Journal of Organometallic Chemistry, 94 (1975) 281—284
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THERMOCHEMISTRY OF METAL CARBONYL COMPOUNDS*

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Introduction

It is well known that there is a large gap in precise thermodynamic data in the field of organometallic chemistry. The information is badly needed in order to test the results obtained by theoretical calculations. It was therefore decided to carry out an investigation into the thermochemistry of metal carbonyl compounds.

In this lecture we will discuss the main purpose of our thermochemical research: the determination of the bond energies of the M—L and M—CO bonds in molecules of the form $M(CO)_{6-x}L_x$, in which M is a Group VIB metal and L is a nitrogen-bound ligand.

The substitution reactions of acetonitrile by carbon monoxide under isobaric conditions were studied in the case where M is tungsten and L is acetonitrile. In order to obtain reliable enthalpies of reaction it is of great importance to have well-defined initial and final compound(s). Evidence for these was obtained by carrying out the substitution reaction on a thermobalance (Mettler, type 1) and by IR-spectroscopic analysis of the products formed.

In the measured enthalpy of reaction the contributions from changes in enthalpies of formation, heat capacities and lattice energies are involved. These values are well known in the literature for all the compounds involved in the substitution reactions [1,2] except for the acetonitrile complexes.

The enthalpy of reaction is measurable in several ways [3-5]. Differential scanning calorimetry, DSC, (Dupont, type 990), was chosen by which experimental method it is also possible to determine the heat capacities of the compounds. The lattice energies are determined by means of a fully automatic vapour pressure measurement apparatus developed in our laboratory [6].

Since the standard enthalpy of formation of $W(CO)_6$ is known from other calorimetric work [7,8], it is possible to study the influence of the replacement of CO by CH_3CN in $W(CO)_6$ on this enthalpy value.

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* Presented at the Symposium on Metal Carbonyl Chemistry, dedicated to Professor Walter Hieber, held at Ettal (West Germany), July 21st-July 27th, 1974.

Results

A. W(CO)$_5$CH$_3$CN

The compound was prepared photochemically [9]. On the thermobalance it can be seen that the CO-substitution reaction under isobaric conditions is quantitative:

$$W(CO)_5CH_3CN + CO \rightarrow W(CO)_6\uparrow + CH_3CN\uparrow + \Delta H_{r(1)}$$

The products formed were identified by IR analysis. The thermogravimetric curve and its derivative show only one reaction step. The DSC-curve of the same reaction has the form shown in Fig. 1A. The form of the curve in this thermogram is remarkable in view of the thermogravimetric results.

It was impossible to find an explanation for the stepwise decomposition. An attempt will be made to obtain more information about this substitution reaction with the aid of matrix IR spectroscopy.

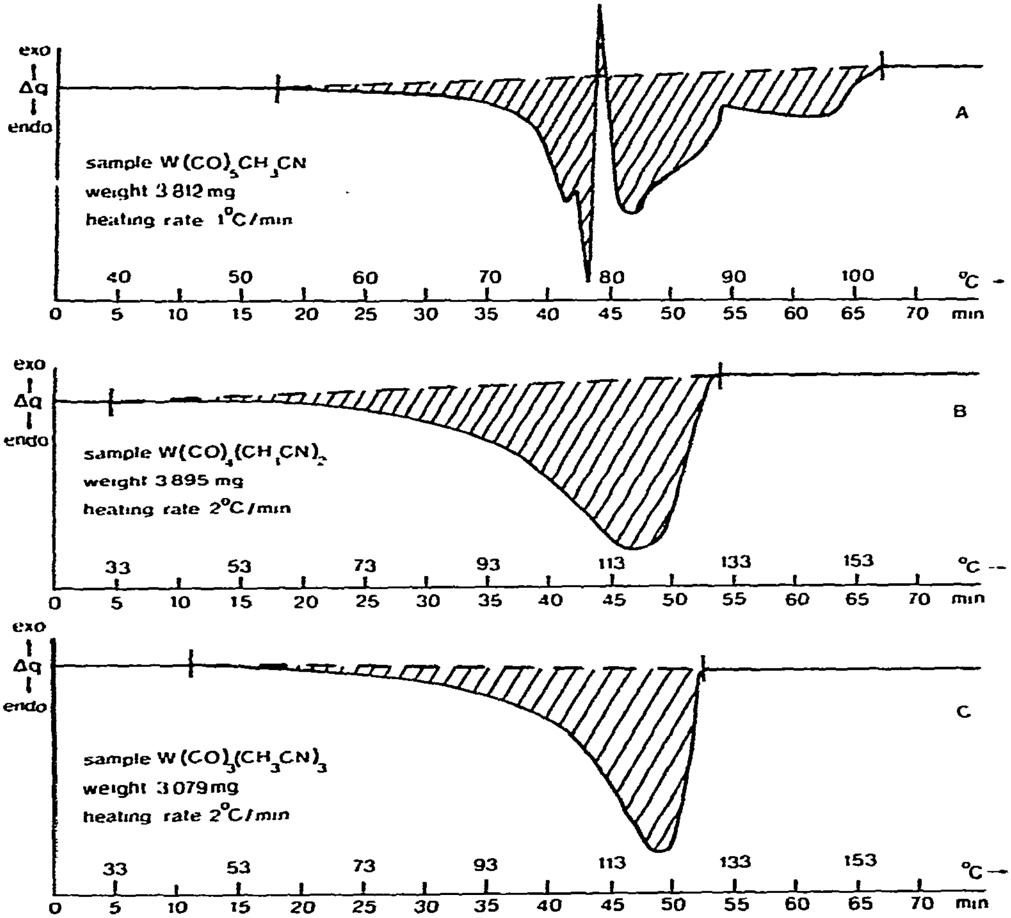

Fig. 1. DSC-curve for CO substitution in W(CO)$_{6-x}$(CH$_3$CN)$_x$. Dynamic CO atmosphere, gas flow 2 l/h.

The DSC-curves obtained from fourteen experiments were reproducible both in form and area. The enclosed area, shaded in Fig. 1, is a measure of the enthalpy of reaction. The value of the molar enthalpy of reaction determined is 16.9 ± 0.6 kcal/mol.

Calculation of the standard enthalpy of formation gives, after reduction to standard conditions (25°C): $\Delta^s H^\circ_{f(1)} = -199.5 \pm 0.6$ kcal/mol, for which the standard deviation is defined as:

$$S = \sqrt{\frac{\sum_i \Delta_i^2}{n-1}}$$

where Δ_i = deviation from the mean, n = number of experiments.

B. *cis*-$W(CO)_4(CH_3CN)_2$ *and cis*-$W(CO)_3(CH_3CN)_3$

The bis-acetonitrile complex is prepared photochemically [9] and the tris-compound is prepared as described in the literature [10]. The substitution of acetonitrile by CO performed under isobaric conditions on the thermobalance is quantitative:

$$W(CO)_4(CH_3CN)_2 + 2CO \rightarrow W(CO)_6{}^{\uparrow} + 2CH_3CN^{\uparrow} + \Delta H_{r(2)}$$

and

$$W(CO)_3(CH_3CN)_3 + 3CO \rightarrow W(CO)_6{}^{\uparrow} + 3CH_3CN^{\uparrow} + \Delta H_{r(3)}$$

The thermogravimetric curves and their derivatives show only one reaction step. The DSC-curves from these reactions are given in Figs. 1B and 1C, indicating only one decomposition step. In the temperature region of the shaded area there is only evidence for $W(CO)_4(CH_3CN)_2$ and $W(CO)_3(CH_3CN)_3$ respectively and $W(CO)_6$.

The optimal reaction temperature is 115°C for the bis-substituted complex; the tris-compound is slightly more stable. Comparison with the mono-substituted complex is difficult since the bis- and tris-substituted complexes are heated at twice the heating rate of the mono-acetonitrile complex. The values of the molar enthalpy of reaction are 17.8 ± 0.9 kcal/mol for the bis-compound and 17.3 ± 1.2 kcal/mol for the tris-substituted complex. Calculation of the standard enthalpy of formation gives, after reduction to standard conditions: $\Delta^s H^\circ_{f(bis)} = -204.7 \pm 0.9$ kcal/mol and $\Delta^s H^\circ_{f(tris)} = -210.4 \pm 1.2$ kcal/mol respectively.

Discussion

Cotton [7] and recently Barnes [8] determined the standard enthalpy of formation of $W(CO)_6$, both values for which are precise and in good agreement with each other. As the heats of formation of $W(CO)_{6-x}(CH_3CN)_x$ have been determined with great precission, it is possible to draw conclusions about the relative stabilities of these compounds (Table 1).

The stability of the acetonitrile-substituted compounds with regard to $W(CO)_6$ is less in all cases. Our impression is that this stability behaviour is caused by a rearrangement of electrons throughout the whole molecule on substituting one CO group in $W(CO)_6$ by CH_3CN. In particular the CO-ligands *cis* to CH_3CN are labilized [9].

TABLE 1

STANDARD ENTHALPY OF FORMATION OF $W(CO)_{6-x}(CH_3CN)_x$ (solid state)

$\Delta^{s}H_f^{o}W(CO)_6 = -227.3$ kcal/mol[a]
$\Delta^{s}H_f^{o}W(CO)_5CH_3CN = -199.5$ kcal/mol
$\Delta^{s}H_f^{o}W(CO)_4(CH_3CN)_2 = -204.7$ kcal/mol
$\Delta^{s}H_f^{o}W(CO)_3(CH_3CN)_3 = -210.4$ kcal/mol

[a] Ref. 7.

The thermal stabilities as shown by Fig. 1, which were corroborated on the thermobalance are understandable in terms of our enthalpy data, viz.: stability hexa > tris > bis > mono. It is difficult (photochemically) to replace one CO-group by CH_3CN in $W(CO)_6$. Once the mono-product has been formed it is much simpler to replace the second and third CO group. The recently described, but not explained, disproportionation reactions of these acetonitrile complexes [11] must be considered in the light of the very small differences in energy content between the different molecules. We must conclude that the energies of activation for the different reactions should be approximately the same.

Appearance potential measurements and the enthalpies of formation of other carbonyl complexes with nitrogen-bound ligands will possibly reveal the bond properties of these ligands. The values of the W—CO and W—$NCCH_3$ bond energies of all these compounds will be published [9].

Acknowledgements

We are indebted to Mr. J. Berke and Mr. J. Oor for the preparation of the pure compounds and to Mr. H.J. van Ballegoy for the accurate thermobalance and DSC measurements.

References

1 Handbook of Chemistry and Physics, 53rd edition, The Chemical Rubber Co press, Cleveland, Ohio, 1972/1973.
2 I. Barin and O. Knacke, Thermochemical Properties of Inorganic Substances, Springer-Verlag, Berlin and Heidelberg, 1973.
3 L.G. Berg and V.P. Egunov, J. Therm. Anal., 1 (1969) 5.
4 S.J. Ashcroft and C.T. Mortimer, J. Chem. Soc. A, (1971) 781.
5 J.A. Connor, H.A. Skinner and Y. Virmani, J. Chem. Soc. Faraday Trans. I, 68 (1972) 1754.
6 R.H.T. Bleyerveld, J.B. Molenaar and F.C. Mijlhoff, J. Phys. E, 8 (1975) 235.
7 F.A. Cotton, A.K. Fischer and G. Wilkinson, J. Amer. Chem. Soc., 78 (1956) 5168.
8 D.S. Barnes, G. Pilcher, D.A. Pittam, H.A. Skinner and D. Todd, J. Less Common Met., 38 (1974) 53.
9 R.H.T. Bleyerveld, Th. Höhle and K. Vrieze, Inorg. Chim. Acta, (1975) in press.
10 D.P. Tate, W.R. Knipple and J.M. Augl, Inorg. Chem., 1 (1962) 433.
11 J.M. Graham and M. Kilner, J. Organometal. Chem., 77 (1974) 247.