Theoretical Studies of the M–CO Bond Lengths and First Dissociation Energies of the Transition Metal Hexacarbonyls $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$

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Quantum mechanical *ab initio* calculations at the CCSD(T) level of theory using MP2 optimized geometries and effective core potentials for the metals predict M–CO bond lengths and first dissociation energies which are in excellent agreement with experimental results obtained from gas phase experiments for $Mo(CO)_6$ and $W(CO)_6$.

The results of experimental[1–3] and theoretical[4] studies of the first dissociation energy of CO from the transition metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, W) yielding the metal pentacarbonyls are in striking disagreement about the order of the reaction enthalpies for reaction (1).

$$M(CO)_6 \rightarrow M(CO)_5 + CO \qquad (1)$$

Kinetic studies of the activation barrier for substitution of CO in $M(CO)_6$ show the order Mo < Cr < W.[1] The same trend is observed in photoacoustic calorimetry experiments,[2] but the error bars for the reported reaction enthalpies are rather high. The only set of experimental data for reaction (1), reported from gas phase experiments, shows a different order for the bond energies Cr < Mo < W.[3] The experimentally reported values for the reaction enthalpies of reaction (1) are shown in Table 1.

Table 1 Theoretically predicted and experimentally observed first dissociation energies [kcal mol^{-1} (1 cal = 4.184 J)]

M	ΔE^a	$\Delta H^{298,a}$	$\Delta E_{calc}{}^c$	$\Delta H_{exp}{}^d$	$\Delta H_{exp}{}^e$	$\Delta H_{exp}{}^f$
Cr	45.8 (32.5^b)	45.3 (32.0^b)	35.1	38.7	37 ± 5	36.8 ± 2
Mo	40.4	40.3	28.4	30.1	34 ± 5	40.5 ± 2
W	48.0	47.8	33.9	39.7	38 ± 5	46.0 ± 2

[a] Calculated at CCSD(T)/II using MP2/II optimised geometries. [b] Calculated at CCSD(T)/II using estimated geometries, see text. [c] DFT/NL, ref. 4. [d] Ref. 1. [e] Ref. 2. [f] Ref. 3.

Table 2 Bond length (ax/eq) (Å) and total energies E_{tot} (au) of $M(CO)_6$, $M(CO)_5$ (M = Cr, Mo, W)

		MP2/II			CCSD(T)/II	experimental^a	
	Symmetry	r_{M-C}	r_{C-O}	E_{tot}	E_{tot}	r_{M-C}	r_{C-O}
$Cr(CO)_6$	O_h	1.8613	1.1676	−764.29085	−764.24425	1.918	1.141
$Mo(CO)_6$	O_h	2.0608	1.1643	−745.46649	−745.49544	2.063	1.145
$W(CO)_6$	O_h	2.0597	1.1655	−745.73214	−745.75970	2.058	1.148
$Cr(CO)_5$	C_{4v}	1.7438/1.8736	1.1917/1.1666	−651.17778	−651.13751		
$Mo(CO)_5$	C_{4v}	1.9296/2.0604	1.1787/1.1650	−632.37243	−632.39739		
$W(CO)_5$	C_{4v}	1.9440/2.0534	1.1778/1.1671	−632.62355	−632.64940		
CO	$C_{\infty h}$		1.1511	−113.02064	−113.03376		1.1150

[a] Ref. 12.

The situation is complicated by theoretically predicted activation energies using density functional theory for reaction (1). Somewhat surprisingly, the results obtained using the local density approximation (LDA) with nonlocal corrections (NL) support the experimental values reported from the kinetic measurements.[4] But the LDA/NL calculations were performed without corrections for zero-point vibrational energies (ZPE) and thermal contributions, using experimental geometries for $M(CO)_6$ and frozen geometries for $M(CO)_5$.[4] The theoretical results are also shown in Table 1.

We have systematically studied the accuracy of effective core potentials (ECP) for calculating transition metal complexes.[5] Here we report quantum mechanical calculations for the first dissociation energies of $M(CO)_6$ (M = Cr, Mo, W) using ECPs[6] for the metals and all electron basis sets for C and O. The geometries are optimized at the MP2[7] level using a (441/2111/N-1) valence basis set for the metals, which is derived from the (55/5/N) minimal basis set optimized by Hay and Wadt[6] (N = 5, 4, 3 for Cr, Mo, W, respectively). A 6-31G(d) all electron basis set is used for C, O.[8a] This basis set combination is denoted II. The dissociation energies are calculated using coupled-cluster theory with singles and doubles and a noniterative estimate of triple substitutions [CCSD(T)].[9] ZPEs are calculated at the Hartree-Fock level using a (441/41/N-1) ECP valence basis set for the metals and 3-21G[8b] for C, O (basis set I). The geometries have been calculated using the program TURBOMOLE.[10] For the CCSD(T) calculations the program ACES II[11] was employed.

Table 2 shows the geometries for $M(CO)_6$ (O_h) and $M(CO)_5$ (C_{4v}) molecules optimized at MP2/II and the experimental values[12] for $M(CO)_6$. The theoretically predicted Mo–C and W–C bond lengths are in excellent agreement with experiment, but the Cr–CO interatomic distance is too short. It is gratifying to learn that the great problems which have been encountered[13] in calculations of the Cr–C bond length in $Cr(CO)_6$ are not encountered when the heavier analogues $Mo(CO)_6$ and $W(CO)_6$ are calculated. It is our general experience that compounds of the second and third row of the transition metals are calculated in much better agreement with experiment than compounds of the first row.[14]

Table 1 shows the calculated first dissociation energies ΔE for reaction (1) at the CCSD(T)/II/MP2/II level of theory.† We converted ΔE into ΔH^{298} values by correcting for ZPE and thermal contributions (7/2 RT). The theoretically predicted ΔH^{298} values for $Mo(CO)_6$ and $W(CO)_6$ are in excellent agreement with the experimental results obtained from gas phase laser pyrolysis.[3] The calculated ΔH^{298} value for $Cr(CO)_6$ is clearly too high [45.3 kcal mol^{-1} (1 cal = 4.184J)]. This may be caused by using the calculated bond length for $Cr(CO)_6$, which is too short. We calculated the first dissociation energy of $Cr(CO)_6$ using the experimental geometry for $Cr(CO)_6$ and an estimated geometry‡ for $Cr(CO)_5$. The theoretically predicted ΔH^{298} value for $Cr(CO)_6$ is much lower (32.0 kcal mol^{-1}) when the estimated geometries are used.

The theoretical results presented here support the experimental values for the first dissociation energies of $M(CO)_6$ measured in the gas phase.[3] The data obtained from kinetic studies of $Mo(CO)_6$ and $W(CO)_6$ refer probably not to dissociation energies, but rather to activation barriers for reactions with an association/dissociation mechanism. Recent mechanistic studies of the substitution reactions of complexes $M(CO)_5$thf (M = Cr, Mo, W) give evidence for a gradual change in mechanism from a more dissociative to a more associative process in the series Cr, Mo, W.[17] The agreement

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† We did not correct the calculated dissociation energies for basis set superposition errors (BSSE). There are two types of errors in calculations using a truncated basis set, *i.e.* the BSSE and the basis set incompletion error (BSIE). These two errors have opposite sign. Both errors can, in principle, be corrected by saturating the basis set. Correcting for the BSSE would leave the BSIE uncorrected. We think that for a comparison with experimental values, directly calculated results should be used rather than estimated data obtained from correction procedures such as the counterpoise method[15] which is not undisputed.[16]

‡ The estimated geometry of $Cr(CO)_5$ was taken from the experimental geometry of $Cr(CO)_6$ and the calculated differences between $Cr(CO)_6$ and $Cr(CO)_5$. Thus, the MP2/II optimized geometry of $Cr(CO)_5$ was used, but the Cr–CO distances were taken as 1.800 Å (axial) and 1.1676 Å (equatorial).

between the LDA/NL calculated dissociation energies[4] and the kinetic data[1] is misleading.§ The theoretical and experimental results suggest the following first dissociation energies ΔH^{298} for the $M(CO)_6$ compounds: $Cr(CO)_6 = 37 \pm 2$ kcal mol^{-1}; $Mo(CO)_6 = 40 \pm 2$ kcal mol^{-1}; $W = 46 \pm 2$ kcal mol^{-1}.

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§ The authors themselves were cautious about their calculated dissociation energies saying '... nor can we exclude that our theoretical results are misleading due to the approximations inherent in the theoretical method'.[1]