

dimers and $\Delta M = 3$ transitions at g ca. 6 for trimers. These are not observed.

The second type of intermolecular contact is of the face-to-face type between benzene rings on neighboring molecules (ring A lies over ring C). In the case of $\text{Tc}(\text{abt})_3$, this leads to a $\text{Tc}\cdots\text{Tc}$ distance of 9.03 Å, and a similar distance is expected for $\text{Re}(\text{abt})_3$. This type of intermolecular contact will give a pathway for intermolecular exchange, but at this stage it is not possible to estimate its magnitude.

The third type of intermolecular contact involves the so-called edge-to-face contacts, between the edge of a benzene ring of one molecule with the face of another benzene ring on an adjacent molecule. A calculation using the crystal structure data of Baldas et al.¹ for $\text{Tc}(\text{abt})_3$ for the two possible edge-to-face contacts discussed by Yamanouchi and Enemark²³ gives $\text{Tc}\cdots\text{Tc}$ distances of 9.65 Å (ring A with edge B) and 11.67 Å (ring C with edge B). We therefore suggest that edge-to-face contacts give another possible pathway for intermolecular-exchange interactions, although such contacts are expected to give less electronic overlap than face-to-face contacts. A number of different trimeric structures can be suggested, all involving different combinations of face-to-face and edge-to-face contacts. The ESR evidence points to the existence of at least three and possibly four combinations, each with different magnitudes of the exchange coupling and hence different values of D . The remarkable feature of these structures is not so much that there is overlap between the π -electron clouds

of the benzene rings (the distances of approach of the carbon atoms are ca. 3.5 Å) but rather that there is a high degree of delocalization of the unpaired electron from the central metal atom.

A number of examples have been reported of systems with exchange coupling between two magnetic centers separated by distances of ca. 10 Å, but most of these have been for cases where the centers belong to the same binuclear species,²⁴ enzyme system,²⁵ or are attached to the same molecular complex.^{26,27} By way of contrast, there have been few observations of intermolecular-exchange interactions between paramagnetic centers where there is no distinct bonding pathway. Most of these observations have been made in the solid state.^{28,29} The novel contribution of this paper is the observation of such effects in dilute frozen solution.

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The Influence of a Second Magnesium Atom in Unsolvated Magnesium-Hydrogen Halide Reactions

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Abstract: Extensive ab initio calculations with the inclusion of electron correlation effects have been used to provide detailed information on the comparative reactions of Mg and Mg_2 with HF. Side-on reaction of HF with dimagnesium is energetically competitive with simple Mg insertion, but radical formation is a process that in the isolated molecule limit will be facilitated by involvement of a second magnesium atom. Magnesium insertion into HCl was also studied, and the transition-state structure was very much like that for insertion into HF, but the activation barrier was lower. Stabilities of dimagnesium reaction products were calculated, and these showed important metal-metal bonding. Comparison calculations on certain beryllium and calcium species show that this metal-metal bonding decreases with atomic number among the group 2 elements.

The reactive nature of elemental magnesium does not seem to be at all simple. While magnesium is generally regarded to form divalent species, we have recently found that formally univalent magnesium salts are stable by around 10–12 kcal in the isolated molecule limit.¹ (We use univalency in this instance in a very specific stoichiometric sense since these salts are of the form XMgMgX with each Mg still participating in two bonds.) The importance of magnesium reactivity, of course, has much to do with Grignard chemistry. In fact, much is still being learned about the very formation of Grignards as revealed by detailed studies on their generation at magnesium surfaces, as reported by Whitesides and co-workers.²⁻⁵ CIDNP spectra obtained by

Bickelhaupt and co-workers^{6,7} have been employed to investigate radical pathways in generation reactions. While Grignard reagents are generally formed and used synthetically in solution or in slurries, recently it has been possible to study these molecules in isolated conditions, free from solvent perturbations, and in turn to probe the reactivity of elemental magnesium more directly.

Skell and Girard⁸ reported the first observation of atomic magnesium reaction by way of matrix deposition. They observed reactivity of ground-state magnesium atoms with water and with alkyl halides at -196°C . A few years later, Ault carried out matrix codeposition experiments that yielded the first spectroscopic characterization of an unsolvated Grignard species.⁹ More recently, Klaubunde's codeposition studies¹⁰ with magnesium and

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a number of other metals provided further evidence of remarkable reactivity of bare metal atoms and also suggested a connection between atomic ionization potentials and reactivity. Magnesium, though, was different from other metals in that results from experiments with varying metal atom flux were indicative of the importance of metal clusters in the observed reactivity.¹⁰ Klabunde's group has since provided definitive experimental evidence of the reactivity of magnesium clusters through vis-UV spectra of the matrix-trapped reaction products.¹¹

The special reactivity of metal atoms or possibly small metal clusters has also been studied in solution and exploited synthetically. In particular, Rieke and co-workers developed a means for producing highly activated metal powders by alkali reduction of metal salts in ethereal or hydrocarbon solvents.¹²⁻¹⁵ Somewhat similar in reactivity, but with certain different properties, are the metal slurries that Klabunde has produced.¹⁶ These are formed by condensation of magnesium atoms and solvents at $-196\text{ }^{\circ}\text{C}$. Upon warming the condensate, a highly reactive slurry is produced.

What accounts for bare metal reactivity for magnesium, and perhaps other group 2 elements, is not entirely clear because of the apparent role of clusters. It may be that clusters provide sites for otherwise forbidden reactions of one magnesium atom or that they initiate reaction steps that cannot occur with one magnesium atom. Unfortunately, what is known about small magnesium clusters is limited. Two magnesium atoms will not bond chemically in the ground state, though there is a ~ 1 kcal van der Waals attraction.¹⁷ Ab initio electronic structure calculations^{18,19} indicate only weak attraction among three magnesium atoms, too. The four-atom cluster is the smallest to display chemical binding. It is bound by at least 10 kcal and as much as 20 kcal according to ab initio calculations²⁰⁻²² at different levels of theory. A value of 15-kcal serves as a good choice from among these calculated values to use for the cluster stability. The bonding in Mg_4 is quite interesting because it arises from electron correlation²⁰ and also requires a significant p and d hybridization of the 3s electrons.^{20,21} Furthermore, while the cluster stability is small, on a per bond per atom basis this stability amounts to almost 50% of the bonding in solid magnesium where the heat of atomization is 36 kcal. Mg_4 is a significant cutoff, then, since smaller clusters may be regarded as unbound while larger clusters will begin to approach the bulk metal bonding, albeit slowly.

In view of the Mg_4 cutoff, results that we have obtained for certain dimagnesium molecules²³ are somewhat surprising. Our ab initio calculations revealed a strong metal-metal bonding that stabilizes species of the form RMgMgX , which is a magnesium cluster alkyl halide. The cluster Grignards that were studied showed a consistent 5-6 kcal enhancement in stability relative to a simple, monomagnesium Grignard (plus a separated magnesium atom). Perhaps more important is the fact that the magnesium-magnesium bonding places an activation barrier in the way of unimolecular decomposition of the species, at least in isolated conditions.

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Table I. Calculated Magnesium Reaction Energies

reaction	exothermicity (kcal)
Monomagnesium Products	
$\text{Mg} + \text{H}_2 \rightarrow \text{MgH}_2$	-10.2 ^a
$\text{Mg} + \text{CH}_4 \rightarrow \text{HMgCH}_3$	20.5
$\text{Mg} + \text{HF} \rightarrow \text{HMgF}$	28.7 ^a
$\text{Mg} + \text{HCl} \rightarrow \text{HMgCl}$	37.7
$\text{Mg} + \text{CH}_3\text{F} \rightarrow \text{CH}_3\text{MgF}$	42.8
$\text{Mg} + \text{CH}_3\text{Cl} \rightarrow \text{CH}_3\text{MgCl}$	53.7
Dimagnesium Products	
$\text{Mg} + \text{HMgH} \rightarrow \text{HMgMgH}$	2.8 ^a
$\text{Mg} + \text{HMgF} \rightarrow \text{HMgMgF}$	7.3 ^a
$\text{Mg} + \text{CH}_3\text{MgF} \rightarrow \text{CH}_3\text{MgMgF}$	5.5
$\text{Mg} + \text{CH}_3\text{MgCl} \rightarrow \text{CH}_3\text{MgMgCl}$	5.4
$\text{Mg} + \text{FMgF} \rightarrow \text{FMgMgF}$	11.7 ^a
Others	
$\text{HMgF} + \text{HF} \rightarrow \text{H}_2 + \text{MgF}_2$	40.0
$\text{HMgCl} + \text{HCl} \rightarrow \text{H}_2 + \text{MgCl}_2$	44.5
$\text{HMgMgF} + \text{HF} \rightarrow 2\text{HMgF}$	32.4
$\text{HMgMgF} + \text{HF} \rightarrow \text{H}_2 + \text{FMgMgF}$	46.6
$\text{CH}_3\text{MgMgF} + \text{Mg} \rightarrow \text{CH}_3\text{MgMgMgF}$	2.0

^a ACCD result; others are SCF results.

Table II. Calculated Beryllium Reaction Energies

reaction	exothermicity (kcal)
$\text{Be} + \text{HBeH} \rightarrow \text{HBeBeH}$	23.5 ^a
$\text{Be} + \text{HBeF} \rightarrow \text{HBeBeF}$	32.8
$\text{Be} + \text{FBeF} \rightarrow \text{FBeBeF}$	38.8 ^a
$\text{Be} + \text{ClBeCl} \rightarrow \text{ClBeBeCl}$	37.3
$\text{Be} + \text{CH}_3\text{BeF} \rightarrow \text{CH}_3\text{BeBeF}$	32.8

^a ACCD result; others are SCF results.

The ab initio calculations reported here probe the effect of a second magnesium atom in the reaction of magnesium with HF or HCl and are the first step in examining reactions of small clusters. Transition-state structures and energetic reaction profiles have been obtained that show how a second magnesium can affect reaction processes. The methods employed and certain of the electronic structure features are discussed following a section on the energetic results.

Results and Discussion

1. Mg Insertion and Stabilities. In view of prior results,^{1,23} and the calculations reported here, it can be concluded that insertion of two magnesium atoms into a single chemical bond is more energetically downhill than insertion of just one atom. In the prototypical case, the reaction of magnesium with H_2 , formation of singlet state MgH_2 is uphill by 10.2 kcal, while $\text{Mg} + \text{MgH}_2 \rightarrow \text{HMgMgH}$ is downhill by 2.8 kcal. (Reaction energetics for magnesium insertion are summarized in Table I.) The formation of a magnesium-hydrogen bond in MgH_2 or, from reaction with methane, HMgCH_3 is endothermic because there is such a low acidity that not enough charge is withdrawn from the magnesium atom. The partial charge on magnesium in MgH_2 based on Mulliken populations is +0.44 e. In HMgMgH , the electron withdrawal from the metal centers by the hydrogens is essentially unchanged, so the magnesiums' charge is only +0.22 e. What is happening in the dimagnesium molecule, though, is that the usually weak Mg-Mg interaction is being strengthened to the point of being a chemical bond. The Mg-H bonds in HMgH and HMgMgH are comparable, so it is the Mg-Mg bond that contributes the extra stability of the cluster species.

The formation of the Mg-Mg bond is illustrated by the simple molecular orbital plots in Figure 1. Conceptually, the antibonding combination of the Mg 3s orbitals participates in forming the Mg-H bonds, leaving a net Mg-Mg bonding electron distribution. We have argued that this is a strong bond because to break it along the Mg-Mg stretching coordinate ($\text{HMgMgH} \rightarrow 2\text{MgH}$) requires about 50 kcal, based on well-correlated, large basis set calculations.²³ In the halogen salts, the Mg-Mg stabilization is more

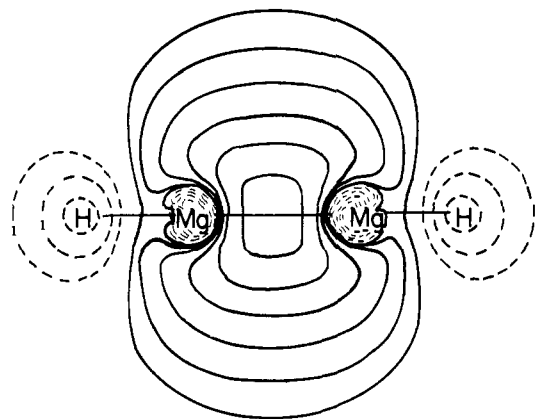


Figure 1. Orbital contours³⁶ of the two highest lying σ_g and the highest σ_u of the molecule HMgMgH . These orbitals are primarily linear combinations of the Mg_2 σ_u antibonding orbital and the hydrogen $1s$ orbitals. The first orbital shows the Mg-Mg bonding that is present in this dimagnesium species, while the other two orbitals are the symmetry-adapted pair of Mg-H bonds.

pronounced and amounts to 10–12 kcal¹ due to the strong halogen electron withdrawing power acting on the antibonding Mg-Mg electrons. Addition of a second magnesium to HMgF has a net exothermicity of 7.3 kcal, again attributed to the halogen's pull on the Mg-Mg antibonding electrons. The total electron density withdrawn from the magnesiums in HMgMgF is +0.84 e. Thus, for each halogen that replaces a hydrogen, the Mg-Mg bond improves by about 4 kcal. For the alkyl halides, Mg-Mg bonding shows the same enhancement and the addition of a second magnesium to CH_3MgF is energetically downhill by 5.5 kcal.

For beryllium, the same type of metal-metal bonding can occur. As the insertion energetics in Table II indicate, all the diberyllium species exhibit an even greater exothermicity of formation than their magnesium counterparts. This is naturally the result of the greater ease at which beryllium's valence s orbital can sp hybridize to participate in linear bonding. At the same time, Be-Be bonding in the metal is about twice that of magnesium and so the exothermicities of the reactions in Table II are still less than the energy required to abstract a Be atom from the solid. Moving down the periodic table to calcium, we find that Ca insertion into CaF_2 is exothermic, but by only 7 kcal. This result is based on energetic evaluations of CaF_2 and Ca_2F_2 with $R(\text{Ca-F}) = 2.10 \text{ \AA}$ and $R(\text{Ca-Ca}) = 3.56 \text{ \AA}$. The set of energies for beryllium, magnesium, and calcium indicates that the trend going down the group 2 elements is a decreasing metal-metal stabilization.

2. Activation Barriers. The transition state for the $\text{Mg} + \text{HF}$ reaction is shown in Figure 2. At this point in the reaction, it is clear that the HF bond has nearly broken. The activation barrier

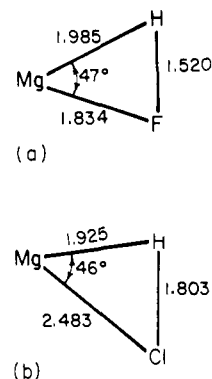


Figure 2. Transition-state structure for the (a) $\text{Mg} + \text{HF} \rightarrow \text{HMgF}$ reaction and for the (b) $\text{Mg} + \text{HCl} \rightarrow \text{HMgCl}$ reaction.

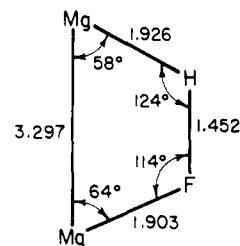


Figure 3. Planar transition state for the reaction of HF with 2Mg .

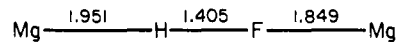


Figure 4. Transition-state structure for the $2\text{Mg} + \text{HF} \rightarrow \cdot\text{MgF} + \text{HMg}$ reaction.

is calculated to be 37 kcal when electron correlation effects, which are sizable at the transition state, are incorporated. The transition state for the $\text{Mg} + \text{HCl}$ reaction is quite similar and is shown in Figure 2b. At the different levels of calculation performed, the barrier for this reaction was always 9–10 kcal less than that of the $\text{HF} + \text{Mg}$ reaction. In addition, the overall reaction is about 20 kcal more downhill for HCl than for HF .

Two magnesium atoms can react with HF through different pathways which for the most part are energetically comparable. If Mg_2 were considered fixed, as if held in an inert matrix, HF could react side-on, by a perpendicular approach, or through some oblique orientation. The activation barrier for the side-on process is within a few kilocalories of the $\text{Mg} + \text{HF}$ barrier. The transition-state structure is shown in Figure 3. The potential surface in the region of this structure was found to be very flat in a number of directions. Of interest is the fact that the HF bond is stretched only to 1.45 Å in this transition state. This four-center reaction can take place earlier in the HF bond breaking to yield the magnesium inserted species. Were the proton replaced with CH_3 or something that could interact more favorably with Mg , the four-center reaction might well occur with a lower activation barrier.

A related idea in explaining the facility of the four-center reaction has been put forth by Klabunde.¹⁰ He suggested a connection between reactivity in a cold matrix and a metal's ionization potential or perhaps some other measure of the transferability of valence electrons. The difference between Mg_2 and Mg seems to fit this picture because of the destabilization of one orbital, the antibonding orbital, upon bringing together two magnesium atoms, thereby lowering the ionization potential of Mg_2 relative to Mg . Our results show that in both the mono- and dimagnesium species, half of the charge transfer found in the equilibrium structures has already occurred at the transition state. This supports the idea that the transferability of charge is important in getting the reaction to occur.

Another route to producing HMgMgF is the barrierless radical recombination of $\text{HMg}\cdot$ and $\cdot\text{MgF}$. Formation of these radicals from 2Mg and HF , however, has a sizable activation barrier of

Table III. Summary of Magnesium Cluster Reaction Energetics

reaction	exothermicity (kcal)
$\text{RMgX} + \text{Mg} \rightarrow \text{RMg}_2\text{X}$	6
$\text{RMg}_2\text{X} + \text{Mg} \rightarrow \text{RMg}_3\text{X}$	2
$\text{RMg}_n\text{X} + \text{Mg} \rightarrow \text{RMg}_{n+1}\text{X}$	$\sim 0^a$ [$n > 2$]
$\text{RMg}_5\text{X} \rightarrow \text{Mg}_4 + \text{RMgX}$	7
$\text{RMg}_6\text{X} \rightarrow \text{Mg}_4 + \text{RMg}_2\text{X}$	13
$\text{RMg}_n\text{X} \rightarrow \text{Mg}_{n-1} + \text{RMgX}$	$36 n$ [n large]

^a Assumed value; energies for reactions following use this value.

38 kcal which is comparable to that of the Mg + HF reaction. The transition-state structure for this reaction, given in Figure 4, has the HF bond stretched only to 1.405 Å. Radical formation with only one magnesium atom is found to be energetically uncompetitive, and so it may be concluded that in the unsolvated limit, the reaction of an HX molecule to form a radical species requires at least a two-atom magnesium cluster. It is interesting then that recent, matrix-isolation EPR results point to magnesium aggregation favoring formation of ion-radical pairs.²⁴

The sizable height of the barrier for all of the magnesium reactions with HF is consistent with the well-known difficulty to initiate X-F bond reactions. For instance, in a recent matrix study of Fe atoms with hydrogen halides, Pearson and co-workers reported reaction products with all HX species studies, except for HF.²⁵ In order to obtain some type of quantitative data on the lowering of the reaction barrier when considering other hydrogen halides reacting with magnesium, we have performed calculations for two reaction pathways of Mg with HCl. Both for the insertion of one Mg into HCl and for collinear dimagnesium attack to form radical species, the activation barrier is again found to be about 10 kcal less than that in the analogous HF reaction.

3. Magnesium Clustering. On the basis of the calculated energetics discussed and the atomization energy of elemental magnesium (36 kcal), an interesting picture of unsolvated cluster reactions emerges. A third magnesium will insert into an RMgMgX species with a small stabilization of ~ 2 kcal, but insertion of subsequent magnesiums is expected to yield a negligible additional stabilization. With this declining stabilization for continued Mg insertion, there will be a magnesium atom number, n , such that $\text{Mg}_{n-1} + \text{RMgX}$ is more stable than RMg_nX . The reaction energetics in Table III illustrate how this develops. The important point is that under unsolvated, matrix deposition conditions, any simple Grignard formed would serve as a "sticky" site for other magnesium atoms, the first bonding to the cluster Grignard and later atoms contributing to the growth of a magnesium cluster. Mg can attach to HMgX in still another way. The species HMgFMg is stable with respect to $\text{HMgF} + \text{Mg}$ by about 6 kcal. (The species FMgFMg is stable relative to $\text{FMgF} + \text{Mg}$ by 8 kcal.) However, unlike HMgMgF which displays true bonding of the second magnesium, HMgFMg is a complex and the activation barrier for its decomposition is its 6-kcal stability. In a like manner, simple Grignards can offer a site for complexing a second magnesium as well. This calculational determination of "stickiness" of Mg atoms to magnesium-containing molecules seems consistent with matrix-isolation observations of a colored complex prior to reaction.

4. Bridged Dimagnesium Molecules. Reaction of a Grignard reagent with excess alkyl halide does not generally lead to formation of the metal salt even though this would be quite exothermic in the isolated limit. Solvent effects undoubtedly lead to preferential stabilization of one or another species, but what is probably the most important energetic factor is the stabilization due to dimerization of Grignards, a process commonly designated the Schlenk equilibrium. Our calculations reveal the driving force for this equilibrium removed from any solvent effects. Dimerization of HMgF is quite exothermic for each of the three possible

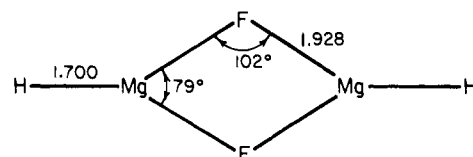
Table IV. Dimerization Energies

dimerization reaction	calcd exothermicity (kcal)
$2\text{HMgF} \rightarrow \text{FMg}[\text{H}_2]\text{MgF}$	26.5
$2\text{HMgF} \rightarrow \text{FMg}[\text{HF}]\text{MgH}$	52.2
$2\text{HMgF} \rightarrow \text{HMg}[\text{F}_2]\text{MgH}$	61.9

Table V. Calculational Tests on the Energetics of the Mg + $\text{HMgF} \rightarrow \text{HMgMgF}$ Reaction

level of calculation ^a	ΔE (kcal) ^b
(8s 4p 1d/5s 3p/2s) SCF	6.7
(8s 4p 1d/5s 3p/2s) ACCD	5.8
(8s 4p 1d/5s 3p/4s 1p) SCF	6.4
(8s 4p 2d/5s 3p 1d/4s 1p) SCF	5.9
(8s 4p 1d/5s 3p 1d/4s 1p) SCEP	5.8
(8s 4p 1d/5s 3p 1d/4s 1p) ^c SCEP	7.3

^a Basis sets are the contracted functions on Mg/F/H. See text for full explanation. ^b Exothermicity. ^c The Mg 2s,2p core electrons, frozen to substitution in the other correlated calculations, were unfrozen in this calculation.

**Figure 5.** Optimized structure of $\text{HMg}[\text{F}_2]\text{MgH}$.

bridged dimers, as given in Table IV. The difluorine-bridged isomer is the most stable being 62 kcal lower in energy than two separated monomers. Its structure is shown in Figure 5. Exchanging halogens with hydrogens in the bridge sacrifices only about 15 kcal for each interchange. Eliminating the bridge entirely, however, and having the magnesiums bond to each other we find to be highly unfavorable.

Theoretical Aspects and Calculational Approach

The ab initio calculations were done for the most part at two levels, with self-consistent-field (SCF) wave functions and with approximate double substitution coupled cluster wave functions²⁶⁻²⁷ (ACCD). ACCD is extremely faithful to the complete CCD treatment²⁸ but is computationally faster because of the neglect of certain small Hamiltonian matrix elements that nearly cancel in most cases. The coupled cluster approach itself incorporates both the dominant pair correlation effects and higher order correlation effects from indirectly interacting configurations.²⁹ The ACCD calculations were carried out with the matrix-oriented concepts³⁰ of self-consistent electron-pair (SCEP) theory.³¹ Certain calculations were performed at the variational CI level, including singly and doubly substituted configurations, and are designated as SCEP results.

Geometrical parameters for transition states were obtained by search along the ACCD potential energy surface. In these particular calculations, all virtual molecular orbitals except those corresponding to the Mg valence 3p or HF antibonding σ orbitals were excluded.³² Within the remaining space, the approximate Brueckner orbitals for the ACCD wave function were obtained. This allows for proper description of breaking and forming single bonds³³ and formally has certain attributes comparable to using

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Table VI. Calculational Tests on Activation Barriers

level of calculation	energy barriers (kcal)		
	HF + Mg	2Mg + HF	Mg + HF + Mg
(8s 4p 1d/5s 3p 1d) SCF	58.5	57.8	55.4
(8s 4p 2d/5s 3p 1d/4s 1p) SCF	56.2	55.9	53.7
(8s 4p 1d/5s 3p 1d/4s 1p) ACCD	36.5	40.1	37.9

Table VII. Equilibrium Bond Lengths^a (Å) of XMgY and XMgMgY Molecules

X	Y	XMgX		XMgMgY		
		R(MgX)	R(MgY)	R(MgX)	R(MgMg)	R(MgY)
H	H	1.712	1.712	1.732	2.920	1.732
H	F	1.692	1.783	1.722	2.882	1.793
F	F	1.770	1.770	1.787	2.841	1.787
Cl	Cl	2.207	2.207	2.240	2.846	2.240
CH ₃ ^b	F	2.081	1.787	2.099	2.888	1.795
CH ₃ ^b	Cl	2.080	2.234	2.099	2.890	2.255
H ^c	CH ₃ ^b	1.726	2.096	1.745	2.924	2.107

^aAll bond lengths listed here were determined at the SCF level.

^bThe methyl group structure was held fixed at $R(\text{CH}) = 1.092 \text{ \AA}$ and $\Delta\text{MgCH} = 111.3^\circ$. ^cDZ hydrogen basis was used.

an MCSCF reference. The effect of this orbital relaxation in the current problem, though, is not large. Final energies were calculated with the original and complete molecular orbital space. Magnesium and fluorine core orbitals were not correlated; however, test calculations where the Mg 2s,2p atomic orbital electrons were correlated showed generally small differences, such as 1.5 kcal in the Mg + HMgF reaction.

For magnesium, the atomic basis set was a 13s 8p 1d/8s 4p 1d contraction.^{30,34} Certain calculations were performed where a less diffuse 3d function, 0.5 vs. 0.14, was added to the basis. This augmentation improves the description of a partially positive (e.g. reacted) magnesium and thereby increases the calculated exothermicities of bare Mg reactions by several kilocalories.¹ However, its effect on the transition-state energetics is negligible as shown by the results in Table VI. Similarly, such a basis enlargement is not necessary for comparing mono- and dimagnesium species. The beryllium basis was a 10s 5p 1d/6s 3p 1d contracted set.³⁰ Dunning-contracted,³⁵ Huzinaga³⁴ double- ζ (DZ) quality sets were used for all other centers, except hydrogen.

Halogen bases were supplemented with a set of diffuse s and p functions with exponents of 0.1 for fluorine and 0.07 for chlorine. Polarization functions were included in the chlorine basis ($\alpha_d = 0.606$) in all calculations and were included for fluorine ($\alpha_d = 0.9$) in selected calculations, including the transition-state calculations. When carbon d polarization functions were used, the exponent was 0.75. Hydrogen bases used were a (6s 1p/4s 1p) Huzinaga set with $\alpha_p = 0.8$; however, only a DZ set was used for hydrogens in a methyl group. As the insertion energies for forming HMgMgF in Table V show, at the SCF level basis set improvement reduces the exothermicity but by less than 1 kcal.

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Table VIII. Total Electronic Energies for Different Computational Levels

molecule	calculation ^a	energy (au)
HMgMgF ^b	(8s 4p 1d/5s 3p 1d/4s 1p) SCF	-499.30828
	(8s 4p 1d/5s 3p 1d/4s 1p) ACCD	-499.56414
CH ₃ MgMgF ^c	(8s 4p 1d/5s 3p 1d/2s/4s 2p 1d) SCF	-538.35191
	(8s 4p 1d/7s 5p 1d/2s/4s 2p) SCF	-898.36623
HMgF (t.s.) ^d	(8s 4p 1d/5s 3p 1d/4s 1p) SCF	-299.55895
	(8s 4p 1d/5s 3p 1d/4s 1p) ACCD	-299.81724

^aBasis sets are given as (Mg/F or Cl/H/C). ^bGeometry was optimized at the ACCD level: $R(\text{H-Mg}) = 1.728 \text{ \AA}$, $R(\text{Mg-Mg}) = 2.898 \text{ \AA}$, and $R(\text{Mg-F}) = 1.768 \text{ \AA}$. ^cGeometry is given in Table VII. ^dGeometry is given in Figure 2a.

Correlation effects are in the opposite direction, and the complete set of values covers a relatively small range. An uncertainty of ± 1 kcal is reasonable.

Table VI gives results that show the sizable correlation effect on the reaction barriers. For the three-centered transition state of the HF + Mg reaction, correlation lowers the barrier by 22 kcal. For the side-on reaction of 2Mg with HF, the lowering due to correlation is less but still a sizable 17 kcal.

Table VII gives calculated bond lengths of mono- and dimagnesium species. From these data, it is seen that there is a qualitative trend of decreasing Mg-Mg distance as the X and Y substituents become more electron withdrawing. Such a trend is consistent with the explanation of the Mg-Mg bonding as given in section 1. The dihalide-substituted species which have the shortest Mg-Mg bonds and are the most stable may be thought of as analogues to the mercurous dihalide salts. Also to be noted is the slight lengthening of the Mg-X and Mg-Y bonds in the dimagnesium molecules relative to the monomagnesium species, indicating some weakening of these bonds.

For comparison with other calculations, total energies from representative calculations are presented in Table VIII.

Conclusions

The calculations that have been carried out were done for isolated molecules. The results are meaningful for low density gas phase and matrix isolation conditions but also serve as the "zeroth order" results from which to discuss solvent effects. The conclusions are the following: (1) Dimagnesium may insert at least as easily as one magnesium into certain chemical bonds because of the possibility of a four-center transition state. (2) Radical formation becomes much more favorable with two magnesiums in the reaction with hydrogen halides. (3) Cluster magnesium species are potentially a source for a more easily released magnesium atom than the bulk metal. While a second magnesium atom complicates the picture because of the greatly expanded reaction paths for even something as simple as reaction with a hydrogen halide, it is clear that this second magnesium can influence or improve the probabilities for certain of the possible reaction steps.

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