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Preliminary communication

Reorganisation Energies and Site Preferences of Carbonyl Ligands: Bond Energies of the Bridging and Terminal Carbonyl Groups of the Iron Carbonyls $Fe_2(CO)_9$ and $Fe(CO)_5$

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Summary

An illustration of how bond energies may be assigned to all the 2-centre links in a bi- or poly-nuclear metal carbonyl, using bond energy-bond length relationships of the form $\underline{E} = \underline{Ad}^{-\underline{k}}$, is given using $Fe_2(CO)_9$ as the example; its C-O and M-C bond energies are calculated to be 947 ± 16 and 241 ± 10 kJ.mol^{-1} respectively for the terminal ligands, and 869 ± 20 and 166 ± 8 kJ.mol^{-1} respectively for the bridging ligands, indicating that the carbonyl ligands may have a slight preference for the bridging sites. A similar treatment of $Fe(CO)_5$ affords values of $\underline{E}$(C-O) = 963 ± 12 kJ.mol^{-1}, and E(Fe-C) = 230 ± 10 and 220 ± 10 kJ.mol^{-1} for its axial and equatorial metal-carbon bonds respectively.

In a recent note, [1], we outlined a new method for assigning bond enthalpies to the metal-metal bonds of metal carbonyl clusters, using the known length and strength of the bonds in the metals themselves as the basis, and using a bond length ($\underline{d}$) - bond enthalpy ($\underline{E}$) relationship of the form $\underline{E} = \underline{Ad}^{-\underline{k}}$, where $\underline{A}$ and $\underline{k}$ are constants. Here, using $Fe_2(CO)_9$ as an example, we indicate how the carbon-oxygen and metal-carbon distances in metal carbonyls of accurately known structure may be used (a) to calculate the C-O bond energy, $\Delta\underline{E}$(C-O), lost by carbon monoxide on coordination to a terminal or bridging site, (b) to assign energies to the metal-carbon bonds of metal carbonyls, and (c) to investigate whether there is a preference by the ligands for terminal or bridging sites.

The interatomic distances in $Fe_2(CO)_9$, which contains six terminal and three bridging carbonyl ligands, are given in Figure 1, [2]. The ligand C-O bonds, like those of metal carbonyls in general, are longer and weaker than those of free CO, which has $\underline{d}$(C-O) = 112.82 ± 0.01 pm [3] and $\underline{E}$(C-O) = 1070 ± 2 $kJ.mol^{-1}$ [4]. Since the energies of carbon-oxygen bonds, ranging from the triple bond of free CO through the double C=O bond of aldehydes and ketones, (typically d = 123 pm and E = 695 kJ [5]), to the single C-O bonds of ethers and alcohols, (typically d = 143 pm and E = 336 kJ), vary with length according to the relationship $\underline{E} = \underline{Ad}^{-5}$, we suggest that this relationship can be used to calculate the C-O bond energies of the ligands of $Fe_2(CO)_9$; hence, for the terminal ligands, we obtain $\underline{E}(\mathrm{C{-}O})_t$ = 947 ± 16 $kJ.mol^{-1}$, and for the bridging ligands, $\underline{E}(\mathrm{C{-}O})_\mu$ = 869 ± 20 $kJ.mol^{-1}$. The terminal ligands have thus lost $\Delta\underline{E}(\mathrm{C{-}O})_t$ = 123 ± 16 $kJ.mol^{-1}$, and the bridging ligands $\Delta\underline{E}(\mathrm{C{-}O})_\mu$ = 201 ± 20 $kJ.mol^{-1}$, relative to uncoordinated carbon monoxide.

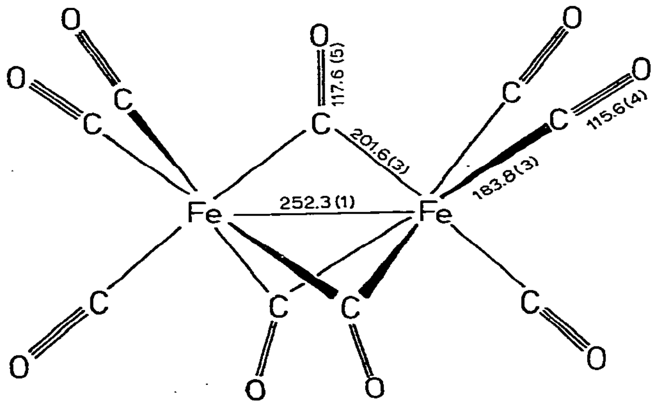

Figure 1. Structure [2] of $Fe_2(CO)_9$ (Distances in pm).

To remove a terminal carbonyl ligand from $Fe_2(CO)_9$ involves cleaving a metal-ligand bond of enthalpy $\underline{E}(\mathrm{Fe{-}C})_t$ and regaining the ligand reorganisation energy $\Delta\underline{E}(\text{C-O})_t$. The dissociation enthalpy, $\underline{D}(\text{Fe-CO})_t$, is thus equal to $\underline{E}(\text{Fe-C})_t$ minus $\Delta\underline{E}(\text{C-O})_t$. To remove a bridging ligand involves cleaving two metal-ligand bonds of enthalpy $\underline{E}(\text{Fe-C})_\mu$ and regaining the reorganisation energy $\Delta\underline{E}(\text{C-O})_\mu$; hence the dissociation enthalpy $\underline{D}(\text{Fe-CO})_\mu$ is equal to $2\underline{E}(\text{Fe-C})_\mu - \Delta\underline{E}(\text{C-O})_\mu$. The overall enthalpy changes associated with the disruption of $Fe_2(CO)_9$ into metal atoms and carbon monoxide molecules are thus as shown in Figure 2. Since the enthalpy change for the process $Fe_2(CO)_9 \rightarrow 2Fe + 9CO$ is 1173 ± 25 kJ.mol^{-1}, [6], and $\underline{E}(\text{Fe-Fe}) = 70 \pm 2$ kJ.mol^{-1}, [1], the total energy assignable to the six terminal and six bridging Fe-C bonds of $Fe_2(CO)_9$ is $1173 + (6 \times 123) + (3 \times 201) - 70 = 2444 \pm 110$ kJ.mol^{-1}.

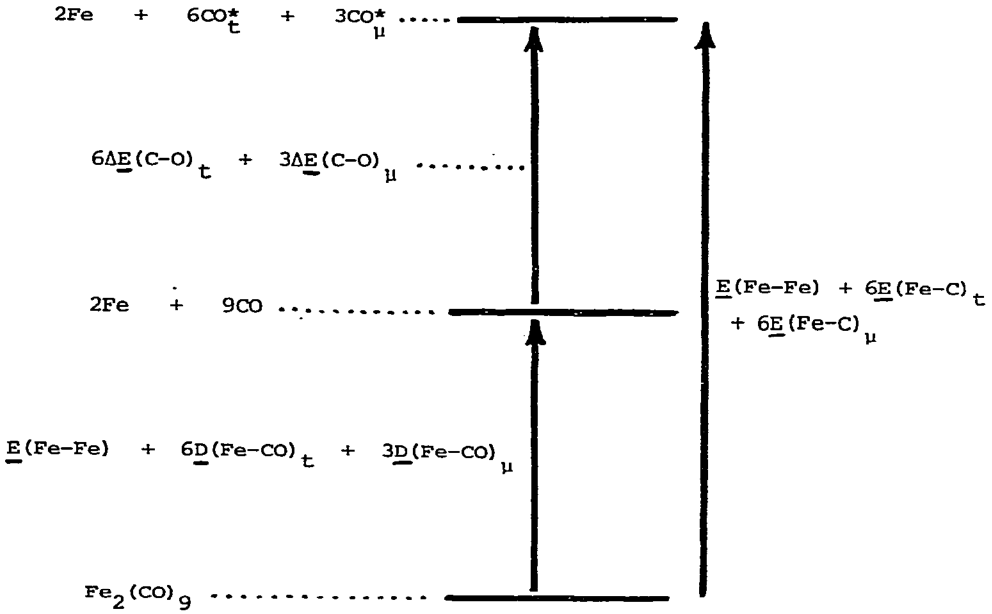

Figure 2. Energy Relationships in the gas-phase disruption of $Fe_2(CO)_9$ into $2Fe + 9CO$

(CO_t^* and CO_μ^* are hypothetical activated CO molecules with bond lengths equal to those of the terminal and bridging ligands of $Fe_2(CO)_9$ respectively)

To allocate this energy appropriately to the two types of metal-carbon bond, we need to know how iron-carbon bonds vary in strength with length. In the absence of any well-established relationship, we consider the relationship $\underline{E} \alpha \underline{d}^{-4}$ to be appropriate, because Fe-Fe bonds have $\underline{E} \alpha \underline{d}^{-4.6}$, and C-C bonds have $\underline{E} \alpha \underline{d}^{-3.3}$. Hence we can write two equations involving the unknowns $\underline{E}(\text{Fe-C})_t$ and $\underline{E}(\text{Fe-C})_\mu$:-

$$\underline{E}(\text{Fe-C})_t = (201.6/183.8)^4 \underline{E}(\text{Fe-C})_\mu$$

$$\text{and } 6\underline{E}(\text{Fe-C})_t + 6\underline{E}(\text{Fe-C})_\mu = 2444 \pm 110 \text{ kJ.mol}^{-1}$$

Solving, we obtain $\underline{E}(\text{Fe-C})_t = 241 \pm 10 \text{ kJ.mol}^{-1}$ and $\underline{E}(\text{Fe-C})_\mu = 166 \pm 8 \text{ kJ.mol}^{-1}$.

The energy, $\underline{D}(\text{Fe-CO})$, needed to remove a carbonyl ligand from $Fe_2(CO)_9$ can now be calculated: for the terminal ligands, $\underline{D}(\text{Fe-CO})_t = 241 - 123 = 118 \pm 25 \text{ kJ.mol}^{-1}$; for the bridging ligands, $\underline{D}(\text{Fe-CO})_\mu = (2 \times 166) - 201 = 131 \pm 25 \text{ kJ.mol}^{-1}$. In view of the uncertainties involved, which stem largely from uncertainties about the precise values of $\underline{d}(\text{C-O})$, the difference between $\underline{D}(\text{Fe-CO})_t$ and $\underline{D}(\text{Fe-CO})_\mu$ cannot be regarded as significant. The carbonyl ligands apparently have much the same affinity for both bridging and terminal sites, though there may be a slight preference for the bridging sites.

A check on whether our bond enthalpy assignments are realistic is provided by a consideration of $Fe(CO)_5$, which has the trigonal bipyramidal structure and interatomic distances shown in Figure 3, [7], and a gas-phase

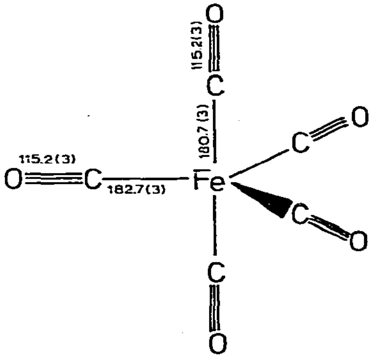

Figure 3. Structure [7] of $Fe(CO)_5$ (Distances in pm).

enthalpy of disruption into Fe + 5CO, $\Delta H_{disrupt}$, of 585 ± 6 kJ.mol^{-1}. From the C-O bond lengths of $Fe(CO)_5$ we calculate that $\underline{E}$(C-O) = 963 ± 12 kJ.mol^{-1} and that $\Delta\underline{E}$(C-O) = 107 ± 12 kJ.mol^{-1}. We can therefore write the following two equations:

$$2\underline{E}(\mathrm{Fe{-}C})_{axial} + 3\underline{E}(\mathrm{Fe{-}C})_{equatorial} = 585 + (5 \times 107)\,\mathrm{kJ.mol^{-1}}$$

$$\underline{E}(\mathrm{Fe{-}C})_{axial}/\underline{E}(\mathrm{Fe{-}C})_{equatorial} = [182.7/180.7]^4$$

Hence $\underline{E}$(Fe-C)$_{axial}$ = 230 ± 10 kJ.mol^{-1} and $\underline{E}$(Fe-C)$_{equatorial}$ = 220 ± 10 kJ. mol^{-1}. These values, which relate to Fe-C bonds of length 180.7 pm and 182.7 pm respectively, may be compared with the value of $\underline{E}$(Fe-C)$_t$ = 241 ± 10 kJ.mol^{-1} for the terminal Fe-C bonds of length 183.8 pm in $Fe_2(CO)_9$. In view of the e.s.d.'s involved, the fact that the Fe-C bonds of $Fe_2(CO)_9$ appear to be a little stronger than the slightly shorter Fe-C bonds of $Fe(CO)_5$ cannot be regarded as significant. Precise determination of $\underline{E}$(Fe-C) by the present method must await yet more accurate determination of $\underline{d}$(Fe-C) and (particularly) of $\underline{d}$(C-O). However, our results for both $Fe(CO)_5$ and $Fe_2(CO)_9$ suggest that $\underline{E}$(Fe-C)$_{terminal}$ probably lies in the range 220-240 kJ.mol^{-1}.

References

1. C.E. Housecroft, K. Wade and B.C. Smith, J. Chem. Soc. Chem. Commun., (1978) 765.
2. F.A. Cotton and J.M. Troup, J. Chem. Soc. Dalton, (1974) 800.
3. P.R. Bunter, J. Mol. Spectrosc., **39** (1971) 90.
4. J. Chao et. al. JANAF Thermochemical Tables, 1965 (Dow Chemical Company, Midland, Michigan) U.S. Dept. of Commerce, Nat. Bureau of Standards, Institute for Applied Technology.
5. F.A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry', Wiley Interscience, New York, 1972, 3rd edn.
6. J.A. Connor, Topics in Current Chem., **71** (1977) 71.
7. B. Beagley and D.G. Schmidling, J. Mol. Structure, **22** (1974) 466.