Hydration of Monomeric Metaphosphate Anion in the Gas Phase

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Abstract: Thermochemical data for the clustering of water molecules onto the monomeric metaphosphate anion PO_3^- in the gas phase are derived from a study by high-pressure mass spectrometry. Experimental details are described, and the enthalpy and entropy changes for the successive addition of the first four water (D_2O) molecules are reported. The results indicate that PO_3^- undergoes simple adduct formation up to the second hydration step, but the third hydration step involves an isomerization of the ion–water cluster into the dihydrate of the dihydrogen orthophosphate anion.

Introduction

Interest in the monomeric metaphosphate anion PO_3^- stems from its proposed intermediary role in phosphorylation and the hydrolysis of phosphate esters[1] and generally from the importance of phosphates to the chemistry of biological systems.[2] Interest in the combustion of phosphorus and phosphorus compounds as impurities in coal-fired magnetohydrodynamic generators has also motivated study of the PO_3^- anion.[3–5] Consequently, along with a basic interest in the bonding and electronic structure of phosphorus compounds, PO_3^- has been the subject of several quantum mechanical treatments.[5–9] In particular, PO_3^- affords valuable comparisons with its nitrogen congener NO_3^-. A recent ab initio study[6] of PO_3^- with assumed D_{3h} symmetry indicates that the P–O bond is highly polar with little double-bond character.

The metaphosphate anion has been shown to be relatively stable and unreactive in the gas phase.[9] However, identification of the species in aqueous solution has been elusive, and there is considerable debate over whether PO_3^- can exist as a free entity in water.[11] In aqueous solution, the free energy change for conversion of PO_3^- into the dihydrogen orthophosphate anion ($HO)_2PO_2^-$ has been determined, by indirect methods, to be −113 kJ/mol.[12]

Investigation of the properties of clusters is a convenient method to bridge the states of matter.[13] Therefore, in order to attempt to understand the apparent discrepancy in the behavior of PO_3^- in the gas phase versus the aqueous phase, we have examined the gas-phase hydration of the ion. Furthermore, study of the clustering of water onto PO_3^- complements our earlier studies of other oxyanions.[14,15] In the present paper, we describe the experimental details and report the measured changes in enthalpy ($\Delta H°_{n,n+1}$),

Table I. Standard Enthalpy, Entropy, and Free Changes for the Successive Addition of Water to PO_3^- in the Gas Phase, Reaction 1[a]

$(n,n+1)$	$-\Delta H°_{n,n+1}$ (kJ/mol)	$-\Delta S°_{n,n+1}$ (J/K·mol)	$-\Delta G°_{n,n+1}$ (kJ/mol)
$(0,1)$ H_2O	53.9 ± 1.4	93 ± 4	26.2
$(0,1)$ D_2O	52.6 ± 0.9	87 ± 2	26.7
$(1,2)$ D_2O	47.8 ± 1.0	92 ± 3	20.4
$(2,3)$ D_2O	68.2 ± 1.2	152 ± 4	22.9
$(3,4)$ D_2O	46.1 ± 1.8	94 ± 5	18.1

[a] Standard state is 1 atm at 298 K. The values for the enthalpy and entropy changes are assumed to be essentially independent of temperature over the experimental temperature range and down to 298 K. ΔH and ΔG are given to the nearest 0.1 kJ/mol to reduce rounding errors when converting to units of kilocalories per mole.

entropy ($\Delta S°_{n,n+1}$), and free energy ($\Delta G°_{n,n+1}$) for the stepwise $(n,n+1)$ hydration gas-phase reactions, nominally expressed as

$$PO_3^- \cdot nH_2O + H_2O \rightleftharpoons PO_3^- \cdot (n+1)H_2O \qquad (1)$$
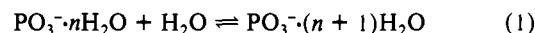
bearing in mind that $PO_3^- \cdot H_2O$ is mass spectrometrically indistinguishable from $(HO)_2PO_2^-$ and hydration may lead to the orthophosphate anion.

Experimental Section

The experimental apparatus and procedure, used to measure the equilibrium constants for reaction 1 and to obtain the thermodynamic quantities, have been described in detail elsewhere.[14,16] Briefly, ions are produced and thermalized in a reaction cell where the pressure is maintained sufficiently high to attain equilibrium of the clustering reaction of interest. This requires a judicious selection of conditions since the pressure must be sufficiently low to avoid an adiabatic expansion leading to additional clustering as the ion clusters exit the reaction cell into vacuum. Ion sampling is accomplished through a 75-μm-diameter orifice into the high-vacuum region of the quadrupole mass spectrometer, where the ions are then mass analyzed and counted. From the measured ion intensities and known partial pressure of water vapor in the cell, the equilibrium constant $K_{n,n+1}$ is determined at the measured temperature of the thermally controlled region of the reaction chamber by using common established assumptions.[16]

As in our earlier work,[14,15] negative ion formation is initiated by the emission of electrons from the passage of current through a $BaZrO_3$-coated filament. To produce gas-phase PO_3^- ions, a small amount (50–100 μL) of concentrated phosphoric acid (made by adding H_2O or D_2O to P_2O_5) is coated onto a surface (the repeller in Figure 1 of ref 16) that is near the filament and heated by the filament. With dry CO_2, N_2O, or O_2 serving as the buffer gas in the reaction cell, this source produces predominantly PO_3^- ($m/z = 79$). The measured isotopic abundances (99.15, 0.13, and 0.72% for $m/z = 79$, 80, and 81, respectively) are in good agreement with the expected natural isotopic abundances. Minor ions at m/z corresponding to CO_3^- (up to 5% of the ion intensity) and PO_2^-, O_2^-, and CO_4^- (each about 1% of the ion intensity) are also observed. With cooling of the reaction cell (to about room temperature), small amounts of the first cluster ions $PO_3^- \cdot H_3PO_4$, $PO_3^- \cdot H_2O$, $PO_3^- \cdot HCl$, and $PO_3^- \cdot SO_2$ (or the deuterated species) are also observed; the presence of the latter two is particularly dependent on the

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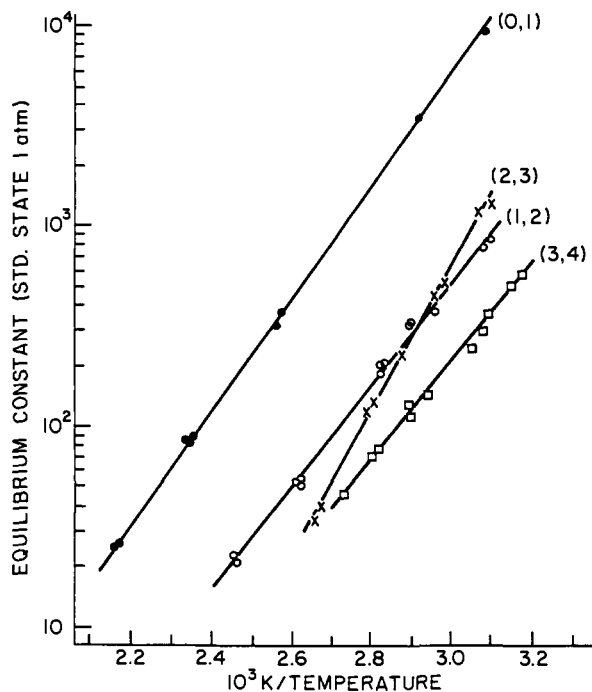
Figure 1. van't Hoff plots of equilibrium constants for the nominal gas-phase reactions $PO_3^- \cdot nD_2O + D_2O \rightleftharpoons PO_3^- \cdot (n + 1)D_2O$. Each is labeled by $(n, n + 1)$.

recent history of the apparatus. With the application of phosphoric acid, the source produces a strong PO_3^- signal over the course of 1–2 weeks before requiring reapplication.

Since phosphoric acid is hygroscopic, the usual procedure of bleeding a gas mixture containing water vapor and buffer gas from a premixed reservoir is avoided. For the present experiments, water vapor is added directly to the reaction chamber where the vapor can equilibrate with the phosphoric acid. The water vapor pressure is then measured with an MKS Baratron, whereafter the water vapor is then diluted, if necessary, by a buffer gas (usually O_2) to achieve an operational total chamber pressure. Data are obtained over a range of 5–100% water vapor with total pressures in the range of about 1–10 Torr. Often, however, for a given temperature and reaction, these ranges are more restricted (a factor of 2 or 3 instead of 1 order of magnitude) due to the experimental requirements for a valid measurement of the equilibrium constant.

Results and Discussion

van't Hoff plots (log K versus $1/T$) for each association step $(n, n + 1)$ of D_2O onto PO_3^- are shown in Figure 1. The thermodynamic quantities are obtained from linear least-squares fits of the plots.[14] The enthalpy changes derived from the slopes and the entropy changes derived from zero (infinite temperature) intercepts of the van't Hoff plots are listed in Table I. Error limits indicate 1 standard deviation of the fit. These limits represent the random error. Because of possible sources of systematic errors, the overall uncertainty of the reported values is estimated to be about 2 kJ/mol for the enthalpy and free energy changes and about 10 J/K·mol for the entropy changes.

Values are given for deuterated water because HCO_3^- hydrates appear when lower temperatures and higher water vapor concentration are employed, and deuteration is required to displace the hydrated PO_3^- mass from the interfering ion peaks. The HCO_3^- ions result from the dissociative attachment of electrons to water and subsequent reactions with water and trace amounts of CO_2. The thermodynamic quantities for the first association step of H_2O onto PO_3^- were determined and are in close agreement with the values for the (0,1) reaction of D_2O onto PO_3^- as expected.

Quantum mechanical calculations suggest that the gas-phase reaction of PO_3^- with water to give the dihydrogen orthophosphate anion $(HO)_2PO_2^-$ is very exothermic. A semiempirical method[9] predicts 122 kJ/mol while an ab initio method[7] yields a value of 150 kJ/mol. The present experimental result is considerably less exothermic at about 54 kJ/mol. In fact, the experimental result

is consistent, when compared to gas-phase hydration of NO_3^-, with simple adduct formation, i.e., association leading to the product $PO_3^- \cdot H_2O$.[17] The small decrease in exothermicity for the (1,2) hydration step is also consistent with a simple clustering reaction.

A glance at Figure 1 readily demonstrates a peculiarity in the (2,3) hydration step. The van't Hoff plot for a series of stepwise clustering reactions typically appears as a sequence of regularly spaced lines with a progressively lessening slope from the first to the last clustering step. The crossing behavior of the (2,3) reaction step is highly unusual. The unusual feature of Figure 1, of course, is also reflected in the peculiar trend in the thermodynamic values listed in Table I. The common trend of decreasing $-\Delta H^\circ_{n,n+1}$ and $-\Delta G^\circ_{n,n+1}$ with increasing n is violated by the (2,3) step. The entropy change for this reaction is also notably different from the others. The mass peaks were carefully checked for the possibility of an underlying interfering ionic species. Substitution of H_2O for D_2O was found to shift the mass 139 (as well as the less abundant mass 142, $DCO_3^- \cdot 4D_2O$) to mass 133, confirming the presence of six hydrogen atoms in mass 139 as expected for $PO_3^- \cdot 3H_2O$. Examination of natural isotopic patterns also suggests that ions with interfering masses are not responsible for the peculiar behavior of the (2,3) hydration step.

The (2,3) reaction also exhibits another pecularity. Generally a small potential (a few tens of volts) is applied to a screened electrode (the top gate) between the ionizing filament and the entrance into the thermally controlled region of the reaction chamber. This potential improves the efficiency of directing ions into and through the reaction cell but also reduces the residence time of the ions in the thermally controlled region. In the vast majority of the ion clustering reactions that we have studied, the measured equilibrium constant for an association reaction is insensitive to the applied potential up to several tens of volts, above which the electrostatic field begins to impart significant translational energy to the ion, and therefore the ion is no longer thermal; thereupon, a concomitant reduction in the measured equilibrium constant is apparent. Unlike the other hydration steps in this study, and indeed most other studies performed in this laboratory, the apparent equilibrium constant for the (2,3) reaction shows a marked decrease as potentials above just a couple of volts are applied. A previous study[15,18] in this laboratory that exhibited such extreme sensitivity to the applied voltage on the top gate was that of the association of HNO_2 onto NO_2^-. In that case, the effect was attributed to the very low concentration of HNO_2 and consequently slow equilibration. The second association of HNO_2 onto NO_2^- was influenced only when applied potentials reached a few tens of volts. Typically if a clustering system shows a sensitivity to the voltage on the top gate, the (0,1) reaction is the most affected.[18,19] In the hydration of PO_3^-, the (2,3) step apparently equilibrates much more slowly than the other hydration steps examined in this study.

With the limitations on water vapor and total cell pressure, the (2,3) association step could achieve equilibration if the applied potential at the top gate is at most 1–2 V. The fact that equilibration is achieved is shown by varying total pressure and/or water vapor partial pressure to demonstrate the requisite independence of the equilibrium constant $K_{n,n+1}$ on all variables except temperature. Figure 2 illustrates the apparent $K_{2,3}$ versus total cell pressure (6.7% D_2O in O_2). From low pressure, equilibrium is approached with increasing pressure due to increase in the ion residence time and the concentrations of the clustering reactant and the stabilizing third body. From previous experience[18] the residence time in the reaction cell for small top gate potentials is in the neighborhood of 2 ms at 5 Torr, but the apparatus is not well suited for determination of rates and rate measurements were not attempted. With further increasing of pressure, clustering is enhanced as the ions exit the cell by collision with D_2O in the adiabatic expansion that develops at higher pressures. The actual

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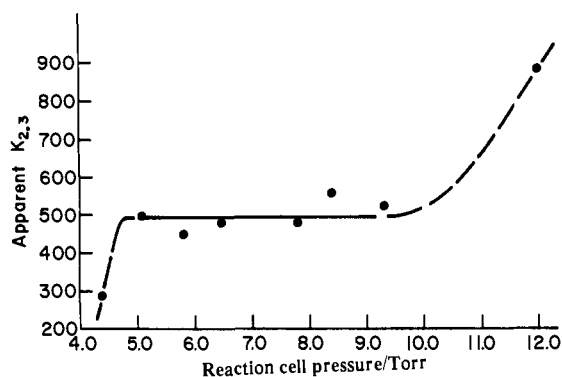
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Figure 2. Dependence of the apparent equilibrium constant $K_{2,3}$ for the (2,3) reaction on the reaction cell pressure consisting of 6.7% D_2O in O_2 at 333 K.

equilibrium constant is determined from the plateau between the two limits. If no plateau region exists, then an equilibrium constant cannot be determined.

Since the many applied tests indicate that equilibrium is attained in the study, the measured result for the (2,3) reaction suggests strongly that this reaction is not the simple clustering of another water (D_2O) molecule onto PO_3^-. In comparison to the initial hydration reactions, the (2,3) step is much more exothermic and exoergic than expected. A plausible explanation is that the PO_3^- hydrate isomerizes to $(DO)_2PO_2^-$ in the presence of three D_2O molecules.

$$PO_3^- \cdot 2D_2O + D_2O \rightarrow (DO)_2PO_2^- \cdot 2D_2O \qquad (2)$$

In the case that gas phase $(DO)_2PO_2^-$ is more stable than $PO_3^- \cdot D_2O$, the results imply that a kinetic barrier to isomerization is reduced by hydration of PO_3^- and that the barrier can be overcome at thermal energies with hydration by three D_2O molecules. However, this situation would seem to preclude the ability to equilibrate the hydration reactions, since the $(DO)_2PO_2^-$ hydrates, once formed, would be expected to equilibrate rapidly among themselves and draw ion intensity away from the less stable PO_3^- hydrates. Equilibration of the (1,2) reaction, however, seems to be unaffected by the presence of the products of reaction 2. Alternatively, if $(DO)_2PO_2^-$ is not as stable as $PO_3^- \cdot D_2O$, then the experimental results imply that $(DO)_2PO_2^-$ is more strongly solvated and that $(DO)_2PO_2^- \cdot nD_2O$ becomes more stable than $PO_3^- \cdot (n + 1)D_2O$ at $n \geq 2$. Equilibration of the hydration reactions is then possible if thermal energies exceed the isomerization barriers.

We may also consider other thermochemical constraints.[20] Deuteration has little effect, so our discussion will take $D_2PO_4^-$ to be equivalent to $H_2PO_4^-$. If we assume that the hydration energies of the reactant PO_3^- and the product $H_2PO_4^-$ in reaction 2 are similar, then the gas-phase heat of formation is given by (all species are gas phase unless indicated otherwise)

$$\Delta H_f^\circ[H_2PO_4^-] = \Delta H_f^\circ[PO_3^-] + \Delta H_f^\circ[H_2O] + \Delta H^\circ_{2,3} \qquad (3)$$

Furthermore, the gas phase acidity of H_3PO_4 is given by

$$\Delta H^\circ_{acid}[H_3PO_4] =$$
$$\Delta H_f^\circ[H_2PO_4^-] + \Delta H_f^\circ[H^+] - \Delta H_f^\circ[H_3PO_4] \qquad (4)$$

The heats of formation of H^+ and H_2O are well-known and are 1530 and −242 kJ/mol, respectively.[21] The value for $\Delta H^\circ_{2,3}$ is determined in the present work to be −68 kJ/mol (see Table I). The gas-phase heat of formation of H_3PO_4 is not known, but we will estimate it. For the liquid, $\Delta H_f^\circ[H_3PO_4] = -1250$ kJ/mol,[22] and we estimate the heat of vaporization from Trouton's rule. Trouton's rule is probably not very accurate for such a polar

hydrogen bonded liquid, particularly since boiling of the liquid at 486 K is accompanied with dehydration,[23] but the estimate of ΔH°_{vap} of about 40 kJ/mol is probably good to a couple of tens of kilojoules per mole. For $\Delta H_f^\circ(PO_3^-)$, Unkel and Freedman[4] report a value of about −800 kJ/mol (from thermochemical constraints on measured conductivities in phosphorus-dope potassium-seeded plasmas) whereas Rudnyi and co-workers[3] report values from about −940 to −990 kJ/mol (from anion-exchange equilibria). The value from Unkel and Freedman leads to $\Delta H^\circ_{acid}[H_3PO_4] = 1630$ kJ/mol, which is about the same as that for water[21] and is therefore not a reasonable result. The determinations by Rudnyi give $\Delta H^\circ_{acid}[H_3PO_4]$ of about 1470 kJ/mol, which is far more reasonable. Our interpretation is therefore consistent with the thermodynamic data of Rudnyi and co-workers.

The uniquely large entropy change for the (2,3) step is also consistent with reaction 2 as opposed to a simple clustering reaction. In a gas-phase clustering reaction, translational and free rotational degrees of freedom are converted into vibrations or internal rotations. The decrease in entropy from loss of translational and rotational degrees is only partially offset by the contribution of low-frequency modes associated with the formation of the weak ion–molecule bond. The translational and rotational contributions to $-\Delta S$ for reaction 2 at 350 K (approximately the middle of the experimental temperature range) are 147.5 and about 51 J/K·mol, respectively. To calculate the rotational contribution, the structures calculated by O'Keefe et al.[7] for the PO_3^- and $H_2PO_4^-$ (assumed the same for $D_2PO_4^-$) were used, and the D_2O molecules were assumed to form linear hydrogen bonds (1.5 Å in length) with the oxygen atoms of the ions. (The magnitude of the rotational contribution is not particularly sensitive to the assumed structure; assuming the product ion to be $PO_3^- \cdot 3H_2O$ yields about 47 J/K·mols.) On the basis of the experimental value, the inferred vibrational contribution is about −46 J/K·mol. For comparison, the inferred vibrational contributions to $-\Delta S$ for the first and second D_2O additions to PO_3^- are −86 and −99 J/K·mol. The significantly smaller magnitude for the vibrational contribution for isomerization compared to straightforward water clustering should be expected because in isomerization there is no net gain in the number of weak ion–water bonds with their associated low-frequency modes that largely contribute to the entropy of the complex. In other words, the six additional vibrational modes in the product of isomerization are associated with the ion $D_2PO_4^-$. These modes are expected to have higher frequencies than the six modes associated with a D_2O loosely bound in a cluster ion. The alterations in the higher frequencies of modes in D_2O and PO_3^- compared to those of $D_2PO_4^-$ contribute relatively little to the entropy change.

The (3,4) reaction behaves more normally, both kinetically and thermodynamically. The thermodynamic quantities are not unreasonable for a third hydration step of $(DO)_2PO_2^-$. The enthalpy change $-\Delta H_{n,n+1}$ for (3,4) is nearly the same as that for (1,2). The $-\Delta H_{n,n+1}$ is expected to increase with decreasing n. Similar to the situation for $HOCO_2^-$,[14] the increase is expected to be significant for $(DO)_2PO_2^-$ on going from (2,3) to (1,2) because of the availability of oxygen atoms as hydration sites. Thus, if the (3,4) reaction actually represents the third or (2,3) hydration steps of $(DO)_2PO_2^-$, then the (1,2) hydration step for $(DO)_2PO_2^-$ should be expected to be considerably more exothermic than the (1,2) step for PO_3^-.

The transformation of an ion at a particular degree of hydration has been reported[24] previously in the literature for the case of the hydration of NO^+ for which the reaction

$$NO^+(H_2O)_3 + H_2O \rightarrow H_3O^+(H_2O)_2 + HONO$$
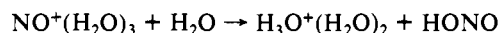
was observed. Recent ab initio calculations[25] have provided an explanation for the ease of formation of H_3O^+ and HNO_2 in the fourth hydration step. A similar study of PO_3^- hydration should

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prove interesting. A previous example of unusual thermochemistry in the hydration of an ion is that of t-$C_4H_9^+$ where the unusual behavior is ascribed to the transfer of charge to water to produce a protonated *tert*-butyl alcohol.[26]

Conclusions

The thermodynamic results of the present study support the conclusion of Henchman et al.[10] concerning the unreactive nature of PO_3^- in the gas phase. Our results suggest that the reaction of PO_3^- with water in the gas phase produces the simple adduct

$PO_3^-\cdot H_2O$. However, hydration of PO_3^- by three water molecules leads to a chemical transformation, presumably to the dihydrogen orthophosphate anion. The thermochemical data on $\Delta H_f^\circ(PO_3^-)$ from Rudnyi and co-workers[3] are consistent with the present interpretation.

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Revised and Modified Mechanisms for the Reactions of Bare Transition-Metal Ions M⁺ (M = Fe, Co, Ni) with n-C₃H₇X (X = NH₂, OH) in the Gas Phase

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Abstract: The metastable ion (MI) decompositions of n-C_3H_7X/M^+ complexes (X = OH, NH_2; M = Fe, Co, Ni) in the gas phase have been studied by tandem mass spectrometry. The analysis of the MI spectra of a large set of isotopomers uncovers processes which require a revision and modification of the previously suggested mechanisms for the activation of CH and CC bonds in these particular systems. Highlights of the novel findings are inter alia the observation that Fe^+-mediated ethylene loss from n-$C_3H_7NH_2$ involves the α- and β-methylene units. "Scrambling" of these two intact CH_2 groups precedes the β-hydrogen transfer which eventually leads to NH_3 and C_3H_6 from $C_3H_7NH_2/Fe^+$. For the Co^+ and Ni^+ complexes this exchange process is not observed, and ethylene loss can be described in terms of the "remote functionalization" concept. In the n-C_3H_7OH/M^+ system, the most unexpected findings concern the mechanism of the competitive formations of CH_3OH and C_2H_4. For M^+ = Co^+, methanol contains the intact methyl and OH groups of the precursor propanol, and C_2H_4 originates from the internal part of the alkyl chain ($C(\alpha)/C(\beta)$). This reaction sequence is to approximately 20% also operative for the Ni^+ system. In addition, the "anchored" Ni^+ induces cleavage of the $C(\alpha)/C(\beta)$ bond to eventually generate C_2H_4 (containing $C(\beta)$ and $C(\gamma)$) and CH_3OH. The methyl group of the latter contains the original α-CH_2 unit and one hydrogen from the CH_3 group of propanol. The results underline the necessity of employing labeled presursors in mechanistic studies of organometallic systems in the gas phase.

Gas-phase experiments with "naked" transition-metal ions offer a unique possibility to probe, in the absence of any solvation, ion-pairing and/or ligand effects, the intrinsic properties of reactive organometallic species and to evaluate the potential role these remarkable transients play in the initial steps of the activation of C–H and C–C bonds.[1]   Not surprisingly, this topic is of fundamental interest in catalysis and has attracted considerable attention in the last decade.[1,2]

Quite a few reactions of transition-metal ions M⁺ with organic substrates can be described by a mechanism (Scheme I), suggested for the first time by Allison and Ridge.[3a] Oxidative addition of the C–X bond (X = functional group) of the organic substrate **1** to M⁺ produces **2** which generates via β-hydrogen transfer the olefin–hydrido complex **3**. Depending on the binding energies, **3** undergoes either alkene detachment (**3** → RCH=CH₂) or reductive elimination of HX.

The selective functionalization of *remote* C–H or C–C bonds, i.e., several carbon atoms away from the activating group X,

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