Inorganic Radicals

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Exergonic and Spontaneous Production of Radicals through Beryllium Bonds

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Abstract: *High-level ab initio calculations show that the formation of radicals, by the homolytic bond fission of Y−R (Y=F, OH, NH_2; R=CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, NO) bonds is dramatically favored by the association of the molecule with BeX_2 (X = H and Cl) derivatives. This finding is a consequence of two concomitant effects, the significant activation of the Y−R bond after the formation of the beryllium bond, and the huge stabilization of the $F^{\cdot}$ ($OH^{\cdot}$, $NH_2^{\cdot}$) radical upon BeX_2 attachment. In those cases where R is an electronegative group, the formation of the radicals is not only exergonic, but spontaneous.*

Since the moment the first free radical was discovered back in 1900,[1] the interest in these species has steadily increased because radicals are involved in a plethora of chemical phenomena, and nowadays their role as intermediates is well established in a huge number of chemical reactions, as well as in the metabolism of biochemical systems.

The formation of neutral radicals usually involves the homolytic bond cleavage of covalent bonds, a process that requires a rather large amount of energy.[2] Boryl, aminyl, phosphinyl radicals, among others, are used as photoinitiating or initiating species[3] even though the formation of these radicals is often hindered by the high amount of energy needed to break a B−H, a N−H, or a P−H bond.[4] Clearly the energy demanded would be much lower when dealing with weak linkages, but even in those cases the amount of energy required is very high. In fact the dissociation of a rather weak covalent bond, such as F−F, still requires 157 kJ mol^{-1}.[2]

However, the strength of a covalent linkage can be altered by protonation,[5] reflecting the relationship between bond energies and electronegativity proposed by Pauling;[6] but also through the binding of a Lewis acid via non-covalent interactions, which normally induces a distortion of the electron density of the two interacting subunits. These distortions are particularly large for molecular linkers based on beryllium bonds,[7] in which the BeXY moiety acts as Lewis acid.

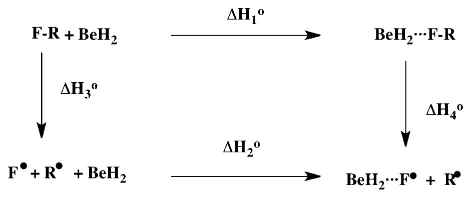
These electron density redistributions are at the origin of 1) very large cooperative effects between beryllium bonds and other non-covalent interactions,[8,9] 2) huge acidity enhancements of the Lewis bases participating in the beryllium bond,[10] 3) the spontaneous formation of ion-pairs in the gas-phase.[11]

Herein, through the use of high-level molecular orbital multi-configurational calculations, which are described in the Supporting Information, we will show that beryllium bonds also strongly favor the formation of radicals. For this purpose, the following compounds: F-R, OH-R and NH_2-R (R = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, NO) and their complexes with BeH_2 have been investigated.

As illustrated in Figure 1, for the set F−R (R = CH_3, NH_2, OH, F, NO), the electron density at the F−R bond critical point clearly decreases on going from the isolated Lewis base to the base in the BeH_2 complex. This F−R bond activation is obviously reflected in a significant lengthening of the corresponding bond (see Table S1 of the Supporting Information). Similar results are found for the HO-R, H_2N-R derivatives (see Figures S1 and S2 of the Supporting Information).

However, the most important finding is the dramatic decrease of the F−R, O−R, and N−R bond dissociation energies on going from the isolated bases to the complex as illustrated in Table 1. Even more importantly, for some systems (F−NH_2, F−OH, F_2, F−SH, F−Cl, F−NO) the bond dissociation is not only an exothermic but also an exergonic process!

The origin of such a dramatic change in the strength of these bonds can be traced through the thermodynamic cycle shown in Scheme 1.



Scheme 1.

The ΔH_3^0 and ΔH_4^0 are the F−R bond dissociation enthalpies for the isolated FR molecule and for the BeH_2:FR complex, respectively (see Table 1). ΔH_1^0 and ΔH_2^0 measure the stabilization of FR and $F^{\cdot}$ upon BeH_2 attachment, respectively. This cycle, clearly illustrates that the dramatic decrease observed in the F−R dissociation energy is not only a consequence of the weakening of the

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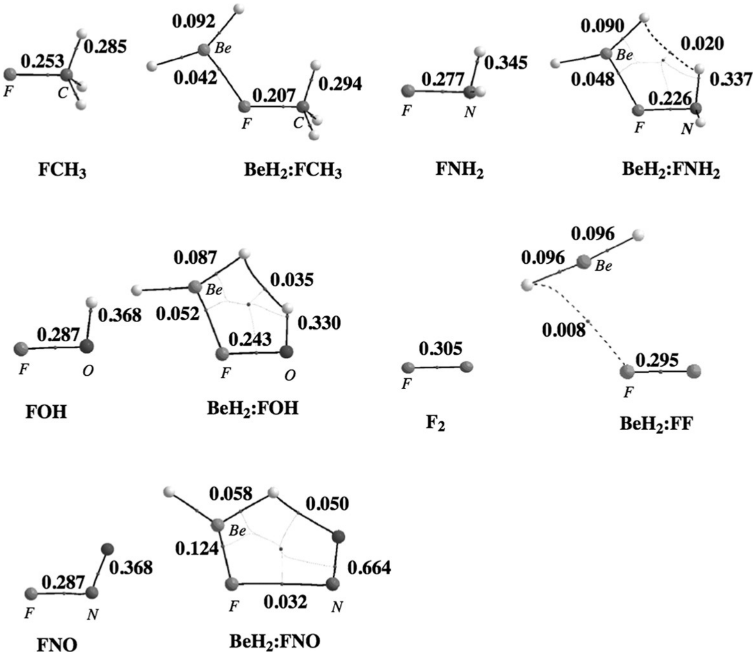


Figure 1. Molecular graphs of F–R (R = CH_3, NH_2, OH, F, NO) compounds and their complexes with BeH_2. Small gray dots on bonds indicate the bond critical points, a small gray dot in a ring system indicates the ring critical point. Electron densities are in a.u.

Table 1: G4 calculated F–R bond dissociation enthalpies (ΔH) and Gibbs energies (ΔG) at 298.2 K, as defined in Scheme 1, for the isolated compounds and for their complexes with BeH_2. $\Delta\Delta H = \Delta H_3{}^0 - \Delta H_4{}^0$ and $\Delta\Delta G = \Delta G_3{}^0 - \Delta G_4{}^0$ measure the changes in these two thermodynamic magnitudes upon association with BeH_2. All the dissociation energies were calculated considering the ground state $^{\bullet}BeH_2F$ radical product.

F–R			Isolated		BeH_2 Complex		Variation	
	$\Delta H_1{}^0$	$\Delta H_3{}^0$	$\Delta G_3{}^0$	ΔH_{exp}[a]	$\Delta H_4{}^0$	$\Delta G_4{}^0$	$\Delta\Delta H$	$\Delta\Delta G$
F–CH_3	−36.7	459.6	420.9	460 ± 8	124.3	79.9	335.3	341.0
F–NH_2	−39.6	289.8	255.1		−42.6	−88.9	332.4	344.0
F–OH	−38.1	200.5	169.7		−133.4	−176.9	333.9	346.6
F–F[b]	−2.96	143.6	113.8	156.9	−212.6	−234.6	356.2	348.4
F–SiH_3	−22.3	633.3	594.6	638 ± 5 636.0	283.6	234.7	349.7	359.9
F–PH_2	−23.1	465.7	429.8	461.5 ± 10.5	116.8	73.4	348.9	356.0
F–SH	−25.4	347.8	316.8		1.2	−40.4	346.6	357.2
F–Cl	−42.1	256.4	274.0	256.2	−73.5	−106.4	329.9	380.4
F–NO	−102.1	257.0	224.4		−12.8	−53.5	269.8	278.0

The stabilization enthalpy of $F^{\bullet}(\Delta H_2{}^0)$ at G4 level of theory is −372.0 kJ mol^{-1}. [a] Values taken from Ref. [2]. [b] Calculated at CCSD(T)/cc-TZVP level of theory. At this level the stabilization enthalpy of F· is −359.2 kJ mol^{-1}.

bond, but it is mostly due to the huge stabilization undergone by the $F^{\cdot}$ radical as compared with the stabilization of the FR compound. Note that the Reaction (1):

$$[BeH_2 \cdots F]^{\bullet} + FR \rightarrow BeH_2{:}FR + F^{\bullet} \qquad \Delta\Delta H = \Delta H_3{}^0 - \Delta H_4{}^0 \qquad (1)$$

is related to what Radom et al. have defined as radical stabilization energy (RSE).[12] As shown in Table 1, the RSE ($\Delta\Delta H$) of $[BeH_2{\cdots}F]^{\bullet}$ is enormous for the different R substituents considered in Reactions (1).

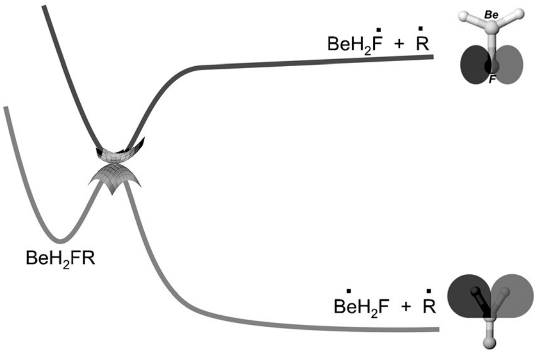
This huge RSE results in a substantial decrease of the enthalpy of Reaction (2):

$$BeH_2F\text{-}R \rightarrow [BeH_2F]^{\bullet} + R^{\bullet} \qquad (2)$$

which for some of species in Table 1 becomes even exothermic. Why? Since, the $BeH_2F^{\bullet} + R^{\bullet}$ dissociation limit must lie necessarily higher in energy than the BeH_2F-R complex, the only possibility of having an exothermic formation of radicals is through a crossing with a second state whose dissociation limit is lower in energy (see Scheme 2). An exploration of the nature of the wavefunction through a multi-configurational approach shows that this lower dissociation limit corresponds to $^{\bullet}BeH_2F + R^{\bullet}$, that is, a radical in which the unpaired electron migrates from the F atom to BeH_2 moiety (See Figure S3 of the Supporting Information and the accompanying explanation). Indeed, the structure in which the unpaired electron is located at the F atom corresponds to an excited state of the system, which lies about 400 kJ mol^{-1}, above the ground state.

The conclusion is that the radical initially formed by the homolytic cleavage of the BeH_2F–R bond (Reaction (2)) in which $BeH_2F^{\bullet}$ is formed, eventually evolves into a much more stable electronic arrangement in which the unpaired electron is mainly localized at the BeH_2 moiety. This process requires however to overpass an activation barrier dictated by the crossing point of the two states involved (see Scheme 2). Therefore, although the dissociation of the BeH_2F–R complex into two radicals is, in several cases exergonic, it is not necessarily a barrierless, and therefore, a spontaneous process. The height of the aforementioned barrier can only be reliably estimated by using multireference methods, because in the area near the crossing of both states, the wavefunction character is necessarily a mixture of several configurations. As suitable model systems to investigate this point we have chosen the BeH_2F–F complex, whose dissociation is the most exergonic process, the $BeCl_2F$–F one, in which we have changed the electron acceptor capacity of the Lewis acid by replacing BeH_2 with $BeCl_2$, and finally the BeH_2F–NO complex, where the NO radical formed is a rather stable molecule.

The results obtained for the BeH_2F–F complex are presented in Figure 2. The curves correspond to the F–F bond cleavage in the isolated F_2 molecule and in the BeH_2FF complex. The curve for the isolated F_2 has the expected shape



Scheme 2.

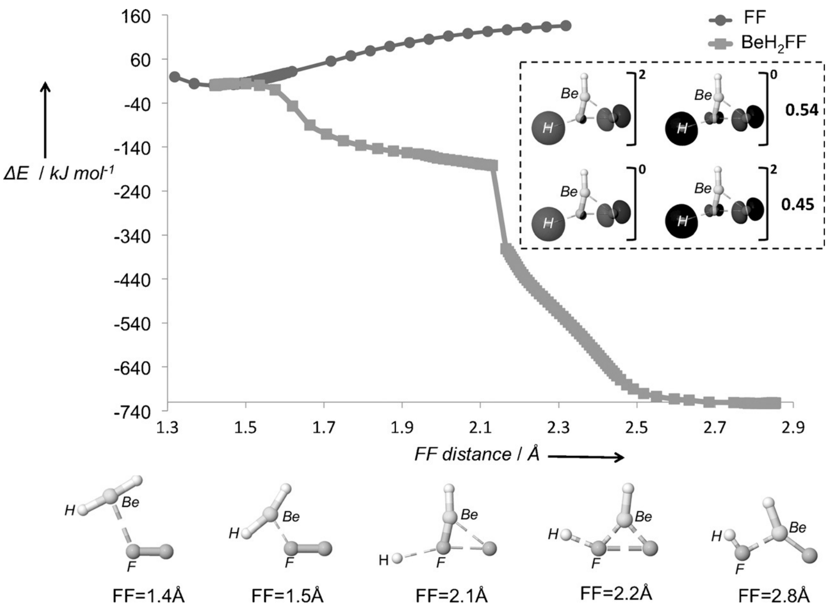


Figure 2. Potential energy curves corresponding to the dissociation of the F–F bond in the F_2 isolated molecule (dots) and in the BeH_2:FF complex (squares). Inset: the character of the wavefunction for an F–F distance of 2.1 Å. FF and BeH_2:FF dissociation profiles were computed, respectively at CASPT2//CASSCF(10,6)/cc-TZVP, and CASPT2//CASSCF(14,9)/cc-TZVP levels of theory.

of an asymmetric parabola, which leads in the asymptotic limit to $F^{\bullet} + F^{\bullet}$. However, the curve for the BeH_2FF complex goes through a negligible activation barrier (ca. 4 $kJ\,mol^{-1}$) to yield $^{\bullet}BeH_2F + F^{\bullet}$. The inset in the Figure 2 shows the two main configurations, of almost equal weight, which describe the system along the dissociation of the F–F bond and that ultimately corresponds to a biradical wavefunction with the two unpaired electrons sitting on the F atom and BeH_2F moiety (see Figure S4 for the evolution of the wavefunction over the reaction pathway). For longer F···F distances the system tries to stabilize the $F^{\bullet}$ so formed, by abstracting a H atom from the BeH_2F moiety, eventually yielding FH + FBeH as the final products. The situation changes only slightly when BeH_2 is replaced by $BeCl_2$: the barrier becomes slightly higher, but still low enough to conclude that the dissociation process is still spontaneous, and the reaction mechanism goes through a radical intermediary (see Figure S5 of the Supporting Information).

The case of the BeH_2:FNO system is particularly interesting, because NO is a rather stable radical. As a consequence, the effect of BeH_2 attachment is already evident in the initial complex which is actually two radical species interacting via hydrogen bond (BeH_2F:NO). Also in this case, the limit FBeH + HNO, in which the NO radical abstracts a H atom from the $[BeH_2F]^{\bullet}$ radical lies lower in energy, however the evolution from $[BeH_2F]^{\bullet} + NO^{\bullet}$ to FBeH + HNO requires surpassing an activation barrier of 32 $kJ\,mol^{-1}$ (See Figure S6). Note that the process is barrierless in practice, since the zero point energy of the complex is higher (ca. 52 $kJ\,mol^{-1}$) than the barrier height.

We can then conclude that beryllium bonds strongly facilitate the formation of radicals from Y–R (Y = F, OH, NH_2; R = CH_3, NH_2, OH, F, SiH_3, PH_2, SH, Cl, NO) molecules as a consequence of two concomitant effects, the significant activation of the Y–R bond, and the huge stabilization of the $F^{\bullet}$ ($OH^{\bullet}$, $NH_2^{\bullet}$) radical upon BeX_2 attachment. In those cases where R is an electronegative group, the formation of the radicals is not only exergonic but spontaneous. There is still a final question to be answered, is always the homolytic dissociation of the Y–R bond dominant? To answer this question let us take FCl as a model compound. In Table 2 we show the homolytic and heterolytic dissociation energies for the isolated molecule and for the complexes in which FCl interacts: a) with BeH_2, FCl acting as a fluorine Lewis base (BeH_2:FCl), b) with methanimine, FCl acting as a Cl Lewis acid (FCl:NH=CH_2), c) with both, acting simultaneously as a fluorine Lewis base and as a Cl Lewis acid (BeH_2:FCl:NH=CH_2; see Table 2).

As expected, the heterolytic dissociation of the FCl molecule is much more endothermic than its homolytic dissociation. Upon association to BeH_2 both processes are favored, the effect being slightly larger in the case of the homolytic bond fission. Nevertheless,

Table 2: G4 calculated F–Cl heterolytic and homolytic bond dissociation enthalpies (Δ*H*, $kJ\,mol^{-1}$).

Reaction	Δ*H*
$FCl \rightarrow F^- + Cl^+$	1305.3
$FCl \rightarrow F^{\bullet} + Cl^{\bullet}$	256.4
$BeH_2{:}FCl \rightarrow BeH_2F^- + Cl^+$	1014.5
$BeH_2{:}FCl \rightarrow [BeH_2F]^{\bullet} + Cl^{\bullet}$	−73.5
$FCl{:}NH{=}CH_2 \rightarrow F^- + [Cl{:}NH{=}CH_2]^+$	619.6
$FCl{:}NH{=}CH_2 \rightarrow F^{\bullet} + [Cl{:}NH{=}CH_2]^{\bullet}$	257.6
$BeH_2{:}FCl{:}NH{=}CH_2 \rightarrow [BeH_2{:}F]^- + [Cl{:}NH{=}CH_2]^+$	379.2
$BeH_2{:}FCl{:}NH{=}CH_2 \rightarrow [BeH_2{:}F]^{\bullet} + [Cl{:}NH{=}CH_2]^{\bullet}$	−21.7

as a result of the very large heterolytic bond dissociation energy of the isolated molecule, the heterolytic F−Cl cleavage in the BeH_2:FCl complex is still extremely endothermic, whereas the homolytic one becomes exothermic. The association with methanimine leads to a dramatic decrease of the heterolytic bond dissociation energy, because the imine strongly stabilizes the Cl^+ cation, whereas the homolytic bond dissociation remains practically unchanged. When the BeH_2:FCl:NH=CH_2 triad is considered, the decrease in the heterolytic bond dissociation energy (926.1 kJ mol^{-1}) is enormous, due to two concomitant effects, the stabilization of the Cl^+ cation and the F^- anion by the imine and the moieties, respectively. However, the decrease of the homolytic bond dissociation energy is much smaller, because as indicated above only the stabilization of the $F^{\bullet}$ by BeH_2 is significant. Still, the homolytic bond dissociation is slightly exothermic, whereas the heterolytic bond cleavage is still endothermic. However, it must be taken into account that in the heterolytic bond fission two ions of opposite sign are forming, that will attract leading to a $[BeH_2{:}F]^-$:$[Cl{:}NH{=}CH_2]^+$ ion pair, which as shown before in the literature, is a very favorable process.[9b]

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