A THEORETICAL STUDY OF MULTIPLE BONDING INVOLVING CARBON AND TITANIUM

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Summary

Multiple bonding involving carbon and titanium is investigated by FSGO calculations on Ti_2H_6, $TiH_2=TiH_2$, $TiH=TiH$, CH_3TiH_3, $CH_2=TiH_2$, and $CH\equiv TiH$. $D_\pi(C=Ti)$ and $D_\pi(Ti=Ti)$ are estimated to be about a third of $D_\pi(C=C)$. The optimum wavefunctions are analysed and the effect of the electropositive titanium on the structure of the multiple bonds is discussed.

Introduction

Titanium has the electronic configuration $KLM\ 4s^2\ 3d^2$ and is therefore the first transition element capable of taking part in multiple bonding similar to that found in carbon systems. However, it has a low electronegativity (1.32 in the Allred-Rochow scale [1]) and so it is probable that like silicon, titanium will not form stable multiply-bonded compounds [2]. Nevertheless, Si=C and Si=Si double bonds have been postulated to occur in certain intermediates [3] and the molecule $Me_2Si=CH_2$, although having a short life, has had its silicon—carbon bond length measured at elevated temperatures [4]. Titanium forms well-characterized homoleptic compounds with alkyl radicals [5] and TiH_4 was prepared several years ago [6], although not much is known about its properties. It is thus not implausible to suggest that intermediates involving the Ti=C and Ti=Ti bonds may have a transient existence.

A π-bond between titanium and carbon, or between two titaniums, is also of considerable theoretical interest. This is because the bond would involve d_π—p_π or d_π—d_π overlap, as opposed to conventional p_π—p_π multiple bonding. Nevertheless, there has apparently been no published ab initio theoretical work. The FSGO approach, used previously in an initial ab initio survey of silicon—carbon multiple bonding [2], has been used to carry out calculations on the structures of Ti_2H_6, Ti_2H_4, Ti_2H_2, CH_3TiH_3, CH_2TiH_2 and CHTiH. Little or no adaptation is

required to facilitate the computations when a d-block element is involved. Full details of the model and method have been given elsewhere [2,7—10].

Calculations

The simple FSGO model was extended slightly in the calculations on the silicon—carbon systems [2] to include p-type functions for the L shell atomic orbitals and for the π-orbitals in the unsaturated molecules. The M shell in titanium is represented in a similar fashion in the present set of calculations. The arrangement of FSGO's in the same as before [2], except that the σ- and π-orbitals in the double or triple bonds were optimised independently. Not only were the orbital exponents different, but in the mixed hydrides the positions of the σ- and π-orbitals along the internuclear axis were varied separately. This permits the analysis of differing σ and π inductive effects.

Results

Table 1 lists the calculated structures, including Frost's results for methane [9] and ethane [8] and a calculation on TiH_4. Experimental results for the hydrocarbons are also included [11]. Limiting geometries [2] for ethylene and acetylene are given, in which the σ- and π-orbitals in the multiple bonds were optimised separately.

The decrease in r_{CC}, r_{CTi} and r_{TiTi} with increasing bond order is observed for each group of compounds, together with the concomitant environmental decrease in r_{CH} and r_{TiH} [2]. Whilst the change from tetrahedral to trigonal coordination in ethane and ethylene is reflected in the HCH interbond angles, this is not the case in the titanium analogues. The slightly smaller than tetrahedral HTiH angle in Ti_2H_4 may reflect the relatively large sizes of the Ti—Ti σ- and π-bonds (vide infra). However, the opposite effect obtains in the mixed hydrides. In CH_3TiH_3/CH_2TiH_2, the HCH angle increases but remains tetrahe-

TABLE 1

CALCULATED GEOMETRIES [a]

Compound	r(CC), r(CTi) or r(TiTi)	r(CH)	r(TiH)	HCH	HTiH
CH_4 [b]		1.115(1.094)			
TiH_4			1.840		
C_2H_6 [c, d]	1.501(1.534)	1.120(1.093)		108.2(109.1)	
C_2H_4 [c]	1.381(1.338)	1.087(1.086)		119.9(117.3)	
C_2H_2 [e]	1.236(1.205)	1.066(1.059)			
Ti_2H_6 [c]	3.180		1.850		108.4
Ti_2H_4	2.843		1.840		106.7
Ti_2H_2	2.574		1.831		
CH_3TiH_3 [c]	2.167	1.133	1.845	105.4	109.6
CH_2TiH_2	2.133	1.106	1.830	109.0	124.7
CHTiH	2.000	1.077	1.830		

[a] Distances in Å, angles in degrees. Experimental results [11] in parentheses. [b] Ref. 9. [c] Staggered conformations. [d] Ref. 8. [e] Limiting geometries (see text).

dral whilst the HTiH angle follows the expected change.

The calculated total energies are given in Table 2. These values were used to estimate the bond energies to be discussed in the next section. The procedure is straightforward; however, large errors are inevitably introduced because correlation energy changes inherent in the Hartree-Fock wavefunction are ignored, in addition to differences in the number and types of functions on either side of a dissociation equation. In the case of FSGO wavefunctions, the latter effect is more important, because bond dissociaiton energies thereby calculated are much larger than anticipated [12]. In order that the results may be compared with empirically determined bond energies, the ab initio dissociation energies were scaled with respect to B(Ti—C). In general, however, when the same number of the same type of bonds are on each side of an equation, values for the heat of reaction agree well with experiment [13].

The torsional barriers in Ti_2H_6 and CH_3TiH_3 are very small, even less than in the silicon analogues [2]. Results for CH_3TiX_3 (X = Cl, Br, I) have been obtained which are about 6 kJ mol^{-1} [14].

The overall dipole moments calculated for the mixed hydrides are given in Table 3. There does not seem to be a standard value for μ(Ti—H) in the literature, so the 1.0 D estimate for the Si$^+$H$^-$ bond was assumed [15]. Using the standard value of μ(C$^-$H$^+$) = 0.4 D [16], the C—Ti bond dipoles listed in the second part of Table 3 were obtained. Since titanium has a lower electronegativity than silicon [1], a higher value for μ(Ti$^+$H$^-$) is expected. this would inevitably lead to larger C$^-$—Ti$^+$ and C$^-$=Ti$^+$ bond dipoles (and reverse the small C$^+$≡Ti$^-$ dipole). The values thus calculated, however, for the C—Ti and C=Ti bonds are very similar to those obtained in the silicon analogues.

Thermodynamics

The calculated heats of reaction given in Table 4 indicate that multiple bonding involving titanium is far less attractive energetically than that which obtains in the hydrocarbons. The comparison between the mixed hydrides in

TABLE 2

TOTAL MOLECULAR ENERGIES (a.u.)

Compound	Energy
CH$_4$ [a]	−33.9921
C$_2$H$_6$ [b, c]	−67.0048
C$_2$H$_4$ [d]	−65.9596
C$_2$H$_2$ [d]	−64.7949
TiH$_4$	−740.8461
Ti$_2$H$_6$ [c]	−1480.7269
Ti$_2$H$_4$	−1479.6388
Ti$_2$H$_2$	−1478.5281
CH$_3$TiH$_3$ [c]	−773.8282
CH$_2$TiH$_2$	−772.7262
CHTiH	−771.5254

[a] Ref. 9. [b] Ref. 8. [c] Staggered geometries. Calculated rotational barriers (kJ mol^{-1}): C$_2$H$_6$ 23.8 [8], CH$_3$TiH$_3$ 1.0, Ti$_2$H$_6$ 1.5 (the eclipsed structures were fully optimised). [d] Limiting geometries (see text).

TABLE 3

DIPOLE MOMENTS

Compound	Dipole moment (Debye)
(i) Molecules	
$\overrightarrow{CH_3TiH_3}$	0.29
$\overleftarrow{CH_2TiH_2}$	1.68
$\overrightarrow{CHTiH}$	1.77
(ii) C—Ti bonds [a]	
C^--Ti^+	1.17
$C^-=Ti^+$	3.07
$C^+\equiv Ti^-$	0.37

[a] Assuming $\mu(C^-H^+) = 0.4$ D [16], $\mu(Ti^+H^-) = 1.0$ D (see text).

the dititanium hydrides is more difficult to make because the change in the number of C—H and Ti—H bonds in the second set of equations would also give endothermic heats of reaction. This assumes that B(Ti—H) is less than B(C—H) [12].

No information is available about the thermodynamic properties of TiH_4 [12] and therefore it is not possible to obtain heats of formation of the various hydrides included in the present study. Nevertheless, expressions for ΔH_f can be written in terms of $T = \Delta H_f(TiH_4)$; this has been done in Table 5. The results give the not unexpected result that the molecules become more endothermic with unsaturation. As to the relative stabilities of the mixed hydrides with respect to the dititanium compounds, this depends upon B(Ti—H) via the relationship

$$4B(\text{Ti—H}) = 1342 - T$$

($\Delta H_f[\text{Ti(g)}] = 470$ kJ mol^{-1}, $\Delta H_f[\text{H(g)}] = 218$ kJ mol^{-1} [17,18]). If T is greater than ca. 140 kJ mol^{-1}, B(Ti—H) would be lower than 300 kJ mol^{-1} (cf. B(C—H) = 413 kJ mol^{-1}, B(Si—H) = 318 kJ mol^{-1} [17]) and the mixed hydrides would then be the less endothermic compounds. However, this does not mean that Ti/Ti is weaker than Ti/C bonding because the carbon—hydrogen bond energy could be even twice B(Ti—H). Table 6 gives the bond energies calculated from the ab initio total energies in Table 2 and B(C—H). These values

TABLE 4

CALCULATED HEATS OF REACTION (kJ mol^{-1})

Reaction	ΔH
$C_2H_6 + TiH_4 \rightarrow CH_3TiH_3 + CH_4$	+80
$C_2H_4 + TiH_4 \rightarrow CH_2TiH_2 + CH_4$	+229
$C_2H_2 + TiH_4 \rightarrow CHTiH + CH_4$	+324
$Ti_2H_6 + CH_4 \rightarrow CH_3TiH_3 + TiH_4$	+117
$Ti_2H_4 + CH_4 \rightarrow CH_2TiH_2 + TiH_4$	+154
$Ti_2H_2 + CH_4 \rightarrow CHTiH + TiH_4$	+390

TABLE 5

HEATS OF FORMATION (kJ mol^{-1})

Calculated ΔH_f			
CH_3TiH_3	$70 + T$ [a]	Ti_2H_6	$28 + 2T$
CH_2TiH_2	$356 + T$	Ti_2H_4	$277 + 2T$
$CHTiH$	$626 + T$	Ti_2H_2	$311 + 2T$

[a] $T = \Delta H_f(TiH_4)$.

have then been scaled with respect to B(Ti—C) = 260 kJ mol^{-1} (an average of two estimates [18,19]) to produce the results given in parentheses in Table 6. Although the ad hoc procedure just outlined is clearly open to criticism, the bond energies thereby determined suggest that D_π(Ti=Ti) and D_π(Ti=C) should be approximately equal and about one third of D_π(C=C). Triple bonding is unfavoured energetically.

Analysis of wavefunctions

In the hydrocarbons, changing the environment from tetrahedral in ethane through trigonal in ethylene to digonal in acetylene produces a reduction in the sizes or polarizabilities of the carbon—carbon σ-orbitals and the carbon—hydrogen bonding orbitals. This orbital contraction, reflected in the bond polarizabilities [10] listed in Table 7, parallels the decreases in bond length. However, these orbital changes occur in reverse for the titanium compounds. The bond polarizability, which is characteristic of an orbital's environment [13], is determined by the most electronegative atom in a bond. In the mixed hydrides and in the hydrocarbons, the bond polarizabilities are controlled by carbon, whereas in the dititanium hydrides, the influence of the hydrogen substituent predominates.

There are interesting comparisons to be made between the polarizabilities of the π-orbitals which make up the multiple bonds. The triple bond π-orbitals are always more compact than the π-orbital in the double bond. In CH_2TiH_2 and Ti_2H_4, the π-orbital is several times larger in size than ethylene's. This is because of the inherently large size of titanium's valence orbitals (for example, Ti ^3F (KLM $4s^2$ $3d^2$) has $\alpha(4s) = 10.0$ Å^3 and $\alpha(3d) = 47.5$ Å^3); a considerable con-

TABLE 6

BOND ENERGIES (kJ mol^{-1})

Standard [a]					
C—H	413	D_π(C=C)	264		
Calculated [b, c]					
Ti—H	379 (267)				
Ti—Ti	451 (318)	C—Ti	369 (260)	D_π(Ti=Ti)	130 (92)
Ti=Ti	581 (409)	C=Ti	496 (349)	D_π(C=Ti)	127 (89)
Ti≡Ti	652 (459)	C≡Ti	364 (256)		

[a] Ref. 2. [b] Calculated from ab initio total energies and standard value of B(C—H) (see text). [c] Values in parentheses have been scaled with respect to B(C—Ti) = 260 kJ mol^{-1} (see text).

TABLE 7

BOND POLARIZABILITIES ($Å^3$)

Compound	α(CC), α(CTi) or α(TiTi)	α(CH)	α(TiH)
CH_4		0.610	
C_2H_6	0.543	0.612	
C_2H_4	0.407(σ)	0.494	
	2.136(π)		
C_2H_2	0.350(σ)	0.439	
	1.255(π)		
TiH_4			1.528
Ti_2H_6	4.712		1.545
Ti_2H_4	5.805(σ)		1.581
	10.419(π)		
Ti_2H_2	7.741(σ)		1.647
	9.671(π)		
CH_3TiH_3	1.076	0.714	1.526
CH_2TiH_2	0.779(σ)	0.541	1.728
	11.795(π)		
CHTiH	0.622(σ)	0.421	1.926
	7.595(π)		

traction is required, especially for the $3d$ orbital, to produce even these relatively polarizable π-orbitals. The large size of both the σ- and π-orbitals in Ti_2H_4 is responsible for the smaller than tetrahedral H—Ti—H angle. This is probably an extreme example of the size effect of a double bond [20].

The results for the binuclear transition metal hydrides serve to emphasise the difficulty with which even a σ or π transition element metal—metal bond can be established [21]. At typical metal—metal distances, the interaction between the centres is only a fraction of first or second row values. This is reflected in the FSGO model by relatively large σ- and π-bonds.

The population analysis given in Table 8 reflects the disposition of the optimum FSGO's. Since the σ- and π-orbitals in the multiple bonds were optimised independently, the most electronegative element, carbon, attracts the σ-orbital, whilst the less tightly bound π-orbital moves towards the electropositive titanium centre. This is because the depletion of σ-electrons produces a simultaneous decrease in the screening at the titanium: it has acquired $-I_\pi$ character. This effect is fortified by the relatively electronegative hydrogen substituents. These remove electrons from the titanium, increasing its positive charge. This may have two effects. It may prevent too great a loss of σ-electrons to the carbon, but it also further facilitates the attraction of the more labile π-electrons to the titanium. This picture of σ—π-orbital separation often occurs when the bonding electrons are shared between two centres which differ substantially in electronegativity [22]. In CH≡TiH, the π-orbitals are not attracted quite so strongly to titanium because the single Ti—H bond makes this centre less positive than in CH_2=TiH_2. In this way, the role of the substituent attached to the electropositive centre is to provide a mechanism both for the attraction and the possible stabilization of the π-orbitals. However, in the case of hydrogen, little stabilization of the π-electrons is thought likely.

Nevertheless, the results for the mixed hydrides demonstrate how the elec-

TABLE 8

VALENCE ELECTRON POPULATION ANALYSIS ^{a}

Compound	$N(C)$	$N(Ti)$	$N(H)$
CH_4	3.232(CH)		1.192(CH)
C_2H_6	1.000(CC) + 3.364(CH)		1.212(CH)
C_2H_4	N_σ: 1.000(CC) + 1.584(CH) N_π: 1.000(CC)	.	1.208(CH)
C_2H_2	N_σ: 1.000(CC) + 0.852(CH) N_π: 2.000(CC)		1.148(CH)
TiH_4		1.335(TiH)	1.666(TiH)
Ti_2H_6		1.000(TiTi) + 1.000(TiH)	1.667(TiH)
Ti_2H_4		N_σ: 1.000(TiTi) + 0.715(TiH) N_π: 1.000(TiTi)	1.642(TiH)
Ti_3H_2		N_σ: 1.000(TiTi) + 0.394(TiH) N_π: 2.000(TiTi)	1.606(TiH)
CH_3TiH_3	1.634(CTi) + 2.620(CH)	0.366(CTi) + 0.995(TiH)	H_C: 1.127(CH) H_{Ti}: 1.668(TiH)
CH_2TiH_2	N_σ: 1.613(CTi) + 1.726(CH) N_π: 0.307(CTi)	0.387(CTi) + 0.790(TiH) 1.693(CTi)	H_C: 1.137(CH) H_{Ti}: 1.605(TiH)
CHTiH	N_σ: 1.622(CTi) + 0.873(CH) N_π: 2.012(CTi)	0.378(CTi) + 0.465(TiH) 1.988(CTi)	H_C: 1.127(CH) H_{Ti}: 1.535(TiH)

^{a} Origin of population is given in parentheses.

tronegative carbon forms a compact σ-bond between itself and titanium, even though the π-bond remains relatively polarizable. This underlines the differences between the covalent carbon—carbon bond, the organometallic bond and the metal—metal bond, although the orbital sizes and populations do not reflect accurately the relative σ- and π-bond strengths.

Conclusions

To sum up, the involvement of titanium in multiple bonding produces the following results (i) that the π-bonds are very labile (ii) that, like the C=Si bond [2], the C=Ti bond is highly polar (iii) that both π_{CTi} and π_{TiTi} have low bond energies but that the D_π values are substantial enough to stabilize a transient existence, similar to that found for molecules including the C=Si bond [3,4]. It is suggested that the substituent may play an important role in the stability of a multiple bond involving the electropositive titanium.

References

1 A.L. Allred and E.G. Rochow, J. Inorg. Nucl. Chem., 5 (1958) 264.
2 P.H. Blustin, J. Organometal. Chem., 105 (1976) 161.
3 L.E. Gusel'nikov, N.S. Nametkin and V.M. Vdovin, Accounts Chem. Res., 8 (1975) 18.
4 P.G. Mahaffy, R. Gutowsky and L.K. Montgomery, J. Amer. Chem. Soc., 102 (1980) 2854.
5 P.J. Davidson, M.F. Lappert and R. Pearce, Accounts Chem. Res., 7 (1974) 209.
6 P. Breisacher and B. Siegel, J. Amer. Chem. Soc., 85 (1963) 1705.
7 A.A. Frost, J. Chem. Phys., 47 (1967) 3707, 3714.
8 A.A. Frost and R.A. Rouse, J. Amer. Chem. Soc., 90 (1968) 1965.
9 A.A. Frost, J. Phys. Chem., 72 (1968) 1289.
10 P.H. Blustin, J. Chem. Phys., 66 (1977) 5648.

11 Chem. Soc. Spec. Publ., 11 (1958) and Supplement.

12 D.M. Hood, R.M. Pitzer and H.F. Schaefer, J. Chem. Phys., 71 (1979) 705.

13 P.H. Blustin and J.W. Linnett, J. Chem. Soc. Faraday Trans. II, 70 (1974) 274.

14 L. Bencivenni, A. Farina, S. Nunziante Cesaro, R. Teghil and M. Spoliti, J. Mol. Struct., 66 (1980) 111.

15 C. Eaborn, Organosilicon Compounds, Butterworths, London, 1960.

16 G.J. Moody and J.D.R. Thomas, Dipole Moments in Inorganic Chemistry, Arnold, London, 1971.

17 D.A. Johnson, Some Thermodynamic Aspects of Inorganic Chemistry, Cambridge University Press, London, 1968.

18 M.F. Lappert, D.S. Patil and J.B. Pedley, J. Chem. Soc., Chem. Commun., (1975) 830.

19 V.I. Tel'noi, I.B. Rabinovich, V.D. Tikhonov, V.N. Latyaeva, L.I. Vyshinskaya and G.A. Razuvaev, Dokl. Akad. Nauk. SSSR, 174 (1967) 1374.

20 H.A. Bent, J. Chem. Educ., 40 (1963) 446.

21 W.C. Trogler, J. Chem. Educ., 57 (1980) 424.

22 P.H. Blustin, Chem. Phys. Lett., 63 (1979) 347.