A Theoretical Study of Mercury Photosensitized Reactions

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Abstract: Some reactions of fundamental importance in mercury photosensitization have been studied by high level quantum chemical calculations. The reactions of Hg* ($^3P_1$) with H_2, CH_4, C_3H_8, and SiH_4 go by initial formation of exciplexes, followed by insertion of Hg* into the reactive X−H bond ultimately giving X radicals and H atoms. Intermediates and transition states have been located, notably the bent triplet ^{3}[H−Hg−H] species. The hydrogen and silane reactions are found to proceed without barriers, whereas the methane and propane reactions require activation energies. In the case of methane the barrier is so high, 12.8 kcal/mol, that the reaction is very inefficient while for propane the barrier is small, 4.9 kcal/mol, leading to the breaking of one of the central C−H bonds. Triplet sensitization of alkenes and the bonding of Hg* with lone-pair ligands are also studied. Very good agreement with the general picture obtained from experiments is obtained. The consideration of both spin-orbit and zero-point vibrational effects are very important for a qualitative understanding of the reactions. Similarities and differences to the corresponding transition metal reactions are discussed.

I. Introduction

Mercury photosensitization[1,2] is one of the cornerstones of photochemistry, yet many of the details of the mechanistic pathways involved remain obscure. This is probably because the area attracted greatest attention in the early 1970s, when the theoretical methods available were inadequate to address the main problems at issue. Crabtree[3] and co-workers have recently shown how mercury photosensitized reactions can be run under conditions which give them practical value in synthetic work, and this has prompted us to look at the main unresolved issues in Hg photosensitization with the powerful modern theoretical methods that are now available.

A number of points concerning mercury photosensitized reactions are widely accepted. In the first step of the process, a mercury atom in the reactor absorbs a 254 nm photon from a low pressure mercury lamp. The ground state mercury is excited to the $^3P_1$ state, commonly referred to as Hg*, which has a lifetime of 1.1×10^{-7} s.[1] Important work by Breckenridge, Jouvet, and Soep has shown that Hg* forms exciplexes with a variety of molecules,[4] which may either luminescence and dissociate, or more commonly, the exciplexes undergo chemical reaction. This reaction normally leads to homolysis of an X−H bond in the substrate molecule, so that H_2 gives H atoms, and cyclohexane gives both cyclohexyl radicals and H atoms, for example. Subsequently, conventional gas-phase radical chemistry leads to the final products.[1-3] There are several excellent reviews of previous work on Hg* photosensitized chemical reactions. In the 1970s, Callear and co-workers were the first to discuss the interaction between Hg(^{3}P) and small molecules.[5] Two reviews by Breckenridge and co-workers cover advances in the field through about 1982,[6,7] and the review by Duval et al.[4] discusses more recent studies of jet-cooled van der Waals complexes of Hg atoms. Several comparisons to the work described in these reviews will be made in the present study, although it should be emphasized that the main objective of this study is to show how well the present theoretical methods can describe the Hg* chemistry in general, and the detailed dynamics of the processes are therefore left for future studies.

A number of features of the Hg* reactions are puzzling. Although the Hg* excited state energy of 112.2 kcal/mol is sufficient to break them, C−H bonds with a bond strength of 100 kcal/mol and above are broken very inefficiently, compared to CH bonds with lower bond strengths. In alkanes, a very good correlation has been found between relative reaction rate and bond strength. Hydrogen, in contrast, is extremely reactive, even though its H−H bond strength is 103 kcal/mol, while C−C bonds in alkanes are almost always unreactive, in spite of the fact that they are much weaker than the CH bonds in the same molecule which are broken. Silanes are comparable to H_2 in reactivity, but the Si−H bond strength is much lower (ca. 90 kcal/mol). This means that the rate of bond cleavage falls off rapidly with the order: H−H, Si−H > C−H > C−C, and for C−H bonds, with the order, tertiary C−H > secondary C−H > primary C−H > $CH_4 \simeq 0$. Neither has there been agreement as to how the Hg* breaks the C−H bond, whether by abstraction of an H atom, energy transfer, or some other mechanism, or whether organometallic intermediates (i.e., having Hg−C bonds) are involved.

Recent theoretical progress in the present context has occurred mainly in two ways. The improvement of computer work stations in combination with the increased understanding of heavy metal complexes has lead to a situation where a large number of systems can be studied in a much shorter time than previously.[8] Also, the increased experience obtained from treating these systems has led to a much better understanding

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of the errors obtained in typical correlated calculations. In fact, recent work has shown that the errors obtained are highly systematic and this fact can be used to vastly improve the accuracy of the information from quantum chemical calculations. In a recently suggested scheme where the correlation energy is scaled[9,10] it has been demonstrated that the accuracy obtained is about the same as that obtained using the most advanced experimental techniques. One major reason to use theoretical methods to study these complicated reactions is that detailed information on the potential energy surfaces including transition states can be obtained with equal ease as that for stable intermediates. This can provide important complementary information and thus help interpret experiments.

II. Computational Details

a. Methods and Basis Sets. In the calculations reported in the present paper on the reaction between the mercury atom and different common first row systems, reasonably large basis sets were used in a generalized contraction scheme. The geometries were fully optimized at a correlated level, and for the evaluation of the energies all valence electrons were correlated using size consistent methods. The energies were then scaled using the PCI-X (parametrized configuration interaction with parameter X) scheme. For mercury a newly developed relativistic effective core potential (RECP) by Wahlgren was used.[11]

The RECP used for mercury treats the 4s, 4p, 5s, 5p, 5d, and 6s electrons explicitly and uses a (14*s*, 11*p*, 8*d*, 3*f*) primitive basis. The 4s, 4p, 5s, 5p orbitals are described by a single ζ contraction, the 6s and 6p by a double ζ contraction, and the 5*d* by a triple ζ contraction. The *f* function was contracted to one function giving a [4*s*, 4*p*, 3*d*, 1*f*] contracted basis for mercury. For carbon, oxygen, and nitrogen the primitive (9*s*, 5*p*) basis of Huzinaga[12] was used, contracted according to the generalized contraction scheme to [3*s*, 2*p*], and one d function was added with exponent 0.63 for carbon, 0.95 for nitrogen, and 1.33 for oxygen. For silicon a similarly contracted basis was used based on the primitive (12*s*, 9*p*) basis of Huzinaga[12] and including one d-function with exponent 0.30. For hydrogen the primitive (5*s* basis from ref 12 was used, augmented with one p function with exponent 0.8 and contracted to [3*s*, 1*p*].

In the geometry optimizations somewhat smaller basis sets were used. First, for the mercury atom an RECP according to Hay and Wadt[13] was used. The 5*s* and 5*p* core orbitals are described by a single ζ contraction while the valence 5d, 6s, and 6p orbitals are described by a double ζ basis and where the outermost 5d basis function is diffuse. The rest of the atoms are described by standard double ζ basis sets.

The geometry optimizations for all the present mercury systems were performed at the MP2 level using the GAUSSIAN-92 program.[14] The correlated calculations were performed using the modified coupled pair functional (MCPF) method,[15] which is a size-consistent, single reference state method. The zeroth order wave-functions were in these cases determined at the SCF level. The present calculations were performed on DEC-alpha work stations and the final energy evaluations were performed using the STOCKHOLM set of programs.[16]

Even though the absolute accuracy of the MCPF calculations is not very high, the fact that the errors are highly systematic can be used to significantly reduce the errors. The accuracy is mainly limited by the basis set size in the final MCPF calculations. The lack of triple excitations is another rather important factor. In comparison to these other errors, the error in the geometry optimization step can normally be neglected. Based on comparisons to calculations of high accuracy and on comparisons to experiments, it has recently been demonstrated that the present type of treatment gives a remarkably stable fraction of the correlation effects. Using the present basis sets and methods it has been shown that this fraction is close to 80%. A simple estimate of the remaining correlation effects is then obtained by simply adding 20% correlation energy to each system. This is the general idea behind the PCI-80 scheme which has recently been proposed.[9,10] It was shown in refs 9 and 10 that this parametrization gives a major improvement of the results compared to an unparametrized treatment. For a benchmark test consisting of the atomization energies of 32 neutral first row systems the PCI-80 scheme gives an average absolute deviation compared to experiments of only 2.4 kcal/mol. Pople et al.[17] have shown that for the same systems the MP2 method using polarized basis sets gives an average absolute deviation of 22 kcal/mol, and for the QCISD method the deviation is actually larger with 29 kcal/mol. For transition metal systems the improvement at the PCI-80 level compared to an unparametrized treatment is sometimes quite dramatic. Tests against a large number of experimentally studied small second row transition metal complexes show that the accuracy of the PCI-80 scheme for bond strengths is probably at least as high as that available from experiments for these systems.[9] The present study is one of the first where the PCI-80 scheme is used for systems containing elements beyond the second transition series and one purpose of this study is therefore to investigate the accuracy of the approach for this new type of systems.

b. Spin-Orbit Coupling and Zero-Point Vibration. The mercury atom is one of the heaviest atoms in the periodic table and it is therefore clear that a reasonable treatment of relativistic effects is absolutely necessary if results of qualitative accuracy should be obtained. Based on comparisons to relativistic all-electron no-pair calculations, the present RECP has been shown to perform very well.[11] This is also verified for the spin-orbit average excitation energy which at the PCI-80 level becomes 116.3 kcal/mol compared to the experimental average value of 119.5 kcal/mol. The RECP should therefore account for all relativistic effects except for the spin-orbit effects. The spin-orbit coupling constant for the $Hg^*(^3P_J)$ multiplets is quite large, 4265 cm^{-1} (12.2 kcal/mol), and these effects therefore cannot be neglected without good reasons when chemical interaction energies are determined. Unfortunately, an adequate treatment of spin-orbit effects combined with a high level of correlation treatment is not yet possible for the present systems. The simplest assumption that can be made is that the main spin-orbit effects are quenched when the chemical bonds are formed. This assumption is used quite regularly and has, for example,

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been shown to work well for platinum and iridium reactions.[19] The basis for this assumption is the chemical situation before spin-orbit effects are added. For the unperturbed Hg* $^3P(6s^1 6p^1)$ atom the three p-directions will be equivalent and lead to degeneracy without inclusion of spin-orbit effects. When the spin-orbit operator is introduced it is then clear that the interaction between these degenerate states will be large. However, when a chemical interaction has taken place the degeneracy is lifted. With a strong interaction as is found in the present insertion reaction, it is not unreasonable to assume that the degeneracy is almost entirely gone. In practice this assumption means that for the unperturbed atom, spin-orbit effects will lead to a lowering of the energy by 6.8 kcal/mol, which is the difference between the calculated average value and the Hg* $^3P_1$ component. For the products of the reaction and for the transition state spin-orbit effects will not lead to any lowering at all. For the products, like HgH and $HgCH_3$ this assumption should be extremely good since the bonding mercury state is Hg $^1S(6s^2)$, where the spin-orbit effects are zero by definition. Also, to first order, spin-orbit effects are zero for $^2\Sigma$ states. For the transition state the assumption should also be quite good, since this state is similar electronically to the products. The situation is quite different for the weakly bound molecular exciplexes formed with the alkanes where the electronic structure is more similar to those in the reactant excited mercury atom. The assumption made here is then that the same lowering of the energy by 6.8 kcal/mol as for Hg* is appropriate for these exciplexes due to spin-orbit effects.

Zero-point vibrational effects also need to be considered for the Hg* reactions. The importance of these effects for the present reactions can be understood in the following qualitative way. Since the mercury atom forms very weak bonds, like the ones in HgH (6.7 kcal/mol) and $HgCH_3$ (1.4 kcal/mol), and mercury is also very heavy, zero-point vibrational energies directly involving mercury will be very small. For a reaction between, for example, Hg* and C_3H_8 forming HgC_3H_7 and H atoms the change of the zero-point vibrational effects will then be almost the same as between C_3H_8 and C_3H_7. This change is quite large being 10.0 kcal/mol for the propane reaction, and can thus certainly not be neglected. In order to adequately account for the zero-point vibrational effects these have been explicitly obtained at the MP2 level.

III. Results and Discussion

The present section is divided into seven subsections. In the first subsection the interaction between the excited mercury atom and lone-pair ligands will be discussed. In the second subsection the rather unusual type of single bonds formed between mercury atoms and hydrogen and different alkyl groups will be described. The bond strengths for the systems discussed in the first two subsections are summarized in Table 1. In the third subsection the results from the calculations on the simplest possible reaction involving an excited mercury atom, that with the hydrogen molecule, will be discussed. In the fourth and fifth subsection the reactions between Hg* and methane and propane are discussed and compared. Experimentally, Hg* is found to react with a high quantum yield with both H_2 and C_3H_8 but not with methane. Finally in the sixth and seventh subsection a few other representative Hg* reactions, such as those with silane and ethylene will be discussed. A summary of the results for the Hg* insertion reactions are given in Table 2 and in Figure 1. A picture of the transition state for the reaction between Hg* and C_3H_8 is given in Figure 2. Before discussing these reactions, it is useful to know the computed bond strengths in the different systems. The H−H bond energy is calculated to be 104.8 kcal/mol, the first C−H bond in methane 102.7 kcal/mol, the central C−H bond in propane 98.2 kcal/mol and the first Si−H bond in silane 88.4 kcal/mol.

a. Molecular Lone-Pair Exciplexes. As mentioned in the computational section, the spin-orbit coupling constant in the Hg*(^3P_J) multiplets is quite large and these effects therefore need to be accounted for in some way. A direct computational treatment of spin-orbit effects to high accuracy is not yet available and the influence of these effects will therefore have to be determined in a qualitative way in the present study. For strong chemical interactions this can be done quite accurately by simply considering the spin-orbit effects as quenched in the molecular systems. For very weak interactions, like in the exciplexes between Hg* and molecular alkanes, an estimate of spin-orbit effects is also easy. However, for the group of systems where the interaction can be expected to be of intermediate strength, like in the bonding to lone-pair donor ligands, estimations of spin-orbit effects is more uncertain. For the purpose of understanding more about the effects in these systems, the experimentally determined interaction energies between Hg* and different ligands like water and ammonia are quite useful.[4]

The present calculations without allowance for spin-orbit effects yield a binding energy for Hg*−H_2O of 13.1 kcal/mol and one for NH_3 of 22.3 kcal/mol. These values can be compared to the experimental bond strengths of 8.1 and 17.4 kcal/mol, respectively, determined with respect to the Hg*($^3P_1$) excited state. Two points are worth noting. First, the experimental bond strengths are smaller than the theoretical ones ignoring spin-orbit effects. Secondly, the difference in theoretical bond strengths is 9.1 kcal/mol, and the corresponding experimental difference is 9.3 kcal/mol. These results are quite consistent with the general picture given above concerning the effects of spin-orbit interaction. First, it is logical that the difference is almost exactly the same for water and ammonia for which the bonding should be very similar. Secondly, the fact that the calculated bond strengths are larger than the experimental ones is expected since the spin-orbit effects should be largest for the unperturbed Hg* atom. With the assumption of total quenching of the spin-orbit effects for the molecular complexes, as described in Section IIb, the bond strength for Hg*−H_2O becomes 6.3 kcal/mol and for Hg*−NH_3 it becomes 15.5 kcal/mol. These values are smaller, but only slightly, than the experimental values, which means that the spin-orbit effects are almost entirely quenched by the lone-pair interaction with ammonia and water, which is a rather surprising result. It is interesting to note that the present conclusion about the quenching of spin-orbit effects is perfectly in line with the conclusion drawn from the experiments.[4] It is stated there that spin-orbit interaction must be reduced by at least a factor of 10 near the potential minima, and they also note that this is a surprising result. The fact that the experimental bond strengths for the lone-pair ligands are smaller than the calculated ones ignoring spin-orbit effects, can also be understood in another, but less useful, way. This point of view focuses on the orientation of the 6p-orbital and is based on the fact that the most favorable interaction is obtained with the Hg 6p-orbital pointing perpendicularly away from the lone-pair, giving a pseudolinear Π-state. This state is accessible without energy from the ^3P state without spin-orbit effects. However, with spin-orbit effects the $\Omega = 0(-)$ and $\Omega = 1$ states have a strong 50−50% mixing of the p_0 and $p_{\pm 1}$ orientations of the Hg 6p orbital. Therefore, with spin-orbit effects included a reorienta-

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Table 1. Different Hg−X and Hg*−X Bond Strengths ΔE (kcal/mol), Obtained at the PCI-80 Level. Spin-Orbit and Zero-Point Vibrational Effects are Included as Described in Section IIb

	ΔE (calcd)	ΔE (exp)
Hg−H	6.7	8.6[a]
Hg−CH_3	1.4	−
Hg−C_3H_7(iso)	3.3	−
Hg−SiH_3	4.1	−
Hg*−H_2O	6.3	8.1[b]
Hg*−NH_3	15.5	17.4[b]
Hg*−CH_4	3.0	2.0[b]
Hg*−C_2H_4	44.9	−

[a] Huber and Herzberg.[20] [b] Duval et al.[4]

tion of the direction of the p-orbital costs energy which therefore also explains the difference between theory and experiment. The main objection to this viewpoint is that it makes it hard to quantify the effect, and the explanation based on a quenching of the spin-orbit effects is therefore more useful and also easier to adopt. It should be added that some part of the difference between the experimental and theoretical results, of course, in principle could be due to a problem in the treatment of the correlation effects. It is not likely that this should be a major problem since, as mentioned above in Section II, a large number of comparisons made for transition metal complexes have shown that the accuracy of the PCI-X scheme is about as high as the one for experiments.

The MP2-optimized geometries for the water and ammonia complexes can also be compared to experiment. The Hg*−O distance of 2.44 Å for the water complex compares well with the measured distance of 2.4 Å. For the ammonia complex the optimized Hg*−N distance is exactly the same as the Hg*−O distance for the water complex with 2.44 Å, while the experimental bond distance is shorter, 2.2 Å. It should first be noted that a difference of this amount on such a weak bond has only a very small effect on the binding energy. Nevertheless, it is expected that even the simple MP2 method should be able to give the difference in bond distance for these very similar complexes more accurately than to 0.2 Å, and therefore the experimental bond distance difference could be questioned.

b. Mercury Single Bonds, Hg−H, Hg−CH_3, and Hg−C_3H_7(iso). The mercury systems with a single bond to either hydrogen or an alkyl group have been obtained in the course of studying the Hg* insertion reactions into H−H and C−H bonds. These systems are worth a few comments since the bonding turns out to be quite unusual. Without electronic promotion the ground state mercury atom with its $^1S(6s^2)$ configuration can only form a weak van der Waals complex with hydrogen or alkyl groups. Therefore, chemical bonding has to be preceded by promotion to the Hg* $^3P(6s^16p^1)$ state. This state will bind to hydrogen with its s-orbital. Following this bonding there will be a polarization of the bond toward mercury to fill up the empty parts of the deep lying 6s orbital, and electron flow in the other direction in the singly occupied orbital from the mercury 6p orbital over to hydrogen. This will lead to a $^2\Sigma^+$ HgH state. This type of bonding is present in the lighter group II hydrides like BeH which has a binding energy of 46.9 kcal/mol. With this analysis the bond strength will depend critically on the excitation energy from the ^1S to ^3P state of the atom. This excitation energy increases going down in the periodic table from beryllium with 62.8 kcal/mol down to mercury where it is as large as 119.5 kcal/mol (average). It is thus expected that the bond strength in Hg−H will be much smaller than in Be−H. The bond strength of 8.6 kcal/mol obtained experimentally[20] agrees with this expectation. The calculated result is 6.7 kcal/mol. It should be added that this result should be almost unaffected by spin-orbit effects since the bond strength is evaluated with respect to the ground state of the mercury atom which is a closed shell singlet. A detailed look at the orbitals indicates that the bonding is in line with the above expectations. The bonding σ^2 orbital has a mercury occupation of 1.29 (mostly 6s) at the SCF level. The singly occupied orbital has an occupation of 0.23 on hydrogen in line with the donation back-donation picture. It can also be added in this context that even though the promotion energy to a bonding state is the most important factor for the bond strength in these MH molecules, it is not the only factor of importance. For example, the promotion energy for Zn is larger than that of Cd, and still the bond in ZnH is stronger than the one in CdH.[21] Clearly, as usual also overlap criteria influence the bond strengths.

The above bonding picture stays qualitatively the same when the mercury atom binds to an alkyl group, but there are some relatively marked changes in the orbitals involved that are interesting. The binding energy in $HgCH_3$ is calculated to be only 1.4 kcal/mol which is considerably weaker than for HgH where it is 6.7 kcal/mol. The mercury occupation in the bonding σ^2 orbital has now increased to 1.54 from 1.29 for HgH at the SCF level. In response to this, the singly occupied orbital has increased its non-mercury contribution to 0.57 from 0.23 in HgH. For Hg−C_3H_7(iso) these changes in the orbital character are even more pronounced. The mercury contribution in the bonding σ^2 orbital is now as large as 1.98 at the SCF level and the non-mercury contribution in the singly occupied orbital is 0.98. At the SCF level it is thus clear that there is no longer any chemical bonding. However, the PCI-X binding energy for Hg−isopropyl is 3.3 kcal/mol, which is actually slightly larger than the binding energy calculated for Hg−methyl. It is easy to consider this as van der Waals binding but the above chemical type of binding is still possible. A natural orbital analysis of the correlated MCPF wave-function indicates that the mercury contribution to the bonding σ^2 orbital has decreased to 1.91 and the non-mercury contribution in the singly occupied orbital has decreased to 0.94. This means that charge-flow, induced when correlation is included, can still be claimed to be responsible for the binding. In reality, of course, both chemical and van der Waals binding is present in a mixture which is impossible to define quantitatively. An interesting aspect of these bonds is that a major origin of the difference of 1.9 kcal/mol between the Hg−CH_3 (1.4 kcal/mol) and HgC_3H_7 (3.3 kcal/mol) binding energies is zero-point vibrational effects. Without these effects included the difference in bond strengths is only 0.1 kcal/mol. It can also be added that the trend of the amounts of covalent and van der Waals character of the Hg−R bonds is as expected. The Hg−H bond should have most covalent character as it has and the Hg−C_3H_7 bond should have the strongest van der Waals bonding as it has.

c. Reaction between Hg* and H_2. The reaction between Hg* and H_2 is the simplest possible one involving excited mercury, yet it has significant technical importance.[3] Mercury photosensitization of H_2 is a very efficient way of forming useful amounts of H atoms under ambient conditions. It is also a representative case containing most of the aspects of reactions involving excited mercury. Initial formation of a molecular exciplex is followed by a bond-breaking, a formation of a (triplet) insertion complex (oxidative addition product), and

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Table 2. Reaction Energies (kcal/mol) for the Insertion Reactions between Hg* and H_2, CH_4, C_3H_8, and SiH_4. The Energy is Set to Zero for the Reactants. Spin-Orbit and Zero-Point Vibrational Effects are Included as Described in Section IIb

	H_2	CH_4	C_3H_8	SiH_4
reactants	0.0	0.0	0.0	0.0
molecular exciplexes	−3.0	−2.6	−5.6	−7.1
transition state	−0.6	+12.8	+4.9	−6.5
insertion complex	−15.6	–	–	–
HgH + R products	−11.7	−12.7	−17.5	−27.6
Hg + H + R products	−5.0	−6.0	−10.8	−20.9

subsequent dissociation into fragments,

$$Hg^* + H{-}H = {}^3[Hg(H{-}H)]^* = {}^3[H{-}Hg{-}H] = HgH + H = Hg + H + H$$

It should be added that the above sequence is only a sketch of a reaction pathway and possible products formed. It is the detailed dynamics that will eventually determine the exact outcome of this reaction. In fact, experimentally it is found that the major product formed is HgH and H with a quantum yield of 0.62 and Hg + H + H is formed with quantum yield 0.31,[18] see further below.

The first interesting part of the potential energy surface in the Hg* + H_2 reaction is the region where H_2 is almost unperturbed. At the MP2 level a minimum is obtained with an H−H distance of 0.75 Å at an Hg−H_2 distance of 2.72 Å. At this geometry the PCI-80 scheme gives a binding energy of 3.0 kcal/mol compared to the initial reactants. Proceeding further along the reaction coordinate a transition state (one imaginary frequency of the Hessian) for H−H bond breaking was determined at the MP2 level with an H−H distance of 1.11 Å and an Hg−H_2 (midpoint) distance of 1.87 Å. The PCI-80 energy with addition of spin-orbit and zero-point vibrational effects at this point is 0.6 kcal/mol below the reactants. This means that from the exciplex minimum the reaction has a small activation barrier of 2.4 kcal/mol. It should be added that both the transition state and the equilibrium are on the lowest $^3B_2$ potential surface. For states with other symmetries, H−H bond breaking will occur at higher energies. The present results are therefore not inconsistent with experiments showing that both $^3[Hg(H{-}H)]^*$ states which are bound and dissociative exist.[18] Since the calculations do not include spin−orbit interaction explicitly, these calculations do not rule out that these $^3[Hg(H{-}H)]^*$ states are slightly modified by spin-orbit interaction.

After the bond-breaking region is passed an interesting region is entered where an insertion product is formed. This $^3[H{-}Hg{-}H]$ was also observed in the theoretical study by Bernier and Millie.[22] They obtained an equilibrium geometry based on CI calculations with a bond angle of 70°, a Hg−H bond distance of 2.01 Å, and a binding energy with respect to the reactants of as much as 25 kcal/mol. Since HgH is bound by 8.6 kcal/mol, H_2 is bound by 103.3 kcal/mol and the excitation energy from Hg(^1S) to Hg*($^3P_0$) is 107.6 kcal/mol, the $^3[H{-}Hg{-}H]$ insertion product should be bound by 12 kcal/mol with respect to the HgH + H products according to their calculations. Another interesting feature was noted by Bernie and Millie concerning this $^3[H{-}Hg{-}H]$ insertion product. In their dynamical simulation they found that as their trajectories traverse this minimum, this leads to a high torque and thus to rotational excitation of HgH as the H atom leaves. This is probably the reason the major product in the reaction between Hg* and H_2 is found experimentally to be HgH[18] and not free atoms. In this context there is an interesting difference to the corresponding reaction with methane where HgH is not formed, see below. In the present study a very similar minimum for $^3[H{-}Hg{-}H]$ was located with a bond angle of 69.8° and a Hg−H bond distance of 1.98 Å at the MP2 level. The PCI-80 binding energy corrected for spin-orbit and zero-point vibrational effects for this geometry is 15.6 kcal/mol with respect to Hg* + H_2 and 3.9 kcal/mol with respect to the products HgH + H. The present study is therefore in agreement with the previous theoretical study that there is a minimum for the insertion product. The bonding in the $^3[H{-}Hg{-}H]$ insertion product is quite complicated and occurs through a donation back-donation charge flow. In B_2 symmetry (C_{2v}), the singly occupied Hg 6p orbital is entirely emptied by donation into the H−H antibonding orbital. In A_1 symmetry there is a mixing between mercury and hydrogen orbitals to form a doubly occupied Hg−H bonding orbital and a singly occupied Hg−H antibonding orbital. Together these two orbitals contain 1.63 Hg 6s electrons at the SCF level. The total number of Hg 6p electrons at the same level is 0.38. It can be added that this triplet insertion state should not be confused with the ground state singlet H−Hg−H complex which should be very stable and is expected to be linear.

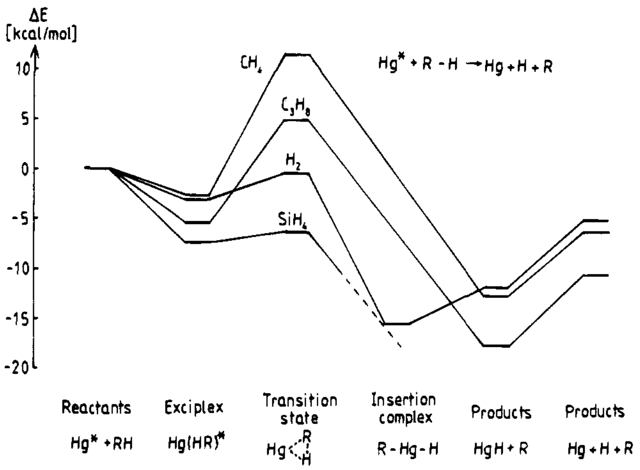

Figure 1. The energetics for the insertion reactions between Hg* and different small molecules.

In summary, the reaction between Hg* and H_2 proceeds over a quite flat potential surface. The reaction goes through a molecular precursor region with a small binding energy of 3.0 kcal/mol, through the bond breaking region with an energy at the MP2 transition state which is 2.4 kcal/mol higher than for the precursor exciplex. After passing the transition state the energy goes down to the lowest point on the potential energy surface which is the insertion product with a binding energy of 15.6 kcal/mol. This insertion product is 3.9 kcal/mol below the HgH + H products which in turn is 6.7 kcal/mol below a complete dissociation into three products. The exothermicity for the insertion reaction going to the HgH + H products is 11.7 kcal/mol.

d. Reaction between Hg* and CH_4. The reaction between Hg* and methane can be written as follows,

$$Hg^* + R{-}H = {}^3[Hg{-}(H{-}R)]^* = HgH + R = Hg + H + R$$

Again the above sequence is only a sketch of a possible reaction pathway, and only detailed dynamics will determine the actual outcome. In this case it is found experimentally that HgH is entirely absent as a product,[4] in contrast to the case of the H_2 reaction, see above. A possible explanation for this difference is mentioned below.

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(22) Bernier, A.; Millie, P. *J. Chem. Phys.* **1988**, *88*, 4843.

There are interesting differences between the Hg* reaction with hydrogen, described above, and the reaction with methane. Experimentally, the hydrogen reaction is known to occur readily while C−H activation of methane hardly occurs at all.[3] The present calculations are in agreement with those findings. In the initial part of the methane reaction a molecular exciplex is formed with a PCI-80 binding energy of 2.6 kcal/mol, which is slightly less than the corresponding molecular hydrogen complex binding energy of 3.0 kcal/mol. The value for methane compares favorably with the experimental value of 2.0 kcal/mol,[4] which supports the present assumption that spin-orbit effects are not quenched for these weakly bound exciplexes. The big difference between the hydrogen and methane reactions occurs in the bond breaking region, where the transition state for the hydrogen reaction is lower in energy than the reactants, while for methane there is a significant barrier. The PCI-80 barrier corrected for spin-orbit and zero-point vibrational effects for C−H activation of methane is 12.8 kcal/mol with respect to the reactants and 15.4 kcal/mol with respect to the molecular exciplex. This result is consistent with the very low quantum yield for CH_4 activation. Another difference between the hydrogen and the methane reaction is that no stable molecular insertion complex is found for methane. At least at the MP2 level of geometry optimization, a starting point around an expected minimum led to a dissociation into HgH and a CH_3 radical. From the results in subsection b and in Table 1, it is known that the HgH + CH_3 dissociation product is lower than the $HgCH_3$ + H dissociation product by 5.3 kcal/mol at the PCI-80 level. Since the HgH_2 insertion product is only bound by 3.9 kcal/mol with respect to HgH + H dissociation, it is therefore not entirely surprising that the more facile methyl dissociation pathway open for $HgHCH_3$ leads to a disappearance of the insertion product minimum. The absence of this minimum could be the origin of the difference in products found for this reaction compared to the one for H_2.[4] For the H_2 reaction the presence of the $^3[Hg(H{-}H)]^*$ minimum leads to a slowing down of the reaction by the introduction of a torque on the system. This leads to rotational excitation of HgH and is the key to the trapping of this product. In contrast, for the R−H reaction the absence of this minimum means that the reaction will just roll over the HgH minimum and dissociate into free radicals.

The simplest explanation for the higher insertion barrier for the methane reaction than for the hydrogen reaction is the same as the one used to explain a similar behavior for transition metal complexes.[23,24] A hydrogen s-orbital is spherical and can overlap simultaneously with metal orbitals and with the s-orbital on the other hydrogen atom in H_2. Therefore, the metal−hydrogen bond can start to form as the H−H bond weakens. The methyl group, on the other hand, has a directed bond. This means that the methyl−hydrogen bond in methane must be broken to some extent and the methyl group tilted before the methyl radical orbital can start to overlap efficiently with metal orbitals. This tilting of the methyl group is what causes the barrier for the C−H insertion reaction. By the same reasoning the breaking of a C−C bond like the one in ethane should lead to even higher barriers since two methyl groups will have to tilt, rather than one as in methane. Higher barriers for breaking C−C bonds than C−H bonds are also found in calculations on this reaction for transition metal reactions,[23,24] and the activation of unstrained C−C bonds is rare. A good argument for this picture of the bond-breaking is given by the fact that the barrier for elimination of CH_4 is roughly half of the elimination barrier of ethane for many metals,[23,24] in line with there being half the number of tilting groups in methane. For the C−C insertion reaction between Hg* and ethane, all attempts to locate a transition state failed. The energy is very high in the C−C bond breaking region and geometry optimizations led to dissociation either into Hg* + C_2H_6 or into Hg* + CH_3 + CH_3. The very high barriers for C−C activation in ethane by Hg* is consistent with the lack of observation of this or similar reactions experimentally.

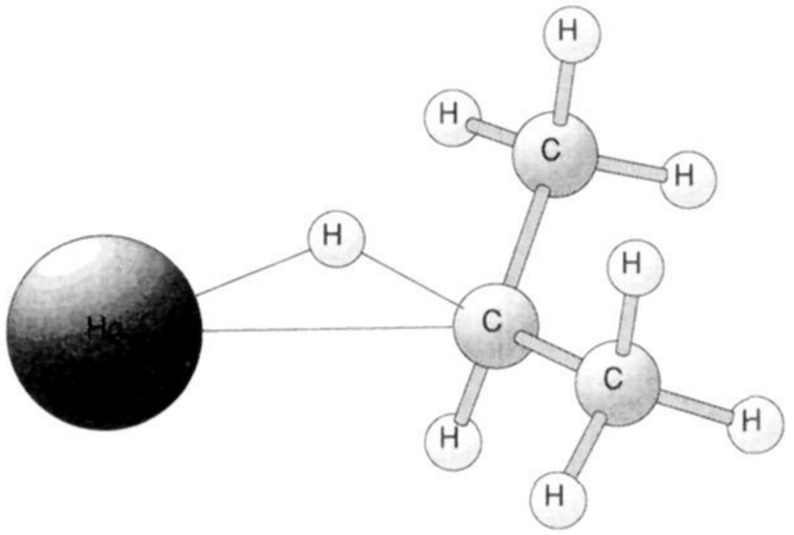

Figure 2. The transition state for the Hg* insertion into a C−H bond on the central carbon in propane. The distances between mercury and the active carbon and hydrogen are 2.91 and 1.83 Å, respectively. The distance between carbon and hydrogen is 1.54 Å.

e. Reaction between Hg* and C_3H_8. The C−H insertion reaction between Hg* and propane is an interesting test case of the present computational model. There are two main experimental facts about this reaction which are worth noting. First, propane is found to be much more easily activated than methane, and secondly, Hg* is known to preferentially break a C−H bond at the central carbon atom and thus form an isopropyl radical. In this context it is useful to know the calculated C−H bond strengths for the terminal carbon (100.6 kcal/mol) and for the central carbon (98.0 kcal/mol). Since the C−H bond in methane is 102.6 kcal/mol (calculated), the ease of activation of the C−H bonds follows the order of the bond strengths, as already mentioned in the introduction.

Three different forms of the Hg*−propane exciplex were investigated. In the first, Hg* is close to one of the C−H bonds on the central carbon atom. In the second, Hg* lies on the back side of the central carbon atom with an interaction to two of the terminal carbon C−H bonds. Finally in the third, Hg* interacts with a C−H bond on one of the terminal carbon atoms. The exciplex with lowest energy turns out to be the second with Hg* inside the C−C−C triangle on the back side of the central carbon. The PCI-80 binding energy for this structure is 5.6 kcal/mol which is 3.0 kcal/mol lower than for the exciplex with methane. The main reason the binding energy is larger than for methane is that for propane Hg* can interact equally strongly with two C−H bonds, one on each of the terminal carbons with an Hg−H distance of 2.81 Å. In this structure the C−H bonds that should be easiest to activate are thus on the terminal carbons, not on the central carbon. Hg* shows the largest interaction with one of the central C−H bonds in the first structure mentioned above, where the exciplex binding energy is 4.1 kcal/mol. In this structure Hg* interacts with only one of the C−H bonds with a Hg−H distance of 2.49 Å. Finally, the exciplex binding energy for the structure with Hg close to one of the terminal carbons is 3.7 kcal/mol, which is only 1.1

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(24) Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1984**, *106*, 8321. Low, J. J.; Goddard, W. A., III. *Organometallics* **1984**, *5*, 609. Low, J. J.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1986**, *108*, 6115.

kcal/mol more than what was obtained for methane. Here the shortest Hg−H distance is 2.69 Å.

It is interesting to compare the above exciplex structures with molecular alkane agostic type structures found for similar transition metal complexes. Several transition metal molecular alkane complexes have recently been optimized. For example, the complexes of methane, ethane, and propane with RhH(CO) and RhCl(CO) and those of a single palladium atom have been obtained at the same level of accuracy as used in the present study. There is one striking difference in this context. While transition metal atoms clearly have an attractive interaction directly with the hydrogen atoms, Hg* appears to interact more directly with the C−H bonds. There are a few examples where this difference is clearly illustrated. For the complex with Hg* outside the central carbon, Hg* prefers to interact with one C−H bond in an η^1 coordination, and Hg* is essentially outside the midpoint of this bond with a Hg−H distance of 2.49 Å. The distance to the other hydrogen is very much longer, 3.94 Å. For the corresponding η^1 coordinated Rh and Pd transition metal complexes mentioned above, the optimal interaction is with a linear metal−H−C orientation. In the cases of η^2 coordination in these transition metal complexes, the metal−hydrogen distances were always found to be equal. From these examples it appears that the type of interaction is rather different. The most important interaction for Hg* is a donation from the 6p orbital over into the C−H anti-bonding orbital, which is optimized with Hg* close to a midpoint of a C−H bond. For a transition metal the most important interaction is the one between the electrons on the hydrogen and an unshielded metal nucleus. The metal is able to move some of its electrons away from the metal−hydrogen region, mainly by sd-hybridization, and unshield the positive nucleus. There is hardly any electron transfer in this interaction, and the bonding is therefore mainly electrostatic. This type of interaction is less efficient for the Hg* systems mainly because the valence electrons in this case are triplet coupled, which prevents efficient hybridization. In line with these differences between Hg* and transition metals the lengthening of the C−H bonds associated with the Hg* interaction is also different, less than 0.01 Å for the present systems, from what it is in the corresponding agostic lengthening of the C−H bonds found in transition metal complexes, where it can typically be on the order of 0.05 Å. It should be noted that in spite of the difference in the character of the interaction, the size of the binding energies for Hg* and for transition metal atoms are quite similar. For example, a calculation on the agostic interaction between a palladium atom and methane gave a binding energy of 3.4 kcal/mol,[25] which is rather close to the binding energy of 2.6 kcal/mol obtained here for Hg* and methane. For transition metal complexes alkane binding energies are commonly larger than 10 kcal/mol. It can be added that van der Waals attraction is also of importance for the bonding in these molecular Hg* exciplexes, but it is unlikely to be the only important interaction in this region. Donation back-donation also has to set in in this region since the R−H bond is eventually broken on the same potential surface. For comparisons to similar complexes of cadmium, see refs 26 and 27.

Two different transition states for C−H activation of propane were determined, one for activation of C−H on a terminal carbon and one on the central carbon. The lowest one of these was found to be activation of C−H on the central carbon with an energy which is 4.9 kcal/mol above the reactants. The geometry for this transition state is given in Figure 2. It can be seen in this figure that C−H activation occurs by what is closest to an insertion mechanism even though the Hg−C bond is rather long, 2.91 Å. The reaction does not go by energy transfer since the lowest excitation energy of alkanes is much higher than the energy available in Hg*. The energy for the other transition state at the terminal carbon was found to be 7.4 kcal/mol above the reactants. From the results discussed above it is further known that the corresponding exciplex binding energies are 3.7 kcal/mol for a terminal carbon and 4.1 kcal/mol for the outside approach on the central carbon. It should be remembered that the most strongly bound exciplex was found to be inside the C−C−C triangle with a binding energy of 5.6 kcal/mol and with closest interaction to the C−H bonds on the terminal carbons. If these transition state energies are compared to the energies of the corresponding molecular exciplexes discussed above, an activation barrier of 9.0 kcal/mol is found for a central C−H bond and one of 11.1 or 13.0 kcal/mol is found for a C−H bond of a terminal carbon depending on which exciplex minimum is used. Irrespective of how these barriers are counted it is thus clear that a C−H bond on the central carbon atom should be easiest to activate in agreement with experiments. It can also be concluded that the height of the barrier is more important than the size of the exciplex binding energy. If the latter energy would have been decisive, activation of a C−H bond on a terminal carbon would have been found experimentally since the exciplex binding energy is largest for that approach (inside the C−C−C triangle).

The results above are therefore in agreement with experiments that the central C−H bond should be easiest to activate. The results are also in agreement with experiments concerning the fact that propane is easier to activate than methane. The energy at the transition state for the propane reaction is 4.9 kcal/mol above the reactants compared to 12.8 kcal/mol for methane. The origin of this difference must be a more effective interaction between the Hg* 6p orbital with propane than with methane, which in turn probably has to do with the initially less negative charge on the central carbon atom in propane than the carbon atom in methane. This difference in charge permits the Hg* 6p electrons to enter more easily for propane. The larger size and the lower excitation energy for propane than for methane probably also contribute. It should be noted that the electron flow from Hg* to propane is still quite local since otherwise the C−C bonds should be broken instead. The C−C bonds are much weaker than the C−H bonds and the lowest excitation energy in propane is to a C−C antibonding orbital.

For the final part of the propane reaction with Hg* it can be concluded from the bond strengths in Table 1 that the total exothermicity is 17.5 kcal/mol which is substantially larger than for methane with 12.7 kcal/mol. This could also be a contributing factor for the observed difference between these reactions. A geometry optimization of an insertion complex for propane also led to a dissociation into products like in the case for methane. Again, the small Hg−C_3H_7 binding energy of 3.3 kcal/mol is apparently not enough to keep the system together.

f. Reaction between Hg* and SiH_4. In these final subsections a few other Hg* reactions, which have also been studied, will be briefly discussed. The reaction between Hg* and silane is one of these where reaction is observed to occur readily.[2] The calculations are in agreement with this finding, see Table 2 and Figure 1. The molecular exciplex, optimized at the MP2 level, is bound by 7.1 kcal/mol, which is 1.5 kcal/mol more than what was found for propane. The PCI-80 energy corrected for spin-orbit and zero-point vibrational effects for the transition state is 6.5 kcal/mol below the reactants. From the exciplex

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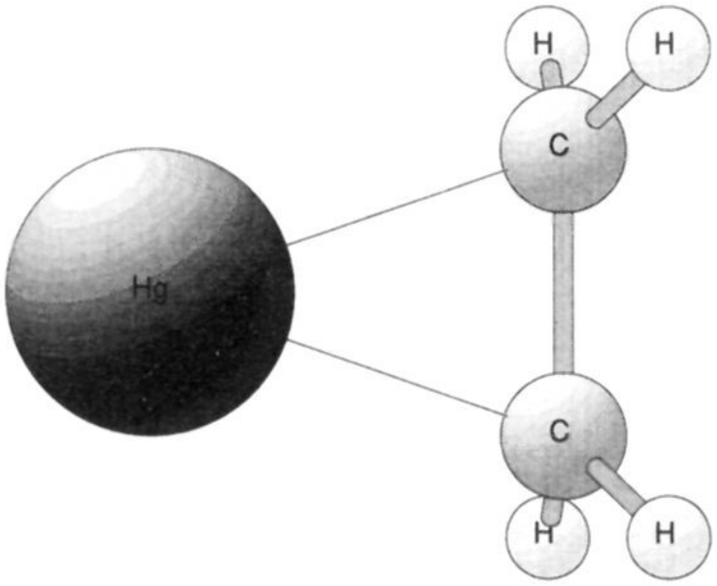

Figure 3. The π-complex between Hg* and ethylene. The mercury to carbon distance is 2.42 Å and the C−C distance is 1.50 Å.

there is thus a small activation barrier for the Si−H bond breaking of 0.6 kcal/mol. The potential surface for the silane reaction is similar to the one for molecular hydrogen discussed above. The exothermicity of the overall reaction for silane is as high as 27.6 kcal/mol, which is much more than for the other reactions studied here.

g. Triplet Sensitization of Ethylene. An important reaction in Hg* chemistry is triplet sensitization, in which Hg* attacks a double bond in an alkene and where the products are triplet alkene and ground state Hg,

$$Hg^* + C_2H_4 = {}^3[Hg(C_2H_4)]^* = Hg + C_2H_4^*$$

In the calculations on the model case of Hg* plus ethylene, a rather deep minimum is found for an $Hg^*{-}C_2H_4$ complex with a binding energy of 44.9 kcal/mol, including spin-orbit and zero-point vibrational effects. The geometric structure of this complex, which strongly resembles transition metal olefin π-complexes, is shown in Figure 3. From the donation back-donation that occurs, the C−C bond distance is increased to 1.50 Å from 1.37 Å for free ethylene obtained at the same level of accuracy. As a comparison the C−C bond distance in triplet ethylene is found to be 1.57 Å. The Hg−C distance in the π-complex is 2.42 Å. The 6s and 6p populations on mercury are 1.50 and 0.51, respectively. From this point the reaction then goes up in energy to the final Hg + $C_2H_4^*$ products with a final energy which is 29.4 kcal/mol below the reactants but 15.5 kcal/mol above the molecular exciplex. The overall reaction energy of 29.4 kcal/mol has been corrected for spin-orbit effects of 6.8 kcal/mol present for the reactants but missing for the products.

IV. Conclusions

There are many similarities between the reaction of Hg* with alkanes and the oxidative addition reaction known for transition metal complexes and alkanes. In particular for the H_2 reaction, the energetics of the reaction are quite similar to those for the many known transition metal examples of this reaction. In both cases the reaction proceeds via a molecularly bound precursor complex, separated by a small activation barrier from an insertion complex. A major important difference, of course, is that the Hg* reactions can then proceed to form atomic hydrogen radicals. This can happen because the mercury atom forms only very weak bonds, almost of van der Waals character. The reason for this is that Hg has a closed shell s^2 ground state with a very high excitation energy to a binding state, the Hg* ($6s^1$-$6p^1$) state. In the case of a transition metal complex the bond strengths are always quite large, for M−H typically on the order of 50 kcal/mol. The reason for this is that the transition metal complexes that are active in breaking bonds also have low excitation energies to binding states. A typical case is Rh(C_5H_5)(CO) with a singlet to triplet excitation energy of the order of 10 kcal/mol.[28]

The present calculations have shown that it is possible to obtain a quantitatively correct picture of these electronically quite complicated Hg* reactions. Both zero-point and spin-orbit coupling effects are very important for the energetics. The explicit treatment of spin-orbit effects is quite difficult and has not been carried out, but fortunately these effects are quite easy to estimate for these reactions. To a good approximation they have disappeared entirely for the products of the reaction where the bonding mercury state is the singlet $6s^2$ state. For the reactants and for the exciplexes the assumption that a spin-orbit averaged value is computed means that 6.8 kcal/mol should be subtracted from the computed energies for these systems. When this is done and zero-point vibrational effects are accounted for, the PCI-80 energies appear to give quite accurate energetics. Our good experience with this scheme for the lighter transition metal complexes[9] is thus now carried over to the heavier mercury-containing systems.

Acknowledgment. We thank a referee for pointing out some of the implications of the theoretical work mentioned in the text.

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