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*Short communications*

# CALORIMETRIC STUDY OF ADDUCT FORMATION AT 300 K BETWEEN $H_2Os_3(CO)_{10}$ AND LEWIS BASES

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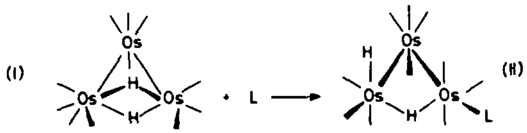
The enthalpies of the reactions $H_2Os_3(CO)_{10}(I) + L = H_2Os_3(CO)_{10}L(II)$, $L = PR_3$, $P(OR)_3$, in chloroform were determined by means of microcalorimetry. Satisfactory agreement was found between the basicity parameters and the measured reaction enthalpies. As concerns the kinetics, qualitative correlation of a thermokinetics parameter with the steric factor of the ligand was observed.

The reactions of transition metal carbonyl clusters have been subjected to intense investigation as these molecules may have an important role in homogeneous catalysis [1].

One way to obtain active homogeneous catalysts is to produce coordinatively unsaturated species in solution. $H_2Os_3(CO)_{10}$ is a well-known stable hydride, which has been employed as starting material in several reactions to form osmium cluster derivatives [2].

In particular, it has been shown that I readily reacts at room temperature with a Lewis base, $L$ ($L$ = carbon monoxide, phosphines, phosphites, etc.), according to the following reaction scheme:



The reactions involving metal carbonyl clusters often give a number of products, so that it may be difficult to acquire detailed information about the reaction mechanism, but the transformation I →II probably represents a case of a single mechanistic step process.

Metal carbonyl clusters have been extensively studied by kinetic methods [3], but direct measurements of the reaction enthalpies are very uncommon [4]; in order to gain more insight into the thermal features of metal carbonyl clusters, we report here some preliminary results concerning the transformation I →II.

## Experimental

All measurements were performed at 300 K, employing a Calvet microcalorimeter (CRMT type) and the calorimetric cell we conceived to study reactions in the liquid phase according to a technique already described [5].

The carbonyl clusters and the tertiary phosphines were both dissolved in chloroform: the solutions of the clusters and the phosphines were thermostated in the calorimeter and then mixed. The concentrations ranged between $4.10^{-3}$ and $1.10^{-2}$ *M*; blank experiments showed that the dilution heats were in all cases negligible.

## Results and discussion

The enthalpies of the reaction $H_2Os_3(CO)_{10}(I) + L = H_2Os_3(CO)_{10}L(II)$ in chloroform are given in Table 1.

$C^{13}$–NMR spectra of adduct II, previously obtained following the addition of L to a $CHCl_3$ solution of I, have shown that this reaction is practically quantitative [6].

Table 1 also gives (i) the reciprocal of the half neutralization potentials, obtained by Streuli [7], who studied the reactions of the same phosphines with perchloric acid in nitroethane solution; (ii) the electronic factor, $\nu$, given by Tolman [8] for the same ligands. Both these quantities reflect the $\sigma$-donor ability of the phosphines and

**Table 1** Comparison of the electronic and steric parameters of the ligands and the enthalpy ($\Delta H$) of the reaction $H_2Os_3(CO)_{10} + L = H_2Os_3(CO)_{10}L$

| *L* | $1/E_{1/2}$, $V^{-1}$ | Electr. parameter, $\nu$, $cm^{-1}$ | Steric parameter, $\theta$ ° | Half-deviation time $t_{1/2}$ min | $\Delta H$, kcal/mole |
|---|---|---|---|---|---|
| $(I\text{-}Pr)_3P$ | 8.33 | 2059 | 160 | 56 | 107.9 |
| $Et_2PPh$ | 3.33 | 2063 | 136 | 27.2 | 89.1 |
| $Ph_3P$ | 1.74 | 2069 | 145 | 6.8 | 30.3 |
| $(PhO)_3P$ | 1.11 | 2085 | 128 | 24.8 | 23 |

phosphites. Comparison of the sets of results reveals good agreement between the basicity parameters and the reaction enthalpies.

It must be remembered, however, that the enthalpy is only an indirect measure of the bond strength between osmium and phosphorus; in fact, it has been well established through the NMR spectra [6] and solid-state structure deermination [9] that synthesis of the adduct II is associated with cleavage of a hydride bridge, with the consequent formation of a terminally bonded hydride on the unsubstituted osmium. The contribution of this internal rearrangement has to be considered in the evaluation of the enthalpy of the reaction.

In Table 1 the half-deviation times of the heat emission peaks are also given. It is well known that this is only a semiquantitative parameter, as the true thermokinetics is very difficult to deduce [10]. In the Table one can observe furthermore the steric factors of the same Lewis bases, defined by the ligand cone angle [8]. Our half-deviation times are in satisfactory agreement with these steric factors (i.e. with increasing $\vartheta$, larger $t_{1/2}$ values are obtained), but in the case of adduct II with triphenylphosphine quite fast kinetics has been observed. This behaviour suggests that transformation I →II must be interpreted with caution and that a single mechanistic step may not be proposed for the reaction of all the tertiary phosphines, since different transient states are probably present.

Further calorimetric studies involving a wide range of Lewis bases are needed, however, to attain a better understanding of the kinetics and the thermodynamics of these adduct formations.

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