The Influence of Metal Electronic Configuration on the Activation Energy for Transition-metal–Carbon Bond Dissociation

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Summary Symmetry arguments suggest that metal electronic configuration can influence the activation energy for metal–carbon homolytic bond dissociation.

It is now generally accepted that the instability of binary transition metal alkyl- and aryl-complexes is not caused by a very weak metal–carbon bond but rather by the possibility of decomposition by low activation energy pathways.[1] The realisation that these activation energies can be greatly influenced by the other ligands co-ordinated to the metal or by substituents on the alkyl- or aryl-groups has led to the isolation of many thermally stable transition metal σ-organo-complexes.[2] Chatt and Shaw[3] suggested that the first step in homolytic metal–carbon bond dissociation involves promotion of an electron from predominantly non-bonding *d* orbitals to antibonding metal–carbon orbitals, and the presence of strong σ- or π-bonding ligands (such as phosphines, carbon monoxide and π-cyclopentadiene) increases the energy gap between these orbitals and hence leads to a higher activation energy. They also pointed out that bulky substituents on aryl-groups could influence the lability of the complex.[4] The Chatt and Shaw dissociative mechanism does present certain difficulties as a general model because it is a photochemical process and the only parameter it allows is the ligand field splitting energy. As a result it is difficult to rationalise the kinetic stabilities of some Cr^{III}, Rh^{III} and Co^{III} alkyls within its framework.[2] Wilkinson and his co-workers[5] have suggested that this difficulty may be overcome if it is assumed that suppression of olefin elimination may be responsible for the stabilities of these substitution inert complexes.

In the absence of detailed kinetic studies it is impossible to evaluate the importance of these different mechanisms, however, the activation energy for homolytic metal–carbon bond dissociation can be influenced by the presence of low lying excited states. This will be illustrated for the octahedral complex MMe_6, and more detailed arguments will be presented later for other co-ordination numbers and geometries.

Bader[6] has shown that the symmetry of the reaction co-ordinate of a unimolecular decomposition reaction may be successfully predicted from a consideration of the excited electronic states of the molecule. The most favourable reaction co-ordinate, which is represented by a normal vibrational mode, is one which mixes the ground and a low lying excited state of the correct symmetry. In terms of group theory this may be stated as follows, for a low activation energy the direct product of the ground and the low lying excited state wave functions must have the same symmetry as the normal vibrational mode, which forms the basis of the reaction co-ordinate for dissociation. In other words, the electronic redistribution associated with forming the activated complex can be facilitated by mixing in an excited state of the correct symmetry. It should be noted that this is not a photochemical effect and does not require promotion of an electron to an excited state.

Table

The ground states and relevant d→d *and* d→p *excited states for octahedral complexes of the type* $[MMe_6]$.

Electronic configuration	Ground state	*d→d* excited state with same spin and symmetry	Relevant *d→p* excited state	Direct product of ground *d→p* excited state
$d^1(t_{2g})^1$	$^2T_{2g}$	None	$^2T_{1u}$	$T_{2g} \times T_{1u} = A_{2u} + T_{2u} + E_u + T_{1u}$
$d^2(t_{2g})^2$	$^3T_{1g}$	$^3T_{1g}(t_{2g})(e_g)$		
$d^3(t_{2g})^3$	$^4A_{2g}$	None	$^4T_{2u}$	$A_{2g} \times T_{2u} = T_{1u}$
$d^4(t_{2g})^4$	$^3T_{1g}$	$^3T_{1g}(t_{2g})^3(e_g)$		
$d^5(t_{2g})^5$	$^2T_{2g}$	$^2T_{2g}(t_{2g})^4(e_g)$		
$d^6(t_{2g})^6$	$^1A_{1g}$	None	$^1T_{1u}$	$T_{1u} \times A_{1g} = T_{1u}$

A low spin transition metal complex MMe_6 has the electronic configuration (ignoring the C–H molecular orbitals); $(a_{1g})^2\ (e_g)^4\ (t_{1u})^6\ (t_{2g})^n\ (e_g^*)\ (t_{1u}^*)\ (a_{1g}^*)\ (n = 0—6)$, and the normal vibrational stretching modes which can form the basis of homolytic metal–carbon bond dissociation have the symmetries a_{1g}, e_g and t_{1u}.[7] A consideration of the ground and one electron excited states for d^1 to d^6 low spin configurations (see Table) leads to the following conclusions:

$(t_{2g})^2$, $(t_{2g})^4$ and $(t_{2g})^5$ electronic configurations have excited states with the same symmetries as the ground states, approximately Δ (the $t_{2g}\rightarrow e_g$ energy separation) above the ground state. Therefore the direct product of ground and excited states contains terms of the correct symmetry to allow the a_{1g} and e_g vibrational modes to form the basis of a decomposition reaction co-ordinate (*i.e.* $T_{1g} \times T_{1g} = T_{2g} \times T_{2g} = A_{1g} + E_g + T_{1g} + T_{2g}$). As Δ is typically rather small for first row transition elements (1—3 eV) rather low activation energies are expected for these complexes. A combination of the a_{1g} and e_g modes will result in the simultaneous dissociation of two *trans*-metal–carbon bonds.

$(t_{2g})^1$, $(t_{2g})^3$ and $(t_{2g})^6$ complexes have no suitable $(t_{2g})^{n-1}$ (e_g) excited states and therefore these complexes are expected to be more inert to homolytic dissociation than analogous $(t_{2g})^{2,4 \text{ or } 5}$ complexes. There are, nonetheless, $(t_{2g})^{n-1}$ (t_{1u}) excited states which can mix with the ground state to lower the activation energy of a dissociation based on the t_{1u} vibrational mode (see Table), (*i.e.* the asymmetric dissociation of one metal–carbon bond). These excited states are approximately equal to the metal $nd \rightarrow (n+1)p$ energy separation above the ground state, and consequently their effect on the activation energy will be much smaller than the low lying $d \rightarrow d$ excited states for analogous $(t_{2g})^{2,4 \text{ or } 5}$ complexes. Approximate considerations based on $nd \rightarrow (n+1)p$ promotion energies suggest that for analogous complexes with the same metal oxidation state the order of lability is $(t_{2g})^6 < (t_{2g})^3 < (t_{2g})^1$, and that the activation energy for homolytic metal–carbon bond dissociation will increase with metal oxidation state. Also for these electronic configurations strong σ- or π-bonding ancillary ligands will only be required for the lower metal oxidation states which have small $nd \rightarrow (n+1)p$ promotion energies.

Thus $(t_{2g})^3$ and $(t_{2g})^6$ complexes are substitution and dissociatively inert, but $(t_{2g})^1$ complexes are substitution labile but dissociatively inert, and complexes with this electronic configuration merit further study. Although olefin elimination may play an important part in determining the stabilities of transition metal ethyl- and substituted methyl- compounds as Wilkinson has suggested,[5] it is apparent that the general stability trends observed for transition metal methyl-, phenyl- and hydrido-complexes may also be rationalised with the assumption that homolytic metal–carbon (or metal–hydrogen) bond dissociation is the dominant decomposition mechanism.

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