, and allylation and hydrolysis transition structures by the MP2 method. This material is available free of charge via the Internet at http://pubs.acs.org.

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