Transition Metal–Carbon Bond Lability and Electronic Configuration: a Comment

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Summary Theoretical explanations of transition metal–carbon bond lability, in terms of configuration interaction among d^n states along the reaction co-ordinates for homolysis, require closer critical scrutiny.

It was believed for many years that π-accepting ligands stabilised transition metal–carbon bonds by suppressing electronic excitations, which in the absence of such stabilisation would cause cleavage,[1] sometimes assumed[2] to be homolytic. This view has recently been questioned. 'Stabilising ligands' are unnecessary;[3] the cleavage of transition metal-carbon bonds commonly takes place by two-electron processes at least at the end of the transition series;[4] and in many cases the excitations invoked require more energy than is thermally available.[5] Recently, a different role for *d–d* excited states has been suggested, in which they can be mixed into the ground state by bond-weakening distortions provided certain symmetry requirements are satisfied. Thus where *d–d* excited states of the correct symmetry exist, bond-weakening distortions are vibronically facilitated, and the homolytic cleavage of metal–carbon bonds is thereby assisted. The stability of Cr$^{\text{III}}$, Co$^{\text{III}}$, and Rh$^{\text{III}}$ complexes is related to the lack of vibronic facilitation in the configurations t_{2g}^3 and t_{2g}^6. A similar stability is predicted for octahedral t_{2g}^1 systems;[6] and indeed such systems (involving Ti$^{\text{III}}$) are known.[7]

This theory must however be questioned for the following reasons: (i) the b_{2g} bond-weakening distortion of d^8 square-planar complexes should in the theory be assisted by the excited state $[d(z^2) \rightarrow d(x^2 - y^2)]$ (to the energy of which π-bonding as such is irrelevant), yet stable transition metal–carbon σ-bonds are probably better documented for this than for any other situation.[2] (ii) The theory does not explain the stability of such species as Os(CO)$_4$R$_2$.[8] (iii) The theory is given as specific to homolysis. It is of the essence of homolysis that the organometallic group (formally regarded as a carbanion) be lost as a radical; thus homolytic loss of one (or two) groups from a d^n complex must leave a fragment with $n + 1$ (or $n + 2$) outer electrons, and it is to the configuration of these fragments that any theory of homolysis must address itself. (iv) It is true that the theory concerns itself with kinetic, rather than thermodynamic quantities; but unless there is an energy maximum along the dissociation co-ordinate the activation energy for a unimolecular decomposition is equal to the relevant dissociation energy. The mechanism suggested could alter the form of the energy–reaction co-ordinate plot, but not the energy of the final fragments. (v) A test of the value of any theory is its validity when applied to fresh situations. In this case, although the theory is put forward specifically for homolysis, it is in principle applicable to any distortion (indeed, this could be presented as a strength). Such an effect should show in a facilitation of the a_{1g} and e_g stretching modes, relative to t_{1u}, for the appropriate configurations. Comparison of frequencies for $Ru(NH_3)_6^{3+}$ and $Ru(ND_3)_6^{3+}$ with those for the Rh^{III} analogues shows the effect to be non-existent or very small.[9] Results for the d^2 hexafluorides appear in better accord with the theory, but PtF_6 does not show the effect, nor in any case does the a_{1g} vibration. Moreover, the origins of the effect lie in interactions of terms within the t_{2g}^n configuration, rather than in the configuration interaction required by the theory.[10]

In conclusion, the theory under discussion conceals complexities which must be further resolved if it is to be used to explain chemical phenomena. While direct tests of the theory are lacking, its extension leads to the prediction of effects that are either absent, or else too small to have gross chemical implications.

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