Kinetic and Spectroscopic Parameters for Some Metal–Metal Bonded Carbonyls

By J. PAUL FAWCETT, ANTHONY J. POË,* and MARTYN V. TWIGG

(*Erindale College and the Department of Chemistry, University of Toronto, Toronto, Canada*)

Summary Activation enthalpies for reactions of several metal–metal bonded carbonyls are shown to correlate well with force constants for the metal–metal vibration, and with energies of a u.v. absorption band that can be assigned to a $\sigma \rightarrow \sigma^*$ transition between orbitals of the metal-metal bond.

ACTIVATION parameters have been obtained for the reactions of $M_2(CO)_{10}$ (M = Mn,[1] Tc,[2] and Re[3]), $MnRe(CO)_{10}$,[2] and $[Mn(CO)_4L]_2$ [L = PPh_3[2] and $P(OPh)_3$[4]] with oxygen in decalin under conditions where they proceed at rates independent of $p(O_2)$ and first order in [complex]. No clearly defined carbonyl products are formed. The activation enthalpies for the decacarbonyls show a good correlation (see Figure) with corresponding force constants[5] for vibration of the metal–metal bond and, therefore, with this particular measure of the relative metal–metal bond strengths. Force constants are not known for the metal–metal vibrations in the substituted carbonyls but electronic spectra can provide another measure of the strength of metal–metal bonds. Gray *et al.* have made a rigorous assignment[6] of the band at 29,200 cm^{-1} in the electronic spectrum of dimanganese decacarbonyl to a $\sigma \rightarrow \sigma^*$ transition involving orbitals from the metal–metal interaction. Corresponding bands for technetium and rhenium decacarbonyls were also assigned, by analogy. These energies can be taken as an approximate measure of the energy required to destroy the metal–metal interaction without drastically changing any of the other interactions in the molecule, and they should therefore provide some measure of the relative strengths of the metal–metal bonds, at least in closely related complexes. The absolute energies so obtained will almost certainly be overestimates of the energies of homolytic dissociation. We have measured the electronic spectra of cyclohexane solutions of MnRe(CO)$_{10}$ and of several substituted decacarbonyls. If we assume that the bands corresponding to those in $M_2(CO)_{10}$ (M = Mn, Tc, and Re) can also be assigned to the $\sigma \rightarrow \sigma^*$ transition then we find the correlation, shown in the Figure, between the activation enthalpies and $h\nu(\sigma \rightarrow \sigma^*)$.

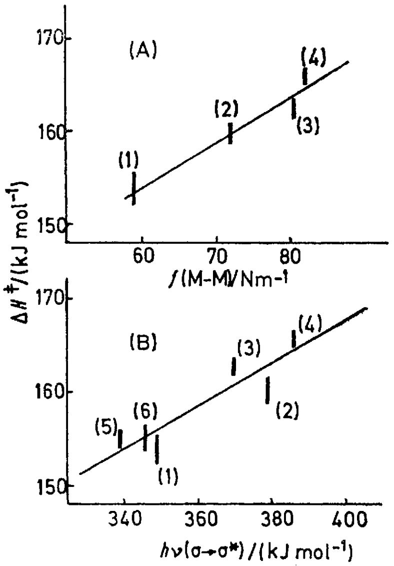

FIGURE. *Correlation of kinetic and spectroscopic parameters for some metal–metal bonded carbonyls.* (A) $\Delta H^\ddagger$ *vs. force constants for metal–metal vibrations.* (B) $\Delta H^\ddagger$ *vs.* $h\nu$ $(\sigma \rightarrow \sigma^*)$. *Kinetic data are for reactions of oxygen with* (1) $Mn_2(CO)_{10}$, (2) $Tc_2(CO)_{10}$, (3) MnRe-(CO)$_{10}$, (4) $Re_2(CO)_{10}$, and (5) $[Mn(CO)_4P(OPh)_3]_2$, *and of carbon monoxide with* (6) MnRe(CO)$_8$(PPh$_3$)$_2$. *Uncertainties, indicated by lengths of vertical lines, are standard deviations.*

In many cases we find that substitutions of carbon monoxide by phosphines, or the reverse, have the same activation parameters as the reactions with oxygen, and we have therefore included data for the reaction of MnRe(CO)$_8$-(PPh$_3$)$_2$ with carbon monoxide,[2] activation parameters for reaction with oxygen not being available. These data also fit with the correlation, as do those[7] for the reaction of $Mn_2(CO)_9P(OPh)_3$ with P(OPh)$_3$. The uncertainty of $\Delta H^\ddagger$ for this reaction is rather large and this example is not included in the Figure. Data for the reactions of Mn_2-$(CO)_9PBu_3$ with PBu$_3$,[7] $Mn_2(CO)_9PPh_3$ with PPh$_3$,[2,7] and $[Mn(CO)_4PPh_3]_2$ with oxygen[2] lie increasingly below the line along that series, to the extent of *ca.* 13, 20, and 30 kJ mol^{-1}, respectively, $\Delta H^\ddagger$ decreasing more rapidly than $h\nu(\sigma \rightarrow \sigma^*)$.

We have also obtained kinetic evidence[2] that reactions of oxygen with $Mn_2(CO)_{10}$ and MnRe(CO)$_{10}$ proceed *via* homolytic fission of the metal–metal bond, this reaction being reversible at higher concentrations of complex and/or lower concentrations of oxygen. A similar mechanism also appears to be operating in reactions of oxygen with [Mn-$(CO)_4L]_2$ [L = PPh$_3$ and P(OPh)$_3$]. Similar evidence for the mechanism of reaction with $Tc_2(CO)_{10}$ and $Re_2(CO)_{10}$ has not been obtained. The correlation of activation enthalpies with metal–metal force constants and with $h\nu(\sigma \rightarrow \sigma^*)$ adds strong support to this mechanism. The relative force constants suggest that the Mn–Re bond is stronger than the Tc–Tc bond, in agreement with the kinetic data, whereas the u.v. data suggest the opposite order. Possibly the u.v. data are a less reliable indication of bond strengths of unsymmetrical metal–metal bonds. The fact that activation parameters for substitution are so frequently identical with, or very close to, those for reaction with oxygen suggests that the substitution reactions are also dependent on metal–metal bond strengths to a similar degree. Those complexes that have activation enthalpies lower than expected from the correlation may suffer from steric strain, due to the substituted phosphines, that is relieved as the metal–metal bond is stretched. The absence of this effect for MnRe(CO)$_8$(PPh$_3$)$_2$ is surprising although data for the reaction of this complex with oxygen are not yet available. Whatever the cause of the deviations however, we believe that these correlations, and the deviations from them, are important in any consideration of the mechanisms for such reactions, and in planning further studies. So far as the strength of the metal–metal bonds is concerned, the enthalpies of activation for the complexes showing the linear correlation span a range of only *ca.* 10 kJ mol^{-1}, whereas the deviations that we have tentatively ascribed to steric effects rise to as much as 30 kJ mol^{-1}. Electronic effects due to substitution of phosphines may therefore be much smaller than was originally thought.[8]

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