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The activation of the C–H bond in acetylene by second row transition metal atoms

P. E. M. Siegbahn

Institute of Theoretical Physics, University of Stockholm, Vanadisvägen 9,
S-11346 Stockholm, Sweden

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Summary. The C–H activation reaction of acetylene by second row transition metal atoms has been studied including electron correlation of all valence electrons. Binding energies have been computed for both π-coordinated complexes and C–H insertion products. It is found that for most atoms the π-coordinated complexes are thermodynamically favoured, just as in the case for the corresponding ethylene reaction. The barrier height for the C–H insertion increases from acetylene to ethylene and to methane. This is in line with the experimental finding that there should be an inverse relation between C–H bond strengths and the difficulty to activate these bonds. To explain the detailed differences between the C–H activation of acetylene and ethylene, the interaction with two, rather than one, π- and π^*-orbitals for acetylene is of key importance. The barrier height for the acetylene reaction increases significantly between niobium and molybdenum going to the right in the periodic table, just as for all oxidative addition reactions previously studied. The origin of this increase is that noibium has one empty $4d$-orbital but for molybdenum all $4d$-orbitals are occupied. Rhodium has the lowest barrier for C–H activation for all systems studied.

Key words: Acetylene – C–H bond – 2nd row transition metals – Activation

1 Introduction

The present issue of this journal is dedicated to Inga Fischer–Hjalmars. This paper which is devoted to a number of reactions involving second row transition metal complexes, is perhaps not directly connected to her work but two clear parallels can still be noted. A large part of Inga Fischer–Hjalmars' work during the last thirty years has been concerned with systems containing metals, mostly transition metals [1]. A difference is that her work has mostly dealt with reactions of biological interest, whereas the present work is related to processes of catalytical concern. This minor distinction is, moreover, basically a matter of time. A natural extension of the present work is towards enzymatic reactions of biological interest. A second parallel between Inga Fischer–Hjalmars' work and the present work concerns the state of quantum chemistry two to three decades ago, in Inga Fischer–Hjalmars'most active period, and the present situation. *Ab initio* theory finds itself today in a similar situation to the one of semi-empirical theory during the 1960's. Semi-empirical theory had gone through a period of intense method development [2], reaching a stage where the methods could no longer be significantly improved. Many quantum chemists feel that the situation for *ab initio* theory is similar today. Inga Fischer–Hjalmars' work on systems of biological interest was one attempt to lead quantum chemistry into a different direction and to apply the methods that had been developed on significant chemical problems. This work is part of a comparable attempt.

The present study on the activation of the C–H bond in acetylene by second row transition metal atoms is part of a series of similar investigations. Among the previously published studies the ones that are most directly related to the present work are the activations of the C–H bonds in methane [3] and in ethylene [4, 5]. There are also clear parallels to the results on the O–H activation of water [6] and the N–H activation of ammonia [7]. All these studies contain results for the entire sequence of second row transition metal atoms. It has been demonstrated in previous studies by Bauschlicher, Langhoff and coworkers [8] and by our group [3–7] that this is a very useful approach to obtain a quantitative analysis of the energetics in reactions involving transition metals. For example, this approach allows for a systematic evaluation of the importance of the positions of the various atomic states on the metal atom for the bonding. Also, the effects of a continuous increase of the ionization potential and an increase of the number of *d*-electrons of the metal can be investigated by going from left to right across the row in the periodic table.

The C–H bond in acetylene is one of the strongest known C–H bonds with a bond-energy of 140 kcal/mol (D_e) [9]. As a comparison, the C–H bond in methane has a bond-energy of 112 kcal/mol and the C–H bond in ethylene one of 118 kcal/mol. Yet, the acetylinic C–H bond is considered so much easier to activate by transition metal complexes that acetylene is regarded as belonging to a different class of molecules in this respect than, for example, alkanes and alkenes [10]. This result is not unique in this context. In fact, one mystifying and surprising result that has emerged from the active research on the C–H oxidative addition reaction is that there is a rather general anti-correlation between the initial C–H bond strength and the difficulty to activate this bond by transition metal complexes [11]. C–H bonds considered in this anti-correlation are the ones in methane, in ethylene, in benzene, in progressively larger alkanes and in substituted alkanes. The C–H bond in acetylene is thus an extreme case since it is one of the strongest C–H bonds known. It should be noted that most observations of C–H activation of acetylene have been made in solution where a two-step process is the most likely mechanism. In the first step of this process acetylene just looses a proton and this occurs rather easily since acetylene is quite acidic. This mechanism can obviously not be in operation in the gas phase and the present calculations, which do not model the effects of the solution, can therefore not be directly compared to these solution experiments.

There are obviously many similarities between the present study of the C–H activation of acetylene and the previous study of the C–H activation of ethylene [5, 6]. In the case of ethylene, there are very few examples where C–H activation has actually been observed experimentally. An interesting finding in our previous study is that this is often not due to large barriers for the reaction, but rather due to the fact that the formation of the π-complex is more favourable. For the acetylene reaction the same type of competition exists between the formation of C–H insertion products and of π-complexes, and an important part of the present study is therefore to determine the relative energies between these two types of complexes.

2 Computational details

In the calculations reported in the present paper for the C–H activation of acetylene by the second row transition metal atoms, the same standard basis sets were used as in all the previous similar studies [3–7]. In some calculations, which are used as benchmarks, larger basis sets were employed. All valence electrons were correlated and size-consistent correlation methods were used.

For the metals the Huzinaga primitive basis [12] was extended by adding one diffuse *d*-function, two *p*-functions in the 5*p*-region, and three *f*-functions, yielding a (17*s*, 13*p*, 9*d*, 3*f*) primitive basis. The core orbitals were totally contracted [13] except for the 4*s*- and 4*p*-orbitals which have to be described by at least two functions each to properly reproduce the relativistic effects. The 5*s*- and 5*p*-orbitals were described by a double zeta contraction and the 4*d* by a a triple zeta contraction. The *f*-functions were contracted to one function giving a (7*s*, 6*p*, 4*d*, 1*f*) contracted basis. For carbon the primitive (9*s*, 5*p*) basis of Huzinaga [14] was used, contracted according to the generalized contraction scheme to [3*s*, 2*p*] and one *d*-function with exponent 0.63 was added. For hydrogen the primitive (5*s*) basis from [15] was used, augmented with one *p*-function with exponent 0.8 and contracted to [3*s*, 1*p*]. These basis sets are used in the energy calculations for all systems, and these were performed using the STOCKHOLM set of programs [16] on the ALLIANT FX-80.

In the geometry optimizations, performed at the SCF level using the GAMESS set of programs [17], somewhat smaller basis sets were used. For the metals a relativistic ECP according to Hay and Wadt [18] was used. The frozen 4*s*- and 4*p*-orbitals are described by a single zeta contraction and the valence 5*s*- and 5*p*-orbitals are described by a double zeta basis and the 4*d*-orbital by a triple zeta basis, including one diffuse function. The rest of the atoms are described by standard double zeta basis sets.

The correlated calculations were in most cases performed using the Modified Coupled Pair Functional (MCPF) method [19], which is a size-consistent, single-reference state method. The zeroth-order wavefunction was determined at the SCF level. Relativistic effects were accounted for using first-order perturbation theory including the mass-velocity and Darwin terms [20].

In a few benchmark calculations on the palladium systems a larger basis set was used. For the metal the same primitive basis as above was used but the three *f*-functions were kept uncontracted. For carbon and hydrogen extended primitive basis sets were contracted using atomic natural orbitals (ANOs). For carbon a primitive (14*s*, 9*p*, 4*d*) basis was used and contracted to give [4*s*, 3*p*, 2*d*] and for hydrogen a (8*s*, 4*p*) basis was used and contracted to give [3*s*, 2*p*] [21]. For the closed-shell PdC_2H_2 systems these benchmark calculations were performed using the single and double excitation coupled-cluster (CCSD) method including a perturbational estimate of connected triple excitations, denoted CCSD (T) [22]. The difference in relative energy between these large calculations and the MCPF calculations using the standard basis obtained for palladium is used as a correction on the reaction energies. The same correction is used for all metals. This correction contains both the effects on the correlation energy from higher excitations and the effects due to the larger basis sets. The correction lowers the insertion barriers by 3.0 kcal/mol. The basis set effect is actually negative by 0.1 kcal/mol which just means that there is a smaller basis set superposition error (BSSE) for the larger basis set. The effect of higher excitations is 3.1 kcal/mol, counted as the difference between the CCSD (T) and the MCPF results using the large basis set. The binding energy of the insertion products is correspondingly increased by 1.8 kcal/mol, of which 0.1 kcal/mol is a basis set effect and 1.7 kcal/mol is the effect of higher excitations. Finally, for the π-bonded acetylene complex the correction is 1.1 kcal/mol. For this system the basis set effect is − 2.5 kcal/mol, indicating a relatively large BSSE for the smaller basis, while the effect of higher excitations is 3.6 kcal/mol.

3 Results and discussion

The oxidative addition reaction between transition metals and the C–H bond of acetylene competes with the formation of the π-coordinated complexes. For the naked metals atoms the π-complexes can be formed essentially without any barriers. The resulting binding energies and geometries for these complexes are given in Table 1 and the structure of a typical complex, that of zirconium, is shown in Fig. 1. The populations are given in Table 2 and the results are discussed in Sect. 3.1 below. The insertion products are discussed in Sect. 3.2 and the geometries

Table 1. Results for the acetylene coordination reaction: $M + C_2H_2 + \Delta E_c \rightarrow MC_2H_2$. The energies are calculated relative to free acetylene and ground-state metal atoms. The ΔE_c values include a correction of − 1.1 kcal/mol for higher excitation and basis set effects estimated from calculations on the PdC_2H_2 system (see Sect. 2)

Metal	State	Configuration	M–C [Å]	C–C [Å]	Tilt angle	ΔE_c [kcal/mol]	$\Delta E_c(C_2H_4)$ [kcal/mol]
Y	$^2A_1$	$\sigma^1 d_{b_2}^2$	2.23	1.37	53.7	− 48.6	− 22.3
Zr	$^3A_2$	$\sigma^1 d_{b_2}^2 d_{a_2}^1$	2.13	1.35	49.0	− 56.9	− 23.0
Nb	$^4A_2$	$\sigma^1 d_{b_2}^2 d_{a_2}^1 d_{a_1}^1$	2.09	1.35	47.5	− 52.2	− 23.6
Mo	$^5B_2$	$\sigma^1 d_{b_2}^2 d_{a_2}^1 d_{a_1}^1 d_{b_1}^1$	2.09	1.32	43.3	− 24.2	− 6.5
Tc	$^4B_1$	$\sigma^1 d_{b_2}^2 d_{a_2}^2 d_{a_1}^1 d_{b_1}^1$	2.05	1.31	39.5	− 15.3	− 0.4
Ru	$^3B_1$	$\sigma^1 d_{b_2}^2 d_{a_2}^2 d_{a_1}^2 d_{b_1}^1$	2.05	1.29	34.1	− 36.8	− 26.8
Rh[a]	$^2A_1$	$\sigma^1 d_{b_2}^2 d_{a_2}^2 d_{a_1}^2 d_{b_1}^2$	–	–	–	− 37.2	− 34.9
Pd[a]	$^1A_1$	$\sigma^2 d_{b_2}^2 d_{a_2}^2 d_{a_1}^2 d_{b_1}^2$	–	–	–	− 28.3	− 30.7

[a] Geometry taken from RuC_2H_2

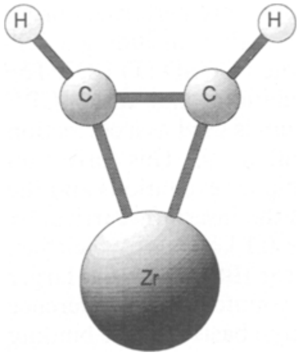

Fig. 1. The π-coordinated ZrC_2H_2 complex

Table 2. Mulliken populations (MCPF) for the ground states of the second row π-complexes of the MC_2H_2 systems

Metal	State	qM	$5s$	$5p$	$4d$	q(C)
Y	$^2A_1$	+ 0.31	0.92	0.40	1.28	− 0.24
Zr	$^3A_2$	+ 0.27	0.85	0.23	2.58	− 0.23
Nb	$^4A_2$	+ 0.24	0.64	0.11	3.96	− 0.21
Mo	$^5B_2$	+ 0.25	0.54	0.18	4.97	− 0.24
Tc	$^4B_1$	+ 0.24	0.42	0.14	6.14	− 0.25
Ru	$^3B_1$	+ 0.17	0.57	0.13	7.07	− 0.23
Rh	$^2A_1$	+ 0.15	0.35	0.15	8.28	− 0.21
Pd	$^1A_1$	+ 0.15	0.34	0.13	9.31	− 0.23

Table 3. Geometries and energies for the ethynyl-hydride products of the C–H insertion reaction: $M + C_2H_2 + \Delta E_c \rightarrow MHC_2H$. The energies are calculated relative to ground-state metal atoms and free acetylene. The ΔE_c values include a correction of − 1.8 kcal/mol for higher excitation and basis set effects estimated from calculations on the $PdHC_2H$ system (see Sect. 2). C_1 and H_1 are the carbon and hydrogen atoms closest to the metal atom

M	State	M–C_1 [Å]	M–H_1 [Å]	$\angle(C_1\text{–}M\text{–}H_1)$ degrees	$\angle(M\text{–}C_1\text{–}C_2)$ degrees	C_1–C_2 [Å]	ΔE_c [kcal/mol]	$\Delta E_c(C_2H_4)$ [kcal/mol]
Y	$^2A'$	2.32	2.01	122.2	179.1	1.22	− 41.4	− 21.1
Zr	$^3A''$	2.25	1.93	131.1	176.9	1.22	− 40.5	− 24.2
Nb	$^4A''$	2.19	1.86	130.5	177.3	1.22	− 35.3	− 20.3
Mo	$^5A'$	2.13	1.76	113.8	177.5	1.22	− 11.1	3.5
Tc	$^6A'$	2.19	1.83	180.0	180.0	1.22	− 19.1	0.9
Ru	$^3A''$	2.02	1.61	99.4	178.3	1.22	− 15.5	− 7.5
Rh	$^2A'$	2.02	1.52	86.8	177.4	1.22	− 25.5	− 16.7
Pd	$^1A'$	1.95	1.50	79.2	176.4	1.21	− 5.4	− 2.2

and binding energies of these systems are given in Table 3. A typical structure is shown for yttrium in Fig. 2 and the populations are given in Table 4. Finally in Sect. 3.3, the transition states and the barrier heights for the oxidative addition reaction are discussed, and these results are given in Table 5. The corresponding populations are given in Table 6. A typical transition state structure is shown for rhodium in Fig. 3. The binding energy curves for the acetylene complexes are shown in Figs. 4–6, in which the corresponding results for ethylene and methane are also shown. Before these results are discussed it is useful to know the C–H bond strengths of the different hydrocarbons. The calculated C–H bond strengths are in acetylene 131.5 kcal/mol, in ethylene 113.4 kcal/mol, and in methane 108.0 kcal/mol. The differences between these bond strengths are rather close to those estimated in [9] based on larger calculations than the present ones. The present calculated absolute values for the C–H bond strengths are 5–8 kcal/mol smaller than the predicted best values.

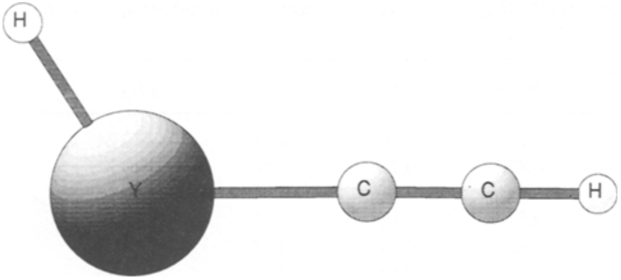

Fig. 2. The product of the C–H insertion reaction between yttrium and acetylene

Table 4. Populations for the ethynyl-hydride insertion products, MHC_2H. C_1 and H_1 are the carbon and hydrogen atoms closest to the metal atom

Metal(M)	M(q)	4d	5s	5p	$C_1(q)$	$C_2(q)$	$H_1(q)$	$H_2(q)$
Y	+.42	1.05	.94	.52	−.20	−.24	−.16	+.18
Zr	+.40	2.28	.86	.41	−.21	−.19	−.18	+.18
Nb	+.37	3.47	.77	.35	−.26	−.14	−.16	+.18
Mo	+.28	4.71	.70	.27	−.22	−.13	−.10	+.17
Tc	+.40	5.22	.81	.53	−.30	−.12	−.16	+.17
Ru	+.15	6.98	.61	.21	−.17	−.15	−.00	+.17
Rh	+.06	8.14	.51	.22	−.13	−.17	+.06	+.17
Pd	+.08	9.12	.54	.19	−.14	−.17	+.06	+.17

Table 5. Transition state geometries and barrier heights for the C–H insertion reaction: $M + C_2H_2 + \Delta E_c \rightarrow MHC_2H$. The energies are calculated relative to ground-state metal atoms and free acetylene. The ΔE_c values include a correction of −3.0 kcal/mol for higher excitation and basis set effects estimated from calculations on the $PdHC_2H$ system (see Sect. 2). C_1 and H_1 are the carbon and hydrogen atoms closest to the metal atom

M	State	$M-C_1$ [Å]	$M-H_1$ [Å]	$\angle(C_1-M-H_1)$ degrees	$\angle(M-C_1-C_2)$ degrees	C_1-C_2 [Å]	ΔE_c [kcal/mol]	ΔE_c (C_2H_4) [kcal/mol]
Y	$^2A'$	2.30	2.16	41.7	178.8	1.27	5.3	15.1
Zr	$^3A''$	2.19	2.11	31.7	143.6	1.23	5.2	14.6
Nb	$^4A''$	2.31	2.09	29.0	141.4	1.21	10.8	6.1
Mo	$^5A'$	2.16	1.99	32.2	145.5	1.22	27.3	27.8
Tc	$^6A'$	2.17	1.68	45.3	168.3	1.22	16.7	27.3
Ru	$^3A''$	2.02	1.64	45.9	166.6	1.22	−2.0	8.0
Rh	$^2A'$	2.00	1.60	46.4	168.0	1.22	−12.9	−2.3
Pd	$^1A'$	1.97	1.53	57.7	171.3	1.21	−4.1	0.3

Table 6. Populations at the transition states of the acetylene C–H insertion reaction. C_1 and H_1 are the carbon and hydrogen atoms closest to the metal atom

Metal(M)	M(q)	4d	5s	5p	$C_1(q)$	$C_2(q)$	$H_1(q)$	$H_2(q)$
Y	+.22	1.20	1.04	.46	−.10	−.28	−.01	+.17
Zr	+.09	2.56	1.06	.24	−.14	−.21	+.07	+.19
Nb	+.00	3.72	1.05	.19	−.17	−.16	+.13	+.20
Mo	+.14	5.19	.50	.12	−.18	−.20	+.06	+.18
Tc	+.10	5.42	.92	.51	−.25	−.11	+.07	+.19
Ru	+.11	7.31	.36	.16	−.18	−.18	+.07	+.17
Rh	+.07	8.33	.37	.18	−.15	−.18	+.09	+.18
Pd	+.09	9.22	.44	.18	−.17	−.15	+.06	+.17

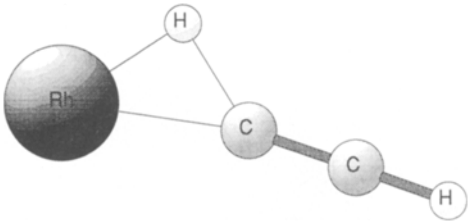

Fig. 3. The transition state structure for the C–H insertion reaction between rhodium and acetylene

3.1 *The π-coordinated complexes*

Before the results of the π-coordinated acetylene complexes are discussed, the results of the previously studied ethylene complexes (also given in Table 1) will be briefly reviewed. The ethylene complexes are most strongly bound for the atoms to the right. For these atoms efficient donation–backdonation bonds can be formed using a 4d-orbital for backdonation which is doubly occupied in the ground state of the atom. The ground states of the atoms to the left do not have doubly occupied 4d-orbitals and the bonding in these complexes is therefore of a more classical covalent type. The structures formed for these atoms are best described as metallacycles where the C–C π-bond has been entirely broken. This is seen on the resulting C–C distances which are typical of single bonds. The binding energies of the π-complexes to the left are 5–10 kcal/mol smaller than those for the atoms to the right. The atoms in the middle of the row, finally, form weakly bound complexes. The bonding is weak because for these atoms, which have many unpaired 4d-electrons in their atomic ground states, there is a large loss of exchange energy when the bonds are formed.

There are many similarities between the results for the π-complexes of ethylene and acetylene but also some major differences. The main difference is perhaps that for the acetylene complexes the bonding is much stronger to the left than to the

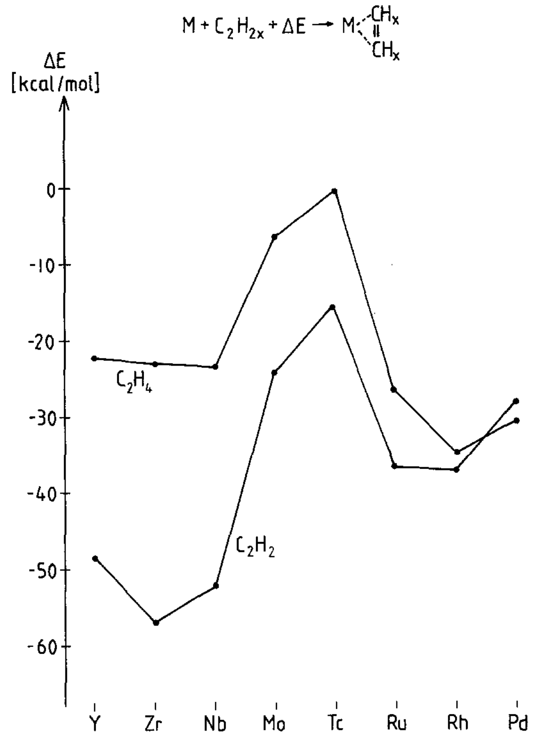

Fig. 4. The binding energy curves for the π-coordinated complexes of acetylene and ethylene

right. For example, for zirconium the binding energy is as large as 56.9 kcal/mol compared to that of rhodium which is only 37.2 kcal/mol. The corresponding binding energies for the ethylene complexes are 23.0 kcal/mol for zirconium and 34.9 kcal/mol for rhodium. Another related difference is that for acetylene there is not such a pronounced minimum in the binding energies in the middle of the row as there is for ethylene. For example, if molybdenum and palladium are compared, the acetylene complexes have similar binding energies with 24.2 kcal/mol and 28.3 kcal/mol, respectively, whereas the corresponding ethylene complexes are bound by 6.5 kcal/mol and 30.7 kcal/mol. These differences are easy to understand if the bonding is studied more in detail and is a good illustration of the usefulness of the present systematic approach where sequences of atoms are studied.

To explain the above differences it is useful to note how the 4*d*-orbitals are gradually occupied as one goes from left to right in the row. For both acetylene and ethylene, the first orbitals to be occupied are an a_1-orbital and a b_2-orbital which form the two covalent bonds in the metallacycle. The a_1-orbital has a mixture of 4*d*- and 5*s*-character on the metal while the b_2-orbital has metal 4*d*-character. The next orbital to be occupied is another a_1-orbital (denoted σ in Table 1) which also accommodates some of the metal 5*s*-electrons. These three orbitals are thus occupied for the yttrium complexes of both ethylene and acetylene and still there is a very large difference in binding energy of the two complexes with 22.3 kcal/mol for the ethylene complex and 48.6 kcal/mol for the acetylene complex. The origin of this difference is the different character of the interaction among the orbitals which are of π-symmetry with respect to the MCC-plane. For the acetylene complex there

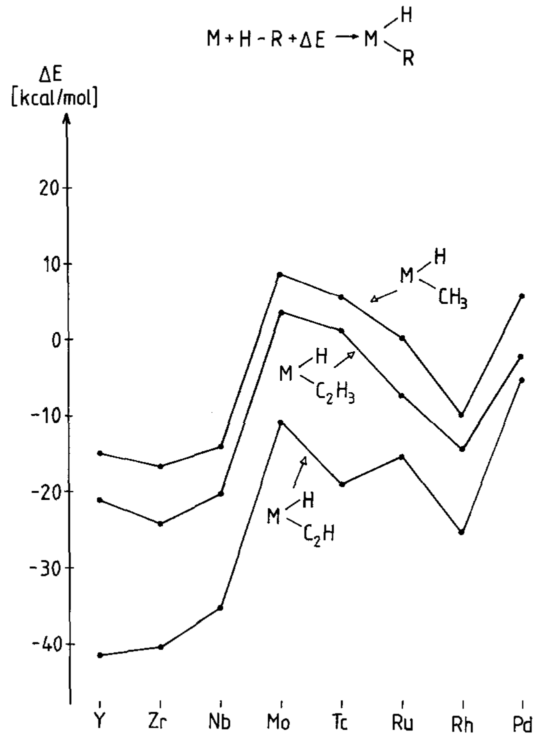

Fig. 5. The binding energy curves for the C–H insertion products of the reaction with acetylene, ethylene and methane

is an attractive interaction between the out-of-plane π-orbital and an empty $4d$-orbital on the metal, which is much more favourable than the interaction between the metal and the C–H bonding orbitals of ethylene, which explains the binding energy difference. The first difference in the filling of the $4d$-orbitals between the acetylene and the ethylene complexes appear for the zirconium complexes. For ethylene the next orbital to be filled is the $4d_{b1}$-orbital, which is the $4d$-orbital with least repulsion towards ethylene. The small repulsion from this orbital can be seen on the binding energies of the yttrium and zirconium ethylene complexes which are almost the same. For acetylene, on the other hand, the next orbital to be filled is the $4d_{a2}$-orbital. The reason for this difference is that the $4d_{a2}$-orbital can donate electrons into the empty out-of-plane π^*-orbital of acetylene. This is an attractive interaction which can be seen on the increase in the interaction energy between the yttrium and zirconium acetylene complexes from 48.6 kcal/mol to 56.9 kcal/mol. The minimum in the binding energy curve of the acetylene complexes for zirconium can be clearly seen in Fig. 4 and is contrasted to the behaviour for the ethylene curve which is flat in this region.

For the complexes in the middle of the row there is a larger decrease in energy for acetylene than for ethylene. The reason for this difference is that the $4d_{b1}$-orbital is significantly more repulsive towards the out-of-plane π-orbital of acetylene than it is towards the C–H bonds of ethylene. However, the main origin of the decrease in binding energy for the atoms in the middle of the row is for both complexes a loss of exchange energy as the bonds are formed and a less favourable interaction between the ligand and the metal as all d-orbitals have become occupied. Going from left to right, niobium is the last metal with empty d-orbitals in its ground state

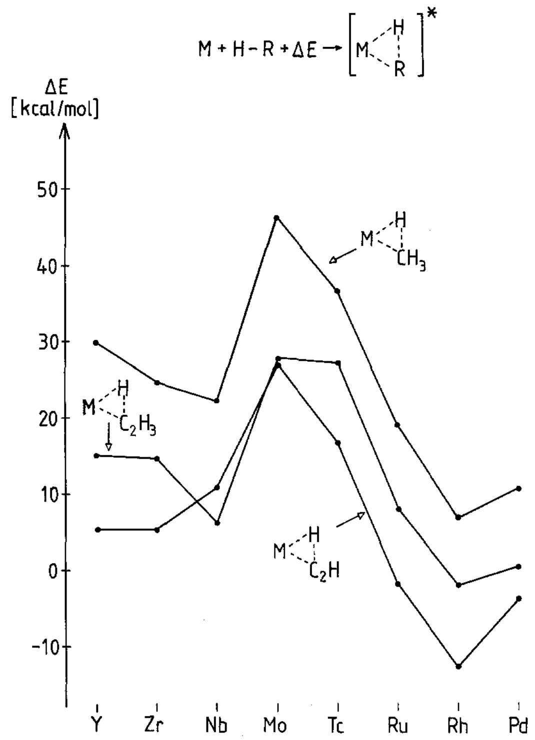

Fig. 6. The barrier height curves of the C–H insertion reaction for acetylene, ethylene and methane

and for practically all systems studied so far there is therefore a large decrease of the binding energy between niobium and molybdenum [3–7].

Going further to the right in the row, repulsive interactions dominate and these repulsions are larger for the acetylene complexes. As the most strongly repulsive orbitals, $4d_{b1}$ and σ, become doubly occupied for rhodium and palladium, respectively, the binding energy difference between the acetylene and ethylene complexes becomes smaller and smaller. This situation is similar to the binding between first row transition metal cations and ethylene and acetylene [23, 24]. In that case the binding energy is also much larger for the acetylene than for the ethylene complexes to the left in the periodic table and slightly smaller to the right. However, it should be noted that this situation, that transition metal cations and neutrals are similar, cannot be considered typical. There are numerous examples where there is a qualitative chemical difference between these systems.

A few comments can be made on the geometries given in Table 1. The most striking result here is the similarity of the structures for the different atoms. The M–C distances are within 0.1 Å with the exception of the yttrium complex and the C–C distance only ranges from 1.29 to 1.37 Å. The largest difference occurs for the tilt angle which is only 34.1 degrees for the ruthenium complex and as large as 53.7 degrees for the yttrium complex. The general similarity of these structures taken together with the rather flat character of the potential surface is the reason the ruthenium structure can be used also for the rhodium and palladium complexes. For these latter systems an SCF optimization partly fails to give accurate geometries. The reason for this is that the binding is weak at the SCF level combined with a situation where the system dissociates properly at this level of treatment. The

SCF M–C distances therefore become too long and the C–C distances too short. The MCPF binding energies for the ruthenium and palladium complexes at the SCF ruthenium geometry have finally been compared to the MCPF binding energies at the MP2 optimized structures, and the ruthenium SCF structures are actually better in both cases. For palladium the difference is small with 1.1 kcal/mol but for the rhodium complex the difference is as large as 8.5 kcal/mol. Other structures for the rhodium and palladium complexes were also tried to investigate the stability of the use of the ruthenium structures. After this investigation it is believed that the energies given in Table 1 should be stable to about 1 kcal/mol with respect to variations of the geometry.

Even though the energetic effects in the binding between the transition metal atoms and ethylene and acetylene are quite different, as discussed above, the resulting populations are in most cases very similar. The metal charges in the two types of complexes are, for example, very similar usually being within a few hundredth from each other. The 4*d*, 5*s*, and 5*p*-populations are also mostly very close for the two systems. The most notable exceptions to this occur for the molybdenum and niobium complexes. For molybdenum the 4*d*-population is significantly higher for the acetylene complex with 4.97 electrons compared to only 4.32 electrons for the ethylene complex. For the niobium complexes the difference is smaller with corresponding 4*d*-populations of 3.96 and 3.71. This effect on niobium and part of the effect on molybdenum are reflections of the larger amount of donation to the metal 4*d*-orbitals from the out-of-plane π-orbital of acetylene than from the C–H bonding orbitals of ethylene. However, the total change in 4*d*-population for molybdenum between the acetylene and ethylene systems is larger than can simply be explained by donation to the 4*d*-orbitals. Instead, there is a change of bonding state where the acetylene complex prefers to bind through a dominant d^5s-configuration and the ethylene complex through a dominant d^4sp-configuration on molybdenum. The origin of this change of bonding state is the larger importance of donations from the 4*d*-orbitals in the acetylene case, where there are two empty π^*-orbitals.

3.2 The insertion products

One of the most important results in Table 3 for the insertion products of the reaction between acetylene and the second row atoms, is that the reaction is *more* exothermic for all atoms than the corresponding ethylene reaction. This is in spite of the fact that the initial C–H bond strength in acetylene of 131.5 kcal/mol (calculated) is much *larger* than the C–H bond strength in ethylene of 113.4 kcal/mol. The difference in exothermicity between the acetylene and ethylene reactions is larger for the atoms to the left. For these atoms the difference is about 20 kcal/mol while the difference for the atoms to the right of the row is about 10 kcal/mol. The inverse relation between exothermicity and initial C–H bond strength is not an entirely new finding, as discussed in the introduction. In fact, it has even been suggested [25] that there should be a linear relationship between M–C and M–H bond strengths, which should give rise to this surprising trend. However, even though the present results are in general agreement with those conclusions a linear relationship is not confirmed at a quantitative level. This can be seen by a comparison of the acetylene and ethylene results to those for the C–H insertion reaction with methane. If there would be a linear relationship as suggested in [25] the reaction energies for the ethylene and methane reactions should be rather close in comparison to the acetylene reaction. The results show that for the atoms to the right ethylene is close to being exactly in between acetylene and methane. For the atoms to the left ethylene is closer to acetylene than to methane but not nearly by as much as would be required for a linear relationship between M–C and M–H bond strengths.

Another important result obtained here is that for all the presently studied systems except for technetium, the energies for the π-coordinated complexes are lower than for the insertion products. This means that even is if there are low barriers for the insertion, C–H activation will still not occur for thermodynamical reasons. This is similar to the situation for ethylene which explains the fact that C–H activation of ethylene has only rarely been observed. The possibility to observe C–H activation of acetylene in the gas phase therefore relies on possibilities to add ligands that would either sterically block the formation of the π-complex or to add ligands that would thermodynamically favour the insertion products. Steric blocking of the π-complex has been used to observe C–H activation in ethylene [26]. In solution the acidic properties of acetylene can be used to achieve C–H activation [10].

A simple explanation for the fact that the reaction energies increase as the initial C–H bond strength increases is based on steric effects and was given already in our previous paper on the ethylene reaction [4]. The most common explanation for the different C–H bond strengths in acetylene, ethylene and methane involves the different amount of *s*-contribution in the carbon *sp*-hybrids in the three systems. One, less common, explanation is that these differences are connected with steric repulsions between the different groups bonded to the carbon atom. For acetylene there are no other hydrogens bonded to the carbon, for ethylene there is one other hydrogen and for methane there are two other hydrogens, which would then lead to increasingly larger repulsion and weaker C–H bonds. When the metal atom takes the place of a hydrogen atom these steric effects should be much larger than for hydrogen since the metal atom is larger. A larger difference in M–C than in C–H bond strengths in the three types of systems is therefore expected, which would lead to the observed result with larger exothermicities the larger the initial C–H bond strength is. However, it should be added that since the exothermicity difference between the three types of reactions is somewhat different across the row of the metals also other effects and interactions play a part in the exothermicity differences (see further below).

One clear trend in the results in Table 3 is that the exothermicity difference between the acetylene and ethylene reactions is larger for the atoms to the left. The simplest rationalization of this trend follows similar lines as the ones in the preceding subsection on the π-complexes. The interactions responsible for this difference are then the ones between the metal and the out-of-plane orbitals of ethylene and acetylene. For the acetylene insertion products there should be an attractive interaction between the out-of-plane π-orbital and empty metal $4d$-orbitals, which can accept electrons. This interaction will then only be attractive for the atoms to the left, which have empty $4d$-orbitals. This explains the larger difference in exothermicity for these atoms. As soon as all the $4d$-orbitals are being partly filled, for molybdenum, the difference in exothermicity decreases.

The binding energy curves in Fig. 5 for methane, ethylene and acetylene have a very similar behaviour across the periodic table with one minor but notable exception, and this is for technetium. The curves for methane and ethylene decrease steadily from molybdenum to rhodium while for acetylene there is a kink in the curve with a marked stabilization for technetium. Exactly the same behaviour of the binding energy curve has been noted before for the O–H insertion products of water [6] and also to some extent for the N–H insertion products of ammonia [7]. The binding of the technetium complex is somewhat different from the binding for the metals next to it. Due to the particular exchange stabilization of the d^5-state of the technetium atom, the bonds in technetium complexes often prefer to be *sp*-hybrids. This tends to lead to a more ionic bonding and also to bond angles close to 180 degrees, which leads to a ligand field stabilization which is larger the more ionic the bonding is. The water insertion products are the most ionic of the systems studied so far and therefore the stabilization kink is most notable in this case. The acetylene and ammonia products are also rather ionic, which is why the stabilization can be seen also for these systems, whereas the products of the methane and ethylene reactions are the most covalent systems studied with no notable ligand field stabilization for technetium.

The M–C–C–H units of the insertion products of the acetylene reaction are remarkably similar to acetylene. The M–C_1–C_2–angles give in Table 3 are never more than four degrees from being linear. This means that there are not any more marked indications on these structures that there should be a strong interaction between the metal and the acetylene π-orbitals. In that case the metal would have had a tendency to bind from the side of the acetylene molecule where the overlap should be best. However, from the above discussion there are other, energetic, indications that there are significant interactions between these orbitals. The only possible sign on the geometries of an attractive interaction between the empty 4*d*-orbitals and the acetylene π-orbitals can be seen on a comparison of the trend of M–C and M–H bond distances. The decreasing M–H bond distances follow the expected decrease in the atomic radii going from left to right. It is seen that the M–H bond distance varies somewhat more than the M–C distance which could be an indication of a compensating attractive interaction to the left. This interaction should then be the attraction between empty 4*d*-orbitals and the acetylene π-orbitals. However, this geometric effect is very small and would not have been noticed if the interaction between second row metals and water and ammonia had not been studied earlier [6, 7]. For these systems the M–O and M–N distances are practically constant across the row, and in these cases the attractive interaction between lone-pairs and empty 4*d*-orbitals is a very plausible explanation.

The populations of the insertion products of the acetylene reaction do not contain any surprises in comparison to the corresponding populations for the methane and ethylene reactions. The details of the bonding are thus very similar in all three cases. For the atoms to the right the bonds are formed mainly from *sd*-hybrids which lead to H–M–C angles of about 90 degrees. The main bonding state is the s^1-state with some admixture of the s^0-state. For the atoms to the left there is considerable *sp*-hybridization in the bonds which leads to H–M–C angles larger than 90 degrees. For these complexes there is some admixture of the s^2-state since this state is the ground state for the atoms to the left.

3.3 The transition states

The barrier heights of the acetylene C–H insertion reaction are for most metals lower than for the corresponding ethylene reaction, which in turn have lower barriers than the methane reaction. This shows that the barriers approximately follow the trend of the exothermicities and not that of the initial C–H bond strengths. Even though the results for the different metals are similar in this general respect, a closer inspection of Table 5 suggests that the results actually fall into three different categories. First, there is the group of atoms to the right from technetium to palladium where the barrier height difference is about 10 kcal/mol both between the ethylene and methane and between the acetylene and ethylene reactions. Secondly, there is the group of the yttrium and zirconium atoms where the barrier height difference is larger between the ethylene and methane reactions than between the acetylene and ethylene reactions. Finally, the atoms niobium and molybdenum fall into a third class where the barrier height differences between the methane and ethylene reactions are similar to those for the yttrium and zirconium atoms, but where the barrier heights are similar or larger for the acetylene than for the ethylene reactions.

The general trend that the barrier heights are lower for the acetylene than for the ethylene reactions which are lower than for the methane reactions, is easiest rationalized as a steric effect. It is easy to see that the metal atom can approach the C–H bond in acetylene essentially without any steric hindrance. In contrast, it is clear that an attack on the C–H bond in methane from the side requires a substantial initial distortion of the methane geometry. The attack on the C–H bond in ethylene is somewhere in between these extremes, which then explains the general trend of the barrier heights for the three reactions. However, since not all the atoms follow the same simple trend it is also clear that there must be other, more directly electronic, effects of importance for the detailed trends of the barrier heights.

To understand the electronic effects involved in the C–H dissociation mechanism for acetylene it is useful to recapitulate the main results for the methane and ethylene reactions. For these reactions the lowest barrier heights of the C–H dissociation reaction were found for the atoms to the right, with the rhodium atom as the extreme case. The reason for this is that for these atoms the s^0-state can mix efficiently into the wavefunction and thereby reduce the initial repulsion. Of the three types of low-lying electronic states of the metal atoms the s^0- the s^1- and the s^2-states, the s^0-state will have the least repulsion towards ligands. For the atoms to the left the s^0-state will have the wrong spin to be mixed into the wavefunction and the barrier heights for these atoms will therefore be higher than for the atoms to the right, in particular for the methane reaction. The second important factor in the size of the barrier height is the position of the s^1-state, which is the leading bonding state for the insertion products. The situation is optimal for the rhodium atom, where both the s^1-state and the s^0-states are low-lying states and this is the explanation for the particularly low barriers for rhodium. The third important electronic effect is the loss of exchange energy when the bonds start to form, and this loss is particularly large for the atoms in the middle of the row which explains the high barriers for these atoms.

The main electronic effect which enters in addition to the ones described above, for the ethylene and acetylene reactions is the interaction between the metal and the π- and π^*-orbitals. The interaction with the π^*-orbital is always attractive and should be largest for the atoms to the right which have more $4d$-electrons to donate. In particular it is generally found that it is much more efficient to donate from a doubly occupied $4d$-orbital. This type of donation can thus only occur for the atoms from ruthenium to palladium, but partly also for the technetium atom, depending on atomic state involved. The interaction between the metal and the π orbitals have both attractive and repulsive components. The repulsion occurs for all atoms but is largest for the atoms to the right due to the larger number of $4d$-electrons for these atoms. It is also important to note that when the reactions from methane to acetylene are compared, the repulsive interaction between the metal and the π-orbitals is larger than the corresponding repulsion towards C–H bonding orbitals. The attractive component of the interaction between the metal and the π-orbital occurs when there are empty $4d$-orbitals. In general, half-empty $4d$-orbitals are not sufficient for any significant acceptance of electrons. Therefore, this attraction is only present for yttrium, zirconium and to some extent, depending on the orientation of the molecule, for niobium.

When the three curves in Fig. 6 for the barrier heights of the methane, ethylene and acetylene reactions are compared, the similarities are most striking. From technetium to palladium the curves are almost perfectly parallel with a general decrease in barrier height going to the right and a marked minimum for rhodium. For the atoms to the left there are also large similarities with a sharp increase in barrier height between niobium and molybdenum, which has been explained above, and for each reaction the curves are rather flat from yttrium to niobium. However, there is one notable irregularity and this occurs for the niobium reaction with acetylene. A significantly smaller barrier for noibium in the acetylene case would have made the curves much more parallel. The explanation for this irregularity concerns the number of empty $4d$-orbitals on the metal. The main reason the barriers for yttrium and zirconium are lower for the acetylene case is that there is a favourabvle attractive interaction with two π-orbitals in that case. For niobium, which has only one empty $4d$-orbital in its ground state, only one of these interactions is attractive for the acetylene reaction. The other interaction, between a π-orbital and a singly occupied $4d$-orbital, is actually more repulsive than the corresponding interaction for the ethylene reaction and makes the acetylene barrier somewhat higher.

4 Conclusions

Of the C–H activations of acetylene, ethylene and methane, acetylene has the lowest barrier followed by ethylene and methane for almost all second row transition metal atoms. This trend is easiest explained as a steric effect. Since C–H activation requires that the metal efficiently interacts in a sideways orientation with the C–H bond, it is clear that this position is easily reached for acetylene. For methane, on the other hand, a substantial initial distortion of the molecule is needed to reach a proper interaction. For ethylene the situation is somewhere in between that of acetylene and methane. The order of the barriers for these three reactions is also connected with the resulting exothermicities which follow the same order. This means that the there is an inverse relation between the initial C–H bond strength and the difficulty to activate the C–H bond. The by far strongest C–H bond, that of acetylene, is thus easiest to activate. One reason the largest exothermicities are obtained for the hydrocarbons with the strongest C–H bonds, is that the same factors that affect the C–H bond strength of the hydrocarbons are active also for the strength of the M–C bonds. These factors are both hybridization effects and steric repulsion effects. The C–H bond is strongest where the carbon atom has the fewest number of additional ligands, that is for acetylene, and the same argument holds for the M–C bond strength but to an even larger extent due to the larger size of the metal atom. Another contributing factor to the differences in exothermicities is the interaction between the metal and the π- and π^*-orbitals of ethylene and acetylene. In particular, the donation from the π-orbitals to the metal is important and leads to larger differences in the exothermicities for the atoms to the left where there are empty $4d$-orbitals. This effect is strongest for acetylene since there are two π-orbitals and for yttrium and zirconium which have two empty $4d$-orbitals.

Even though the barriers for C–H insertion of acetylene are small for many metal atoms, actually absent for Ru, Rh and Pd, this reaction will not take place in the gas phase without additional ligands for most metals. The reason for this is that for all atoms except one, the binding energies of the π-coordinated complexes are larger than for the insertion products. One possibility to observe C–H activation of acetylene in the gas phase could be to make this process kinetically favoured by sterically blocking the formation of the π-complex, as has been successfully done for a case of C–H insertion in ethylene [26]. The possibility to add ligands which would actually make the C–H insertion product of acetylene more stable than the π-coordinated complex does not appear to be as promising as for ethylene. For ethylene, all atoms to the left have insertion products with binding energies very close to those for the π-complexes, while the corresponding energies for acetylene much more strongly favour the π-complexes. The only exception to these results for acetylene is technetium which actually has a more stable insertion product. However, at the same time technetium has one of the highest barriers for C–H insertion of 17 kcal/mol. The possibility to observe the C–H activation for technetium is therefore not very high either.

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