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Reductive hydrogen elimination by an iron metal center. Fe^q (q=+1,0,-1). A semiempirical molecular orbital study

Morella Sánchez[1*] *y Fernando Ruette*[2]
[1]*Departamento de Química, IUT Federico Rivero-Palacio, Apdo. 40347, Caracas, Venezuela*
[2]*Laboratorio de Química Computacional, Centro de Química, IVIC, Apdo. 21827 Caracas, Venezuela*

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Abstract

The present work deals with the applications of the semiempirical MINDO/SR method to study the reductive elimination of molecular hydrogen from $[H\text{-}Fe\text{-}H]^q$ and H + $[FeH]^q$ (q=-1, 0, +1) systems. In the case of the neutral molecule (H-Fe-H) a very high elimination barrier is observed. However, an excitation from the 2^5B_1 to the 1^5B_1 state will produce dissociation into Fe + H_2. For the negative molecule ($[H\text{-}Fe\text{-}H]^-$), the excited $^4B_2$ state can lead to the formation of Fe + H_2^- with an energy barrier of about 31 kcal/mol. The H_2 elimination from $[H\text{-}Fe\text{-}H]^+$ passes through an intermediate complex $[FeH_2]^+$ and exhibits an energy barrier of about 38 kcal/mol. This barrier can be surmounted because the formation of the dihydrogen complex is a highly exothermic process. The reaction of H with $[FeH]^q$ (q = -1, 0, +1) leads to hydrogen elimination, if the geometry of the collision permits the interaction between the hydrogens. Otherwise, the reaction product will be $[H\text{-}Fe\text{-}H]^q$ (q =-1, 0) for large H---$[Fe\text{-}H]^q$ approach angles.

Key words: Reductive elimination; semiempiric MINDO/SR method.

Eliminación reductiva de hidrógeno por un centro metálico de hierro. Fe^q (q=+1,0,-1). Estudio semiempírico basado en la teoría de orbitales moleculares

Resumen

El presente trabajo es una aplicación del método semiempírico MINDO/SR que trata sobre el estudio de la eliminación reductiva de hidrógeno molecular a partir de los sistemas $[H\text{-}Fe\text{-}H]^q$ y H + $[FeH]^q$ (q=-1, 0, +1). Para el caso de la molécula neutra (H-Fe-H) se observa una alta barrera de eliminación. Sin embargo, una excitación del estado 2^5B_1 a 1^5B_1 produce disociación a Fe+ H_2. Para la molecula negativa ($[H\text{-}Fe\text{-}H]^-$), el estado excitado $^4B_2$ conduce a la formación de Fe + H_2^- con una barrera de energía de 31 kcal/mol. La eliminación de H_2 a partir de $[H\text{-}Fe\text{-}H]^+$ pasa a través de un complejo intermediario $[FeH_2]^+$ y muestra una barrera de energía de 38 kcal/mol. Esta barrera puede ser superada debido a que la formación del complejo dihidrógeno es un proceso altamente exotérmico. La reacción de H con $[FeH]^q$ (q = -1, 0, +1) conduce a la eliminación de

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[*] Autor para la correspondencia.

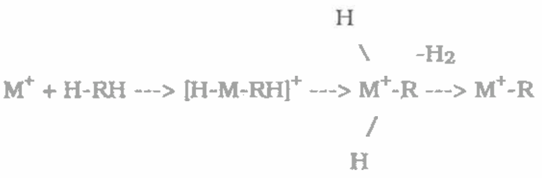
hidrógeno si la geometría de las colisiones permiten la interacción entre los hidrógenos. En otros casos, el producto de la reacción es $[H\text{-}Fe\text{-}H]^q$ (q =-1, 0) para ángulos grandes de acercamiento de $H\text{---}[Fe\text{-}H]^q$.

Palabras clave: Eliminación reductiva; método semiempírico MINDO/SR.

Introduction

The oxidative addition and reductive elimination of hydrogen by a metallic center and the formation of metal hydride and metal dihydrogen intermediates are of great interest in organometallic chemistry, heterogeneous catalysis, and experimental ion beam investigations (1-8).

Many dehydrogenation reactions of alkanes proceed by interaction with metal ions. Oxidative insertion of positive metal ions, such as iron, into the C-H and C-C bonds of alkanes has been largely studied in the gas phase (1-8). In general, the oxidative addition of metal ions occurs across the C-H bond is followed by a β-hydride shift onto the metal. The reaction mechanism goes through an intermediary, with two hydrogens bonded to the metal that subsequently undergoes a reductive elimination of hydrogen (9-10):

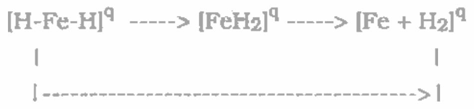


$$M^+ + H\text{-}RH \text{--->} [H\text{-}M\text{-}RH]^+ \text{--->} \overset{H}{\underset{H}{M^+}}\text{-}R \xrightarrow{-H_2} M^+\text{-}R$$

As far as we know, an analysis of energetic and geometrical factors that influence the H_2 formation from [illegible] adducts, in different electronic environments, has not been completed yet. Modifications of the electronic distribution on a modeled center site can be carried out by a [illegible] number [illegible] ligands, modifying the electronic charge, or changing the electronic state. Theoretical calculations have been carried out using one single metal atom as a model of an adsorption site, for example, H_2 on Ni (11) and $[Fe]^q$ (q = -1, 0, +1) (12); O_2 on $[Fe]^q$ (q = -1, 0, +1, +2) (13); $[Co]^q$ (q = -1, 0, +1, +2, +3) (14), and $[Ni]^q$ (q = 0, +2) (15); N_2 on $[Fe]^q$ (q =-1, 0, +1) (16); and CH_4 on $[Fe]^q$ (q=-1, 0, +1) (17). In these calculations, different electronic environments in the adsorption site have been considered by varying the charge and the electronic state.

There is experimental evidence for the formation of mononuclear iron complexes with metal hydrogen bonds. The oxidative insertion of iron into a C-H bond of CH_4 has been reported in FeO^+ (18, 19) and in a photoexcited neutral Fe atom (20,21). The reaction of Fe^+ with methane or ethane is observed with an electronically or translationally excited single Fe^+ atom (4). Otherwise, Fe^+ reacts exothermically with alkanes larger than ethane. In the case of a negative ion, McDonald et al. (22) showed that the $(CO)_2Fe^-$ complex reacts with H_2 to produces $(OC)_2Fe(H_2)^-$ and $(OC)_2Fe(H_4)^-$. The reaction of this complex with methane produces $(OC)_2Fe(CH_4)^-$; with acyclic and cyclic alkanes it yields the corresponding adducts $(OC)_2Fe(R)^- + H_2$.

In a recent paper (12), we have presented theoretical calculations for the oxidative addition reaction of H_2 with a single iron atom in different oxidation states. Here, we discuss the inverse process, i.e. the elimination of hydrogen from $[FeH_2]^q$ systems (q=0,+1,-1), including the possibility of the formation of $Fe(H_2)$ adducts. In addition, hydrogen elimination by the interaction between a hydrogen atom and a $[FeH]^q$ molecule is explored, in order to simulate the formation of FeH_2, H-Fe-H, and $[Fe + H_2]^q$ species in the reaction of -hydrogen in alkanes with a metallic center. The following processes were studied:



$$\begin{tikzcd} {[H\text{-}Fe\text{-}H]^q} \arrow[r] \arrow[rr, bend right] & {[FeH_2]^q} \arrow[r] & {[Fe + H_2]^q} \end{tikzcd}$$

|--------> $[FeH_2]^q$------->|
| |
H + $[Fe-H]^q$-------------->$[Fe + H_2]^q$
| |
|-------> $[H-Fe-H]^q$----->|

Methodology

Calculations were carried out with the semiempirical SCF MINDO/SR method. Details of the method have been reported previously (23). These include symmetry-adapted functions and selective occupation of molecular orbitals, which permits us to maintain, in most of the cases, fixed electronic states along the reaction coordinate. The calculated Fock matrix, at a given point, is used as the initial guess for the next point in the H_2 elimination curves, assuring the convergence to a selected electronic state. The parameters used in this work are presented elsewhere (12). The reference state used for the Fe atom corresponds to a $^5F(d^7s^1)$, because it is well-known that an electronic promotion s^2d^6 --> s^1d^7 (24-25) is required to bind Fe with a ligand.

Results and Discussion

Elimination of H_2 from $[FeH_2]^q$

In order to study the reductive elimination reaction of $[FeH_2]^q$ systems (q=0,+1,-1), potential energy curves were calculated as a function of the distance between the iron atom and the dihydrogen molecule. The resultant curves for the most significant states of neutral, negative and positively charged systems (12) are shown in Figures 1, 2 and 3, respectively.

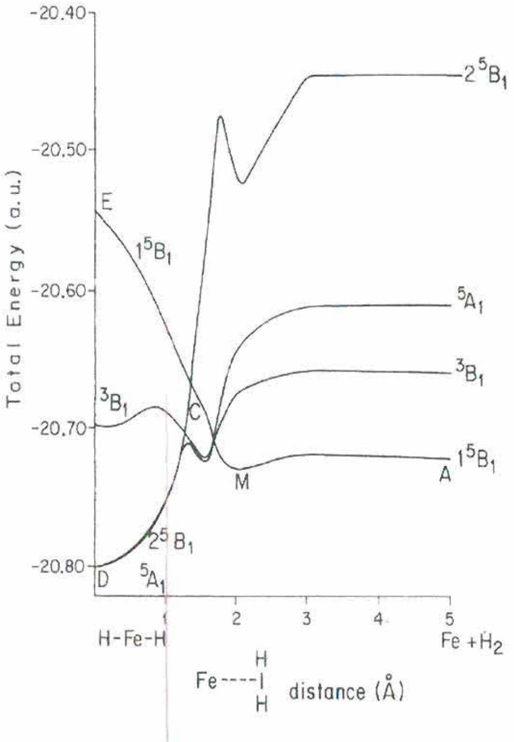


Figure 1. Potential Energy Curves for the Reductive Elimination of H_2 from $[FeH_2]^0$.

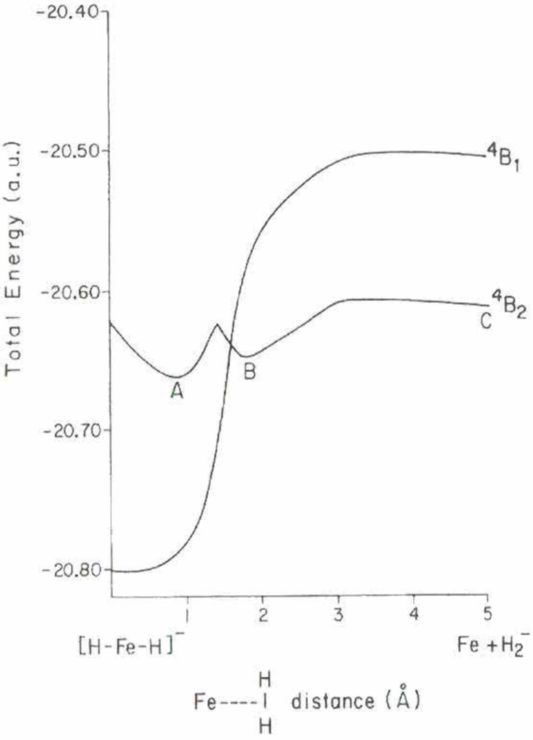


Figure 2. Potential Energy Curves for the Reductive Elimination of H_2 from $[FeH_2]^-$ system.

The H_2 elimination of the neutral HFeH molecule, in its most stable state (2^5B_1), associated to the electronic configuration $\alpha{:}3a_12b_1a_2b_2$; $\beta{:}a_12b_1$, presents a barrier of about 85 kcal/mol, as can be seen from points D, C and A in Figure 1. A vertical excitation (D->E) from this state to the excited 1^5B_1 state ($\alpha{:}4a_1b_1a_2b_2$; $\beta{:}2a_1b_1$) leads to a reductive elimination of H_2, with a small activation barrier (see points D, E, M and A in Figure 1). The HOMO orbital in the 2^5B_1 state is formed by the bonding combination between the p(Fe) atomic orbital with the antibonding combination (σ_u) of the hydrogens. The LUMO orbital in the 1^5B_1 state is the antibonding combination of the s-p(Fe) atomic orbitals on the iron with the bonding (σ_g) combination of the hydrogens. So, this excitation (the transfer of an electron from b_1 (HOMO) in 2^5B_1 to an orbital a_1 (LUMO) in 1^5B_1) favours the scission of the Fe-H bond and the formation of the H-H molecule. This result agrees with experimental results of reductive elimination of dihydrogen from photoexcited FeH_2, reported by Ozin and McGraffrey [9] in solid matrices at 12 K. The stability of FeH_2 (high reaction barrier) with respect to reductive elimination of H_2 has also been observed by Halle et al. [10], using guided ion beam techniques.

The dissociation limit for each state is different because the symmetry and the multiplicity are maintained along the hydrogen recombination pathway. Thus, 2^5B_1 ends up with $Fe(p^1d^7)$ + $H_2{}^*(\sigma_g\ \sigma_u)$ and 1^5B_1 with $Fe(s^1d^7)$ + H_2. Another two stable states ($^5A_1$ ($\alpha{:}3a_12b_1a_2b_2$; $\beta{:}2a_1b_1$) and $^3B_1$ ($\alpha{:}3a_1b_1a_2b_2$; $\beta{:}3a_1b_1$)) were also included here; however, both lead to highly endothermic elimination processes. The dissociation limit for $^5A_1$ was a quintuplet $Fe(p^1d^7)$ + H_2, and for $3B_1$ a triplet $Fe(s^1d^7)$ + H_2.

The potential energy curves for the reductive elimination of negatively charged $[FeH_2]^-$ species, in the two most significant states, according to previous work [3b], are shown in Figure 2. The most stable state ($^4B_1$, with the configuration $\alpha{:}3a_12b_1a_2b_2$; $\beta{:}2a_12b_1$) leads to a negatively charged H_2 molecule and an excited $Fe(d^7p^1)$ atom, through a very high activation barrier. The dissociation of the H-H bond in the $^4B_1$ state is highly favoured respect to H_2 recombination, because part of the electronic charge in the system is transferred to the $H_2(\sigma_u)$ molecular orbital, weakening the H-H bond.

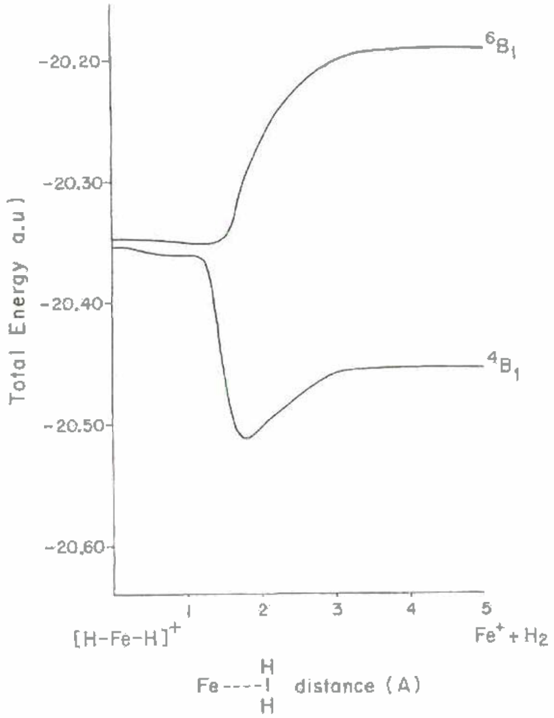


Figure 3. Potential Energy Curves for the Reductive Elimination of H_2 from $[FeH_2]^+$.

If an electron is supplied to the neutral 1^5B_1 state, an a_2 orbital will be filled, and then the system will arrive to the $^4B_2$ state. This excited state ($^4B_2$) with a configuration ($\alpha{:}4a_1b_1a_2b_2$; $\beta{:}2a_1b_1a_2$), exhibits two stable bent geometries (see points A and B in Figure 2.) with respect to Fe + $H_2{}^-$. The recombination process requires to surmounting two barriers: one of about 25 kcal/mol in going from A to B, and the other of 31 kcal/mol from B to C. This process leads to a neutral (d^7s^1) atomic iron and a negatively H_2 charged molecule. There is no experimental data related to the recombination of hydrogen in $[HFeH]^-$. However, kinetic studies carried out by Pearson and Mauermann [11] for the reductive elimination of H_2 in monometallic iron complexes ($H_2Fe(CO)_4$), indicate an activation energy of 26 kcal/mol. Note that CO ligands are generally considered as electron donors and, therefore, the Fe atom will exhibit a partial negative charge in $H_2Fe(CO)_4$ [12].

In the case of positively charged systems, two states ($^4B_1$ (α:$3a_1b_1a_2b_2$; β:$2a_1b_1$) and $^6B_1$ (α:$3a_12b_1a_2b_2$; β:$2a_1$)) were analyzed. It can be seen in Figure 3 that, in the $^4B_1$, state a relatively stable dihydrogen adduct can be formed in the interaction between Fe^+ and H_2. Therefore, an energy barrier for hydrogen elimination is observed (about 38 kcal/mol). There is experimental evidence of the formation of dihydrogen adducts in positively charged mononuclear iron complexes such as $[FeH(H_2.)(dppe)_2]^+$ [13].

Hydrogen elimination can be performed if one electron (b_1) is subtracted from the neutral [H-Fe-H] molecule in the $^5A_1$ (α:$3a_12b_1a_2b_2$; β:$2a_1b_1$) state [3b]. The resultant positively charged dihydride ($^4B_1$) may eliminate hydrogen, because the energy released by the formation of the dihydrogen complex is so high that the elimination barrier can be overcome. It is well established that hydrocarbons are dehydrogenated by Fe^+ [2]. The gas phase collision of an ion M^+ with an alkane molecule may produce adducts, with high internal energy that can be utilized for molecular rearrangement and fragmentation (M^+ + RHH --- $HMRH^+$ ----> $HHMR^+$ ----> H_2 + MR^+)[1c].

The other studied state ($^6B_1$) does not form adducts with H_2 and has a great tendency to form dihydride molecules with, of course, a very high elimination barrier.

Formation of H_2 from $[FeH]^q$ + H

The oxidative insertion of positive metals ions in alkanes is generally followed by a β-hydride transfer from the hydrocarbon to the metal, previous to the reductive elimination of hydrogen. Therefore, we studied the elimination of H_2 from the reaction of $[FeH]^q$ with an H atom and the formation of $[FeH_2]^q$ and $[HFeH]^q$ molecular complexes.

The potential energy curves for the reaction of an H_A atom with the neutral FeH_B molecule are shown in Figure 4. Two different approaches of the hydrogen atom (H_A) were considered. These approaches, and states, were chosen in such a way that the system arrived at the two geometries discussed in the last section (points D and M shown in Figure 1). The reaction coordinate, in the first case, corresponds to a hydrogen atom (H_A) approaching the Fe-H_B molecule by the opposite site to the H_B-iron bond. The FeH_B exhibits a $d^6\sigma_g2\sigma_u$ configuration where the iron atom has a $s^{1.1}p^{0.6}d^{6.0}$ population. This FeH_B configuration was selected as result of calculations in which H_A-Fe-H_B (2^5B_1) is dissociated in FeH_B + H_A. All coordinates were optimized, except the H-Fe-H angle. The results, shown in Figure 4, reveal that the formation of a linear H-Fe-H molecule is exothermic and occurs without activation barrier, for this special FeH state. As expected, the most stable state (2^5B_1) was obtained.

For the other reaction coordinate, the H_A atom is approached with an angle of 22° with respect to Fe-H_B (H-Fe-H angle in point M of Figure 1). The electronic configuration of the FeH molecule was $d^7\sigma_g2$ with an $s^{0.4}p^{0.3}d^{7.0}$ iron atom population. In this case the H_A-H_B bond starts to be formed at a distance H_A-Fe of about 3 Å. At slightly shorter distances, the Fe-H_B bond is weakened and the Fe-H_B distance varies from 1.5 Å to 2.0 Å. The H_2 molecule is formed and could be either eliminated with a small activation barrier, (see broken line depicted in Figure 4), or could be attached to the iron atom by forming a dihydrogen adduct, as shown in Figure 1 for the state 1^5B_1.

In the case of negatively charged systems, the calculated potential energy curves are depicted in Figure 5. Once again the

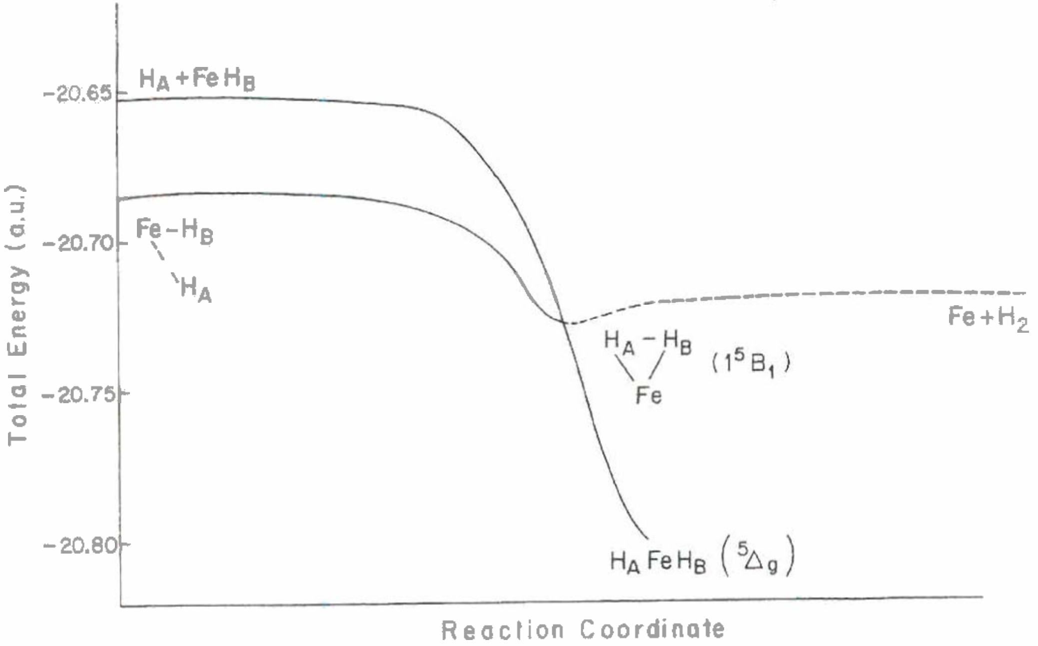


Figure 4. Potential Energy Curves for the Reductive Elimination of H_2 from $[FeH_B]^0 + H_A$ systems. Continuous line means that H_A is approaching to FeH_B. Dashed line represents H_2 going away from Fe.

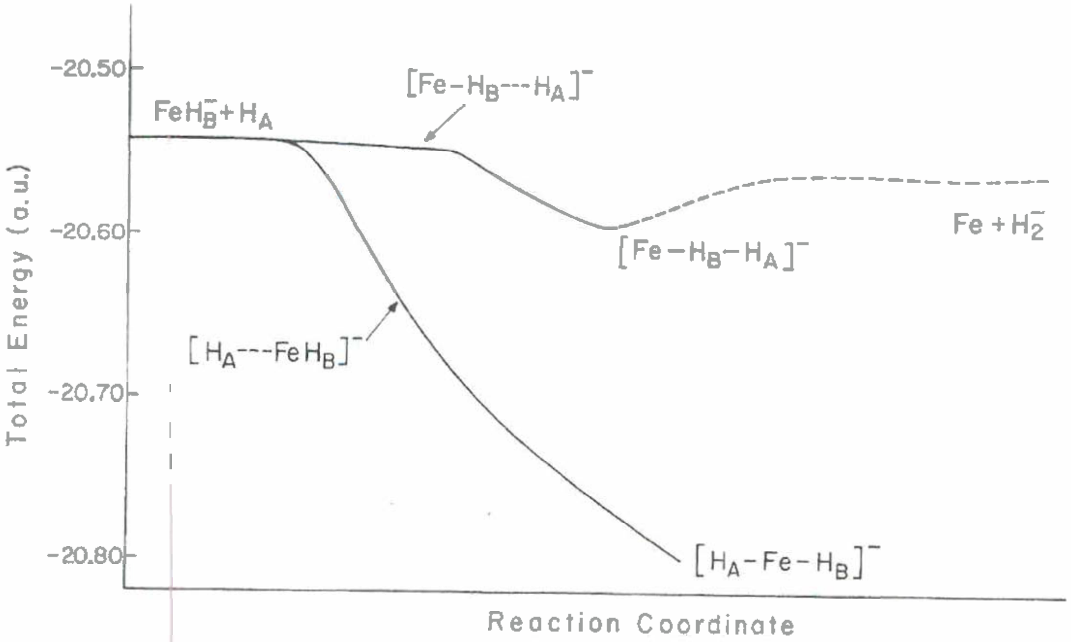


Figure 5. Potential Energy Curves for the Reductive Elimination of H_2 from $[FeH_B]^-$ + H_A systems. Continuous line means that H_A is approaching to $[FeH_B]^-$. Dashed line represents H_2- going away from Fe.

geometries were chosen in such a way the system will arrive at the most significant states. The $[FeH_B]^-$ configuration corresponds to a $d^7\sigma_g2\ \sigma_u$ with a $Fe(s^{1.0}p^{0.5}d^{7.0})$ atom. Two approaches were considered: one in which the H_A-Fe-H_B angle is 180° and other with an angle Fe-H_B-H_A of 180°. In the first case, the process is exothermic and the formation of a linear $[H\text{-}Fe\text{-}H]^-$ molecule occurs without an activation barrier, as in the neutral case. In the second case, the approach of the incoming hydrogen is on the side of the hydrogen atom in $[Fe\text{-}H_B]^-$ and it leads to the formation of a $[Fe\text{-}H\text{-}H]^-$ adduct. The Fe-H bond is weakened by the formation of the H-H bond, giving an activation barrier of about 17 kcal/mol for the dissociation of $[FeH_2]^-$ in Fe + H_2-. From the experimental point of view, the formation of a similar $[Fe\text{-}H_2]^-$ adduct has been reported in the reaction of the negative $(OC)Fe^-$ ion with H_2 ($(OC)_2Fe(H)_2$-) [14].

For positively charged systems, potential energy curves for two different approaches of a hydrogen atom (H_A) to the diatomic molecule $[FeH_B]^+$ are shown in Figure 6. The electronic configuration of $[FeH_B]^+$ resulted in a $d^7\sigma_g2$ where the Fe atom exhibits a $s^{0.8}p^{0.2}d^{6.0}$ electronic population. In one approach the H-H-Fe angle was 180°, in the other the chosen H-Fe-H angle was 22° (the geometry of the stable dihydrogen adduct shown on Figure 3). In both cases, the reactions are exothermic and the final products are Fe^+ and H_2. As the H_A atom approaches the $[Fe\text{-}H]^+$ molecule, the Fe-H_B bond is weakened and the H-H bond begins to be formed. The Fe-H_B bond length abruptly varies from about 1.47 Å to about 2.3 Å when the incoming atom is at a distance of about 2.5 Å. This is reflected in Figure4 by a large slope change in the potential energy curve. This means that the approaching H_A atom is able to relax the H_B atom bonded to the iron. Stable dihydrogen adducts are formed in all cases. The energies liberated in the $[FeH_B]^+ + H_A$ ----> $[Fe(H_2)]^+$ reactions are 96 and 108 kcal/mol for 180 and 22° approaches, respectively.

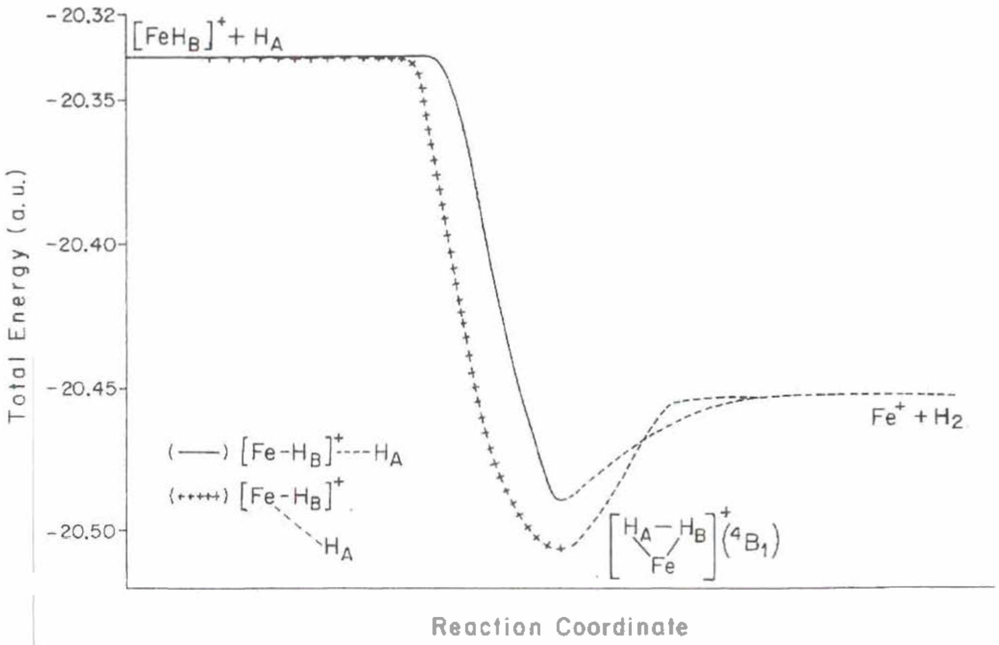


Figure 6. Potential Energy Curves for the Reductive Elimination of H_2 from $[FeH_B]^+ + H_A$ systems. Continuous line means that H_A is approaching to $[FeH_B]^+$. Dashed line represents H_2 going away from Fe^+.

This energy is enough to induce the dissociation of the molecular complex into $Fe^+ + H_2$.

The inverse reaction ($Fe^+ + H_2$ -----> $[FeH]^+ + H$), has been studied by Elkind and Armentrout [15] and by Halle et al. [10], using guided ion techniques. The variation of the cross section with the kinetic energy is characteristic of an endothermic reaction with a thermodynamic threshold equal to the bond energy of H_2 (104 kcal/mol), in agreement with our theoretical results.

To eliminate H_2 from $H + [FeH]^q$ it is necessary for the H atom bonded to the Fe in $[FeH_B]^q$ systems to interact with the incoming H atom. This only occurs when the angle of attack of the hydrogen atom is small. That would not be the case in the interaction between Fe^+ and methane. After the metal insertion, the H-Fe-H angle is so large that the intermediary would be a dihydride ($HHFeCH_2$) which must have a high H_2 elimination barrier, as shown above.

Conclusions

Hydrogen elimination from $[H\text{-}Fe\text{-}H]^q$ (q=-1,0,+1) molecules is feasible mainly for positively charged systems. In this case, the formation of the $[Fe(H)_2]^+$ complex from $[H\text{-}Fe\text{-}H]^+$ is highly exothermic and the system may retain enough internal energy to eliminate H_2.

Excited [H-Fe-H] and $[H\text{-}Fe\text{-}H]^-$ systems are able to eliminate H_2. In the neutral case, no elimination barrier was observed. On the other hand, a barrier of 31 kcal/mol for the reaction $[H\text{-}Fe\text{-}H]^-$ -----> $[Fe\text{-}H_2]^-$ ----->$Fe + H_2^-$ was calculated.

The elimination of H_2 from $H^- + [FeH]^q$ occurs if the angle of attack of the hydrogen atom is small. At large angles, close to 180, the tendency is to produce $[H\text{-}Fe\text{-}H]^q$ systems.

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