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Reduced Variational Space Analysis of Methane Adducts

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Introduction

Methane is the major component of natural gas, and hence its catalytic conversion to functionalized products (e.g., methanol) is of great interest.[1] A variety of transition metal complexes have been investigated experimentally for the selective activation of methane.[2] Recent experiments[3,4] and computations[5] suggest that weakly bound methane adducts play a pivotal role in metal-mediated methane activation. Calculation of the intrinsic reaction coordinates for methane activation by d^0 imidos indicates that the adduct lies along the pathway for methane activation.[6] Isolation of a stable methane adduct, suitable for experimental characterization, would be aided by a greater understanding of their chemistry. Given the short-lived nature of these adducts and the limited direct experimental information, computational chemistry is a useful tool for understanding the bonding and structure of these catalytic intermediates.

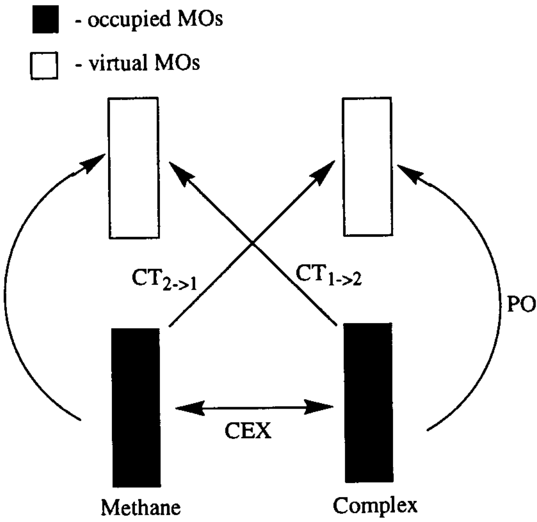
This research investigated the bonding forces in methane adducts of transition metal (TM) complexes. The calculations reported here employed effective core potential (ECP) methods[7] within the Hartree−Fock approximation using the GAMESS quantum chemistry program.[8] The "reduced variational space" self-consistent field (RVS-SCF) method developed by Stevens and Fink was employed.[9] This technique was used to analyze the Coulomb and exchange energy (CEX), polarization energy (POL), and charge transfer energy (CT) contributions to the binding energy (ΔE_{add}) of methane to a TM complex. Adducts of high-valent (d^0) transition metal complexes were studied, Table 1. The role of metal, ligand, and charge on the different contributions to the binding energy were analyzed. The energetic components are depicted graphically in Scheme 1 (arrows denote the flow of electron density). The CT terms measure the energetic contribution arising from electron transfer between the fragments; in this research, the adducts were $LnM^-(RH^+)$, as indicated by a Mulliken population analysis, suggesting greater charge transfer from methane to the adduct than the reverse. The POL term assesses the energetics of deformation of a fragment's electron density caused by the other fragment; the results below indicated that the methane was more polarizable than the metal complex. The CEX term is the energetic contribution arising from the repulsion between the occupied molecular orbitals of the two fragments.

Table 1. RVS-SCF Analysis of Methane Adducts[a]

complex	CEX	POL_1	POL_2	$CT_{1\to2}$	$CT_{2\to1}$	total with BSSE
$Sc(NH_2)_3$	2	0	0	−1	−1	0
$Ti(NH_2)_2({=}NH)$	3	0	−1	−1	−2	−1
$Zr(NH_2)_2({=}NH)$	3	0	−1	−1	−3	−3
$Hf(NH_2)_2({=}NH)$	4	0	−2	−1	−4	−4
$V(NH_2)({=}NH)_2$	5	0	−1	−1	−6	−4
$Nb(NH_2)({=}NH)_2$	4	0	−2	−1	−6	−5
$Ta(NH_2)_2({=}NH)$	6	0	−3	−1	−9	−7
$Mo({=}NH)_3$	5	0	−3	−1	−8	−7
$W({=}NH)_3$	6	0	−3	−1	−10	−10
$[Re({=}NH)_3]^+$	11	−1	−8	−1	−20	−21
$[Ta({=}NH)_3]^-$	5	−1	−1	−2	−3	−2
$[Tc({=}NH)_3]^-$	9	−1	−7	−1	−15	−16
$Ti(OH)_2({=}NH)$	4	0	−2	−1	−5	−3
$Cl_2Ti{=}CH_2$	5	0	−2	−1	−6	−4
$Cl_2Ti{=}NH$	6	0	−3	−1	−8	−6
$Cl_2Ti{=}O$	7	0	−6	−1	−8	−8
$Cl_2Zr{=}CH_2$	4	0	−3	−2	−5	−5
$Cl_2Zr{=}NH$	5	0	−4	−1	−6	−7
$Cl_2Zr{=}O$	5	0	−5	−1	−6	−8
$Cl_2Hf{=}CH_2$	6	0	−3	−1	−8	−7
$Cl_2Hf{=}NH$	6	0	−5	−1	−8	−8
$Cl_2Hf{=}O$	6	0	−6	0	−8	−9
$[Cl_2Ta{=}CH_2]^+$	11	−1	−9	−1	−19	−21
$[Cl_2Ta{=}NH]^+$	11	−1	−12	−1	−21	−25
$[Cl_2Ta{=}O]^+$	11	−1	−12	−1	−23	−27

[a] Energies are reported to the nearest kcal/mol and were determined using the SBK(d) valence basis set scheme (see Computational Methods). In this work fragment 1 is the metal complex and fragment 2 is methane; abbreviations are given in Computational Methods and depicted graphically in Scheme 1.

Scheme 1



Computational Methods

Calculations employed the parallel and serial versions of the GAMESS program.[8] The standard Stevens, Basch, Krauss, Jasien, SBK(d), valence basis set/ECP scheme was used along with a much larger basis set: SBK with f functions for the transition metals,[10] SBK-(d)+ for the main group elements, -311G+ for hydrogen. ECPs replace

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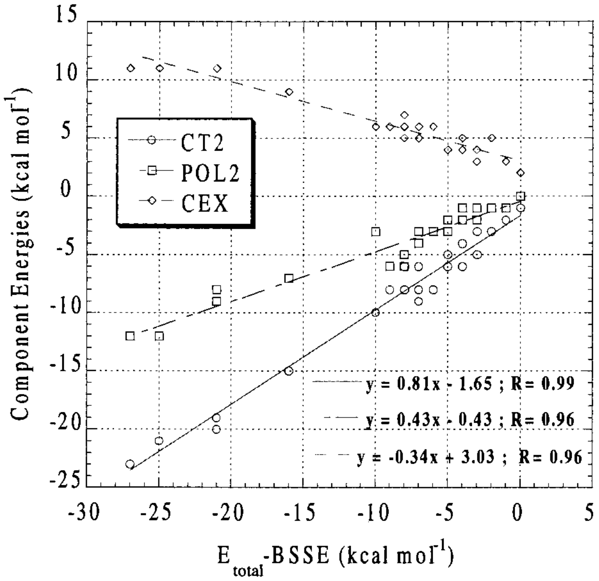

Figure 1. Component energies compared with E_{total}.

the innermost core orbitals for TMs and all core orbitals for main group (MG) elements. Thus, the *n*s, *n*p, *n*d, $(n + 1)$s, and $(n + 1)$p are treated explicitly for the d block; for the main group, *n*s and *n*p are treated explicitly. TM ECPs are created from all electron Dirac−Fock calculations and thus include Darwin and mass velocity relativistic effects.[7] The Stevens−Fink reduced variational space self-consistent field method was employed to analyze the Coulomb and exchange energy (CEX), polarization energy (POL), charge transfer energy (CT), and basis set superposition error (BSSE) contributions to the binding energy (ΔE_{add}) of methane to a TM complex.[9]

Results and Discussion

1. Effect of Basis Set. A larger basis set was researched to ensure that the standard SBK(d) basis sets accurately described the adducts and their interactions even though it was used with success in a previous study of d^0-methane adducts.[5] The standard Stevens, Basch, Krauss (SBK(d)) valence basis set/ECP scheme was compared with the much larger SBK(d)+f basis set. On average the SBK(d)+f basis set yields ΔE_{add} which are only 0.5 kcal/mol lower than those obtained with the SBK(d) basis set. The component energies calculated with the two basis sets were in good linear correlation with each other; the R^2 (correlation coefficient for least-squares line) values were greater than 0.998.

The results suggested that, at least at the Hartree−Fock level, the effect of basis set beyond the standard SBK(d) scheme was minimal. Furthermore, the results showed that charge transfer from the methane to the metal complex ($\text{CT}_{2\rightarrow1}$) was a major contributing factor to the overall stability of the adduct along with polarization energy of the methane (POL_2). These stabilizing interactions were counterbalanced by a repulsive CEX contribution. Indeed, analysis of the three major components, Table 1 and Figure 1, suggested that CEX and POL_2 largely cancel each other out, resulting in $\text{CT}_{2\rightarrow1}$ as the major determinant of trends as a function of metal and ligand.

2. Periodic Trends. i. The Effect of the Transition Metal, M. The stability of the methane adducts followed discernible trends as a function of metal. The complexes studied with three nitrogen-based ligands were $\text{Sc(NH}_2)_3$; Ti-, Zr-, and $\text{Hf(NH}_2)_2({=}\text{NH})$; V-, Nb-, and $\text{Ta(NH}_2)({=}\text{NH})_2$; and Mo- and $\text{W}({=}\text{NH})_3$. These complexes are models of the putative active species in potent methane activating systems.[3,11−14] The adduct binding energies displayed the following general trends: the farther to the right the TM was in the transition series, and the heavier the TM, the more stable the methane adduct. This can be rationalized in steric terms. A larger TM results in less steric hindrance to methane coordination, and thus a more stable product (i.e., methane adduct). Additionally, the 3-coordinate scandium- and titanium-triad complexes assume a planar ground state geometry, while the 3-coordinate vanadium- and chromium-triad complexes are pyramidal. Coordination to a pyramidal complex is expected to result in reduced steric hindrance as compared to a planar complex. Additionally, perturbation from a trigonal planar to trigonal pyramidal geometry lowers the energy of the dσ acceptor orbital on the TM.[5] This is reflected in increased $\text{CT}_{2\rightarrow1}$, Table 1.

ii. The Effect of the Activating Group, E. As with the amido/imido complexes, multiply bonded group IVA adducts ($\text{Cl}_2\text{M}{=}\text{E}\cdots\text{HCH}_3$) had increasing stability down a TM triad. More interestingly, the stability of the adducts also increased as the electronegativity of the activating ligand (E) increased. For example, the Ti−methylene complex was the most weakly bound ($\Delta E_{\text{add}} = -4$ kcal/mol), with the imido complex more stable ($\Delta E_{\text{add}} = -6$ kcal/mol), and the oxo complex being the most tightly bound of this series ($\Delta E_{\text{add}} = -8$ kcal/mol). The RVS-SCF analysis suggested that this trend is due to more exothermic $\text{CT}_{2\rightarrow1}$ and POL_2 coupled with only small changes in the CEX component as a function of *E*, Table 1.

iii. The Effect of Charge. Charge also played an important role in the stability of the adduct. The RVS-SCF analysis indicates that cationic, Ta adducts had a significantly larger CEX (5 kcal/mol on average) repulsion than their neutral Hf counterparts. However, this destabilization was more than made up for by a significantly more negative POL_2 (−6 kcal/mol on average) and $\text{CT}_{2\rightarrow1}$ (−13 kcal/mol on average). Analysis of the energetic components for $[\text{Mo}({=}\text{NH})_3\cdots\text{HCH}_3]$ versus $[\text{Tc}({=}\text{NH})_3\cdots\text{HCH}_3]^+$ and $[\text{W}({=}\text{NH})_3\cdots\text{HCH}_3]$ versus $[\text{Re}({=}\text{NH})_3\cdots\text{HCH}_3]^+$ showed similar trends. Hence, the RVS-SCF analysis suggested that charge transfer from methane to the metal complex is the major factor in engendering increased binding energy to cationic adducts.

Summary

An analysis of the binding of methane to transition metal complexes using the RVS-SCF technique was reported. The major, important conclusions of this research are as follows. First, basis set effects on the energetic decomposition were found to be minimal. Second, three energetic components dominate the binding of methane to the metal complex: Coulomb and exchange repulsion, polarization of methane, and charge transfer from methane to the metal complex. The latter two are stabilizing interactions. Third, energetic changes in the Coulomb and exchange repulsion are largely counterbalanced by changes in the methane polarization component. As a result, trends as a function of metal, ligand, and charge on the methane binding energy are largely due to changes in the degree of charge transfer from methane to the metal complex. Hence, attempts

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to isolate a stable methane adduct, suitable for experimental characterization, would be most profitable by the development of complexes which maximize this energetic component.

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