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Gas-Phase Reactions

Molecular Salt Effects in the Gas Phase: Tuning the Kinetic Basicity of $[HCCLiCl]^-$ and $[HCCMgCl_2]^-$ by LiCl and $MgCl_2$**

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Dedicated to Professor J. Barrie Peel

Abstract: *A combination of gas-phase ion–molecule reaction experiments and theoretical kinetic modeling is used to examine how a salt can influence the kinetic basicity of organometallates reacting with water. $[HC{\equiv}CLiCl]^-$ reacts with water more rapidly than $[HC{\equiv}CMgCl_2]^-$, consistent with the higher reactivity of organolithium versus organomagnesium reagents. Addition of LiCl to $[HC{\equiv}CLiCl]^-$ or $[HC{\equiv}CMgCl_2]^-$ enhances their reactivity towards water by a factor of about 2, while addition of $MgCl_2$ to $[HC{\equiv}CMgCl_2]^-$ enhances its reactivity by a factor of about 4. Ab initio calculations coupled with master equation/RRKM theory kinetic modeling show that these reactions proceed via a mechanism involving formation of a water adduct followed by rearrangement, proton transfer, and acetylene elimination as either discrete or concerted steps. Both the energy and entropy requirements for these elementary steps need to be considered in order to explain the observed kinetics.*

Heterobimetallate complexes that contain one or more of the alkali metals date back to at least 1858, when Wanklyn reported the synthesis of $NaZnEt_3$.[1] Some classes of these complexes have been used in organic synthesis for decades (e.g. organocuprates[2,3]). The design of new heterobimetallate complexes continues to be of great interest as a paradigm for the concept that "the sum is greater than the parts".[4] Indeed, in the quest for more reactive or selective reagents to transform organic substrates, readily available organometallic reagents such as organolithiums, organomagnesiums or organozincs have been combined with various additives (e.g. ligands, inorganic salts such as LiCl, or organometallic bases). Examples of new reagents developed include Knochel's "Turbo-Grignards", formulated as "RMgCl·LiCl"[5] and the bases "Bu_4MgLi_2",[6] "LiZn*t*Bu_2(TMP)",[7] and [(TMEDA)·Na(μ-TMP)(μ-*t*Bu)Zn(*t*Bu)], (with TMP = 2,2,6,6-tetramethylpiperidide).[8] The latter complex, which zincates benzene, can be tamed by replacing *t*Bu with CH_2SiMe_3 to mildly zincate cyclic ethers, a remarkable achievement since they normally undergo base-induced ring-opening reactions.[9] A key challenge though in developing robust protocols for the use of bimetallate reagents is that "the true nature of those mixed-reagents… is generally unknown and they are frequently treated as black-box mixtures".[10,11]

Mass-spectrometry-based methods can provide information on the structure[12] and reactivity[13] of organometallates. Since the stoichiometry of ions can be determined from their m/z values and isotopic signatures, information on the aggregation states can readily be gleaned, as has been demonstrated in reports on the electrospray ionization mass spectra of organocuprates[12a–e] and organozincates.[12f–h] By studying the gas-phase reactions of mass-selected organometallic ions, it is possible to directly probe the intrinsic role of the metal, R group, ligand and cluster size on reactivity.[13,14] We previously showed that the addition of a second $MgCl_2$ enhances the kinetic basicity of $[RC{\equiv}CMgCl_2]^-$.[13d] Here we use a combination of experimental kinetic measurements and theoretical kinetic modeling to explore molecular salt effects of LiCl and $MgCl_2$ by comparing the gas-phase reactivity of water towards $[HC{\equiv}CLiCl]^-$, $[HC{\equiv}CMgCl_2]^-$, $[HC{\equiv}CLi_2Cl_2]^-$, $[HC{\equiv}CMgLiCl_3]^-$, and $[HC{\equiv}CMg_2Cl_4]^-$.

Electrospray ionization (ESI) in combination with multistage mass spectrometry (MS^n) experiments was used to: 1) generate the organometallates $[HC{\equiv}CMg_xLi_yCl_z]^-$ by collision-induced dissociation (CID) of the carboxylate precursors, $[HC{\equiv}CCO_2Mg_xLi_yCl_z]^-$ and 2) study the ion–molecule reactions of the mass-selected organometallates with water. The desired decarboxylation reaction [Eq. (1a)],

$$[HC{\equiv}CCO_2Mg_xLi_yCl_z]- \rightarrow [HC{\equiv}CMg_xLi_yCl_z]- + CO_2 \qquad (1a)$$

although dominant,[13d,g] was found to be in competition with cluster fragmentation reactions in the case of the binuclear clusters [$x=0$, $y=2$ and $z=2$, $x=1$, $y=1$ and $z=3$; $x=2$, $y=0$ and $z=4$; Figures S1–S5 in the Supporting Information and Eqs. (1b)–(1d)].

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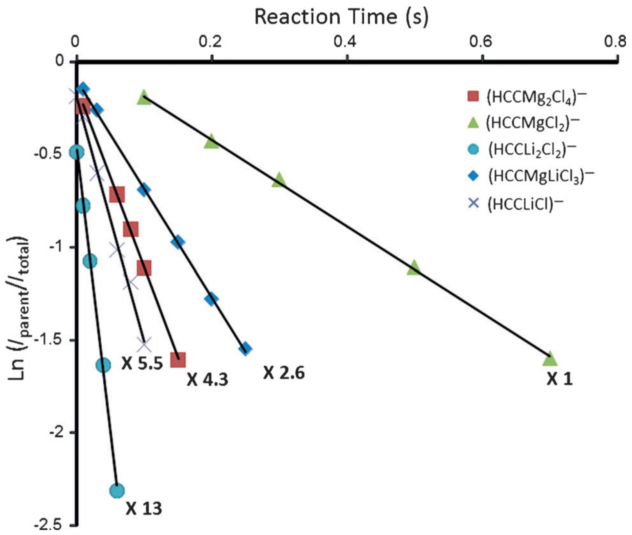

Figure 1. Pseudo-first-order kinetic plots for the reaction of the organometallates, [HC≡CCO$_2$Mg$_x$Li$_y$Cl$_z$]$^-$, with water in the LTQ mass spectrometer (ca. 3×10^9 molecules cm^{-3}). The rates, relative to [HC≡CMgCl$_2$]$^-$, are represented next to each plot.

Figure 1 presents reaction rate data for ion–molecule reactions of the organometallate ions formed by Eq. (1a) with water (Figures S6–S10) where all of the complexes react via the acid–base reaction shown in Equation (2).[15]

$$[\mathrm{HC{\equiv}CMg}_x\mathrm{Li}_y\mathrm{Cl}_z]^- + \mathrm{H_2O} \rightarrow [\mathrm{HOMg}_x\mathrm{Li}_y\mathrm{Cl}_z]^- + \mathrm{HC{\equiv}CH} \qquad (2)$$

Table 1 shows that the rate coefficients for the binuclear clusters are higher than their mononuclear counterparts.[13d] Hence, the addition of a molecule of LiCl to [HC≡CMgCl$_2$]$^-$ increases its rate by approximately 2.6 times, whereas the addition of MgCl$_2$ to that same ion increases the rate by approximately 4.3 times. In a similar fashion, the addition of LiCl to [HC≡CLiCl]$^-$ increases its rate by approximately 2.4 times. In contrast, the addition of MgCl$_2$ to this ion seems to reduce the reaction rate by a factor of approximately 2.1 (a "salt effect" of 0.5).

Table 1: Kinetics associated with the ion–molecule reactions of organometallates [HC≡CMg$_x$Li$_y$Cl$_z$]$^-$ with water. The salt effect is relative to the mononuclear species.

Reactant anion	k [$\times10^{-10}$][a]		Efficiency[b]		Salt effect[c]
	Expt.	ME	Expt.	ME	Expt.
[HC≡CMgCl$_2$]$^{-}$[d]	0.53	0.2	3.0%	0.9%	–
[HC≡CMgLiCl$_3$]$^-$	1.36	1.2	7.8%	7%	+LiCl ×2.6[e]
[HC≡CMg$_2$Cl$_4$]$^{-}$[d]	2.27	6.0	13.1%	34%	+MgCl$_2$ ×4.3
[HC≡CLiCl]$^-$	3.07	10.8	16.4%	58%	–
[HC≡CLi$_2$Cl$_2$]$^-$	7.00	11.2	39.1%	62%	+LiCl ×2.4

[a] Rate coefficients in cm^3 molecule^{-1} s^{-1} for the reaction with water from experiment and from master equation (ME) simulations with G3SX energies. [b] Reaction efficiency = $k_{\mathrm{expt}}/k_{\mathrm{ADO}}\times100$, where k_{ADO} is the ion–molecule collision rate constant obtained from the average-dipole orientation (ADO) theory [16a], calculated using the Colrate program [16b]. [c] The molecular salt effect is defined as k(expt.) for the binuclear metallate divided by k(expt.) for the corresponding mononuclear metallate. [d] The rates are slightly different to those reported in Ref. [13d] (see Ref. [15]). [e] The salt effect for the addition of MgCl$_2$ to [HC≡CLiCl]$^-$ is ×0.5.

To gain insight into the mechanism of these acid–base reactions, ab initio energy diagrams were developed for the reaction of water with each of the organometallate ions. Results at the G3SX level of theory are presented in Figure 2 (M06-2X data is provided in Figure S11). Transition-state structures are illustrated in Figure 3. Each of the reactions begins with barrierless H$_2$O addition to form a reaction adduct in which water is bound to a metal site(s). In the case of [HC≡CLiCl]$^-$ and [HC≡CMgLiCl$_3$]$^-$ this adduct can directly undergo an intramolecular proton transfer to produce a hydroxide that is now complexed to acetylene (**TS2** in Figure 3). For the other systems, however, an additional reaction step is required in which the acetylide moiety undergoes a change in bonding mode from a σ M−C≡CH bond to a π M(C≡CH) complex proceeding via **TS1**. This

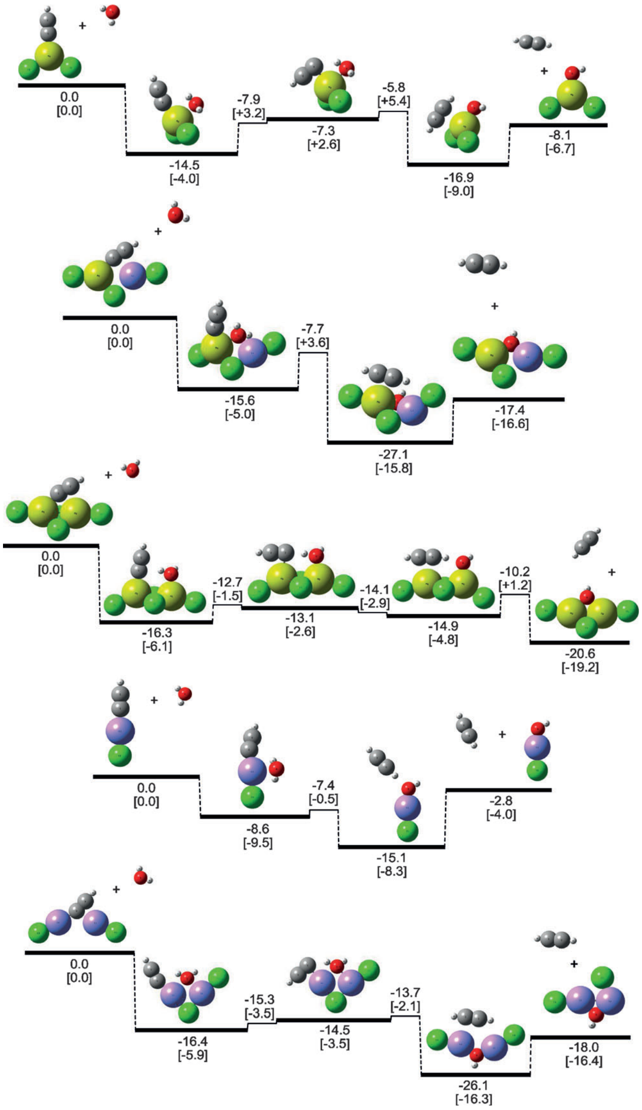

Figure 2. Energy diagrams for reaction of (from top to bottom) i) 1[HC≡CMgCl$_2$]$^-$, ii) [HC≡CMgLiCl$_3$]$^-$, iii) [HC≡CMg$_2$Cl$_4$]$^-$, iv) [HC≡CLiCl]$^-$, and iv) [HC≡CLi$_2$Cl$_2$]$^-$ ions with water. Energies are G3SX theory 298 K enthalpies/[free energies] in kcal mol^{-1}.

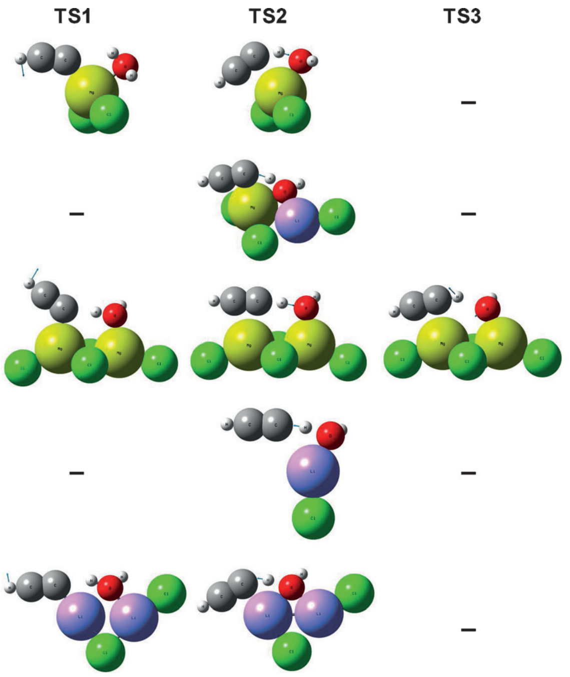

Figure 3. Optimized transition states in the reactions of water with the organometallates, $[HC{\equiv}CMg_xLi_yCl_z]^-$. Calculated at the M06-2X/6-31G(2df,p) level of theory. Imaginary frequency displacement vectors illustrated.

activating step facilitates proton transfer from water to the HCC moiety. Following proton transfer, acetylene is typically lost in a final barrierless step to yield the observed reaction products. The exception is the $[HC{\equiv}CMg_2Cl_4]^- + H_2O$ system, where a significant barrier to eliminate HCCH (**TS3**) exists, which arises because of the exothermic formation of the $[HOMg_2Cl_4]^-$ anion.

A complex interplay of factors is found to control the reactivity of the metallate ions with water. Typically, proton transfer (**TS2**) provides the largest energetic barrier to reaction, although for $[HCCMg_2Cl_4]^-$ and $[HC{\equiv}CLiCl]^-$ the controlling transition state appears to be on the exit channel for acetylene elimination. However, in terms of free energy the largest barrier to reaction in the $[HC{\equiv}CLiCl]^-$ system actually corresponds to **TS2**, indicating an entropically controlled process. These effects are illustrated in Figure 4, where the highest overall barrier to reaction (in terms of both enthalpy and free energy), relative to the reactants, is plotted for each system against the experimentally determined value of ln*k*. When enthalpy alone is considered a reasonable linear correlation between barrier height and ln*k* occurs, except for the outlying $[HC{\equiv}CLiCl]^-$ reaction. When entropic effects are incorporated, this outlier can be brought into better agreement, resulting in a satisfying relationship where decreasing barrier heights correspond to increasing reactivity. On the other hand, if only the enthalpy requirement for the proton transfer is considered, no real trend can be discerned between barrier height and reactivity (see Figure S12).

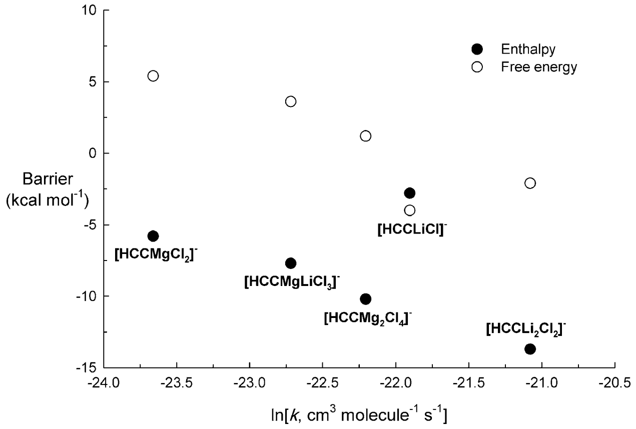

Figure 4. Relationship between highest barrier heights (298 K enthalpy and free energy) and experimentally determined ln*k* for hydrolysis of the organometallate ions. Energies calculated at the G3SX level of theory.

The results presented in Figure 4 provide qualitative support for the proposed reaction mechanisms. They do not, however, provide a direct comparison because of the multi-step nature of these reactions, where multiple barriers are providing an impediment to hydrolysis. Another deficit of this analysis is that we assume the ions to be thermalized (at 298 K), which is particularly significant when evaluating the entropic contribution to the free energy. In reality, however, the bimolecular reactions are chemically activated processes in which the chemical reaction is coupled with vibrational relaxation. These effects can explicitly be accounted for by coupling microcanonical rate coefficients from RRKM theory with time-dependent master equation simulations of the coupled chemical and vibrational relaxation problem under conditions representative of the ion trap.[23] Rate coefficients calculated purely from theory in this manner are provided in Table 1, along with reaction efficiencies determined relative to the ion–molecule collision rates. Overall there is reasonable agreement between the experimental and theoretical rate coefficients, with deviations typically within around a factor of two. Pleasingly, the reactivity order is also the same as that determined experimentally. These results provide further support for the theoretically postulated reaction mechanisms. The trend for theory to overestimate the rate of reaction (except for the slowest two reagents using the G3SX energies) may arise from one or a combination of factors including: the well-documented uncertainties in the theoretically determined energies; systematic errors in the measured water concentration; the assumption that the temperature of the ions in the ion trap are at 298 K.[17c]

The theoretical calculations presented above allow us to now explain the differing kinetic basicities of the magnesium and lithium metallate ions, as well as their molecular salt effects. For the mono-metallic systems, the significantly increased reactivity of $[HC{\equiv}CLiCl]^-$ versus $[HC{\equiv}CMgCl_2]^-$ is the result of a much-reduced entropy penalty for hydration of the former, effectively due to the large entropy loss upon complexation of the linear $[HC{\equiv}CLiCl]^-$ ion with water. For both monometallic ions, addition of an LiCl salt molecule increases reactivity by providing a second metal center upon which to conduct the reaction, resulting in less-strained transition states from which to undergo proton transfer

(**TS2**), significantly reducing the controlling barrier to reaction. Upon the addition of $MgCl_2$, a similar effect is observed for $[HC{\equiv}CMgCl_2]^-$, however, in the case of $[HC{\equiv}CLiCl]^-$ a reduction in reactivity is observed (Table 1, salt effect about 0.5). This result can be explained by the increase in the free-energy barrier upon the addition of the salt to $[HC{\equiv}CLiCl]^-$ (Figure 2). In the case of LiCl addition to $[HC{\equiv}CLiCl]^-$ this effect is offset somewhat by the greater entropy penalty discussed above for the 3D versus 2D (i.e., non-linear vs. linear) structure of the reactant. For LiCl addition to $[HC{\equiv}CMgCl_2]^-$ the mismatched radii of the Mg and Li metal centers, to which the respective acetylene and hydroxyl ligands are coordinated, works to increase the barrier height of the controlling transition state over that found in the matched bimetallic systems. The addition of $MgCl_2$ to $[HC{\equiv}CMgCl_2]^-$ then exhibits the largest molecular salt effect, and the lowest barrier for intramolecular proton transfer. In this instance, reduction of this barrier is so significant that the ultimate elimination of acetylene becomes the rate-controlling step, limiting the magnitude of the salt effect.

In conclusion, this work provides one of the first examples of salt effects on the reactivity of organometallic reagents in the gas phase and provides mechanistic insights into how the addition of a single salt molecule can enhance reactivity. In the condensed phase, the adduct is expected to be quenched with the solvent, however the barrier heights for hydrolysis are sufficiently low that the reaction should proceed by thermal activation even at room temperature, which could produce even more pronounced salt effects. Further work is now underway to develop a gas-phase kinetic basicity scale for organometallates.

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