Journal of Organometallic Chemistry, 213 (1981) 151—156
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

MICROCALORIMETRIC STUDIES OF DODECACARBONYL(DIIRON)RUTHENIUM AND DODECACARBONYL(IRON)DIRUTHENIUM. ENTHALPY CONTRIBUTION OF HETEROMETALLIC METAL—METAL BONDS *

ALEXEI K. BAEV, JOSEPH A. CONNOR *, NABILA I. EL-SAIED and HENRY A. SKINNER

Department of Chemistry, University of Manchester, Manchester M13 9P1 (Great Britain)

(Received February 11th, 1981)

Summary

Microcalorimetric measurements at 520—550 K of the heats of thermal decomposition of $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$ and $Ru_3(CO)_{12}$ lead to values of the standard enthalpy of formation (ΔH_f°, c/kJ mol^{-1}) as follows: $Fe_2Ru(CO)_{12}$ —(1820 ± 14); $FeRu_2(CO)_{12}$ — (1891 ± 16); $Ru_3(CO)_{12}$ —(1903 ± 18). Enthalpies of sublimation are estimated and the iron—ruthenium bond enthalpy contribution is derived as E(Fe—Ru) = (95 ± 20) kJ mol^{-1}.

Introduction

Various approaches to the thermodynamic description of transition metal clusters are developing, but there is a lack of experimental information [1]. In particular, there is no information about the bond enthalpy contributions of the metal—metal bonds in heterometallic transition metal compounds [2]. This information would be useful in a detailed description of large metal clusters [3] containing more than one type of metal atom, such as $[NiRh_6(CO)_{16}]^{2-}$ [4] or $[Mo_2Fe_4C(CO)_{18}]^{2-}$ [5]. We have made calorimetric measurements on the trinuclear dodecacarbonyls $[M^1_xM^2_y(CO)_{12}]$ (M^1, M^2 = Fe, Ru; $x + y = 3$) to provide a basis for development and discussion.

Experimental

The samples of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ were generously provided by Professor G.L. Geoffroy of the Pennsylvania State University. The sample of $Ru_3(CO)_{12}$ (Strem Chemicals) was resublimed before use.

---

* Dedicated to the memory of Professor Paolo Chini.

The Calvet twin-cell high-temperature microcalorimeter supplied by Setaram (Lyon) was adapted to the drop microcalorimetric technique as previously described [6]. The thermopile output was amplified (NV 724A nanovoltmeter amplifier) and the thermograms were recorded (Rikadenki DBE 2). Thermogram areas were simultaneously evaluated by the ITC integrator and printer. The calorimeter was calibrated from measurements of the enthalpy of sublimation of iodine, benzoic acid and naphthalene.

Auxiliary data

All heat quantities are given in joules (J) or kilojoules (kJ). The following auxiliary heats of formation (kJ mol^{-1}) were used in evaluating the experimental results: ΔH_f^0 (CO, g) = $-(110.524 \pm 0.17)$ [7]; ΔH_f^0 (Fe, g) = (417.0 ± 1.2) [8]; ΔH_f^0 (Ru, g) = (656.9 ± 6) [8]; ΔH_f^0 ($Fe(CO)_5$, g) = $-(723.8 \pm 8)$ [8]; ΔH_f^0 ($Fe_2(CO)_9$, g) = $-(1334.7 \pm 25)$ [9]; ΔH_f^0 ($Fe_3(CO)_{12}$, g) = $-(1753.1 \pm 30)$ [9]. Enthalpies of sublimation of $Fe_2(CO)_9$ and of $Fe_3(CO)_{12}$ are not known and values have been estimated [9]. Estimates are used here for ΔH_{sub} of $Fe_2Ru(CO)_{12}$, $FeRu_2(CO)_{12}$ and $Ru_3(CO)_{12}$: these are based on the increase of ca. 3 kJ mol^{-1} in ΔH_{sub} in moving from $Cr(CO)_6$ to $Mo(CO)_6$. We suggest that replacement of Fe in $Fe_3(CO)_{12}$ by Ru raises ΔH_{sub} by the same amount, to give the following values of ΔH_{sub} $Fe_3(CO)_{12} \sim (96 \pm 20)$; $Fe_2Ru(CO)_{12} \sim (99 \pm 20)$; $FeRu_2(CO)_{12} \sim (102 \pm 20)$ and $Ru_3(CO)_{12} \sim (105 \pm 20)$ kJ mol^{-1}.

Results

1. Dodecacarbonyl(diiron)ruthenium

Attempts to measure the enthalpy of sublimation by the vacuum sublimation microcalorimetric technique [10] were made at 393 K but were not successful because thermal decomposition accompanied sublimation and a metallic film formed in the exit tube from the reaction vessel.

Thermal decomposition measurements were made at 545 K. The thermograms showed slight endothermal tailing (possibly due to surface absorption of carbon monoxide) for which approximate corrections were made by extrapolation. The results are shown in Table 1, in which Δh is the enthalpy change measured in the calorimetric experiment. Integrator counts are a measure of the thermogram area, related to heat flow by $\Delta H = k$(counts). From calibration

TABLE 1

THERMAL DECOMPOSITION OF $Fe_2Ru(CO)_{12}$

$FeRu_2(CO)_{12}$ (mg)	Integrator counts	Δh (J)	ΔH_{dec}^{545} (kJ mol^{-1})
2.230	2201	2.42	596.0
3.140	3187	3.51	613.0
1.805	1818	2.00	608.0
2.915	2868	3.16	594.0
2.550	2520	2.77	597.0

Mean $\Delta H_{dec}^{545} = (601.6 \pm 7)$ kJ mol^{-1}

$\Delta H_{dec}^{298} = (494 \pm 7)$ kJ mol^{-1}

TABLE 2

THERMAL DECOMPOSITION OF $FeRu_2(CO)_{12}$

$FeRu_2(CO)_{12}$ (mg)	Integrator counts	Δh (J)	ΔH^{523} (kJ mol^{-1})
3.340	3390	3.729	663.3
3.969	3935	4.329	648.0
3.966	4019	4.421	662.3
2.595	2674	2.941	673.3

Mean $\Delta H_{\text{dec}}^{523}$ = (661.7 ± 10) kJ mol^{-1}

$\Delta H_{\text{dec}}^{298}$ = (565 ± 10) kJ mol^{-1}

experiments on the sublimation of naphthalene $k = (1.10 \pm 0.01) \times 10^{-3}$ at $T \sim 530$ K. This value leads to ΔH_f^0 [$Fe_2Ru(CO)_{12}$, c] = —(1820 ± 14) kJ mol^{-1}. Assuming $\Delta H_{\text{sub}} \sim$ (99 ± 20) kJ mol^{-1} gives ΔH_f^0 [$Fe_2Ru(CO)_{12}$, g] = —(1721 ± 24) kJ mol^{-1}.

2. *Dodecacarbonyl(iron)diruthenium*

Attempts to measure ΔH_{sub} by the vacuum sublimation technique were unsatisfactory. At 375 K, sublimation occurred but was accompanied by considerable thermal decomposition, depositing a metallic mirror near the neck of the reaction vessel, and in the exit tube.

Thermal decomposition measurements were made at 523 K, and for sample weights 2.5—4.5 mg, the metal deposited entirely within the reaction vessel. Samples were dropped in the argon-filled reaction vessel and in some cases a second and third sample drop was made after the initial sample had decomposed. The results are shown in Table 2. This value leads to ΔH_f^0 [$FeRu_2(CO)_{12}$, c] = —(1891 ± 16) kJ mol^{-1}. Assuming $\Delta H_{\text{sub}} \sim$ (102 ± 20) kJ mol^{-1} gives ΔH_f^0 [$FeRu_2(CO)_{12}$, g] = —(1789 ± 25) kJ mol^{-1}.

3. *Dodecacarbonyltriruthenium*

The vacuum sublimation microcalorimetric method was applied to measurement of ΔH_{sub} at 403 K and at 365 K, but even at the lower temperature there was considerable thermal decomposition accompanying sublimation, with the formation of a bright metallic mirror in the reaction vessel and the exit tube.

Thermal decomposition was studied at 523 K and at 545 K. The results are

TABLE 3

THERMAL DECOMPOSITION OF $Ru_3(CO)_{12}$

$Ru_3(CO)_{12}$ (mg)	T (K)	Integrator counts	Δh (J)	ΔH^T (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
2.345	523	2200	2.42	659.8	563.6
3.055	545	2912	3.20	670.3	564.5
3.620	545	3551	3.906	689.9	584.1
1.915	545	1841	2.025	676.1	572.3
4.220	545	4227	4.65	704.4	598.6

Mean $\Delta H_{\text{dec}}^{298}$ = (576.6 ± 13) kJ mol^{-1}

shown in Table 3. This value leads to ΔH_f^0 [$Ru_3(CO)_{12}$, c] = —(1903 ± 18) kJ mol^{-1}. Assuming $\Delta H_{sub} \sim (105 \pm 20)$ kJ mol^{-1} gives ΔH_f^0 [$Ru_3(CO)_{12}$, g] = —(1798 ± 27) kJ mol^{-1}.

Discussion

The results of measurements on [$Fe_xRu_y(CO)_{12}$] ($x, y = 0$—3; $x + y = 3$) and on $Fe(CO)_5$ and $Fe_2(CO)_9$ [9] are shown in Table 4, which includes values of $\Delta H_{disrupt}$ for the process

$$Fe_xRu_y(CO)_{12}\ (g) \rightarrow x\ Fe\ (g) + y\ Ru\ (g) + 12\ CO\ (g)$$

Figure 1 shows the steady increase in $\Delta H_{disrupt}$ with increasing ruthenium content in [$Fe_xRu_y(CO)_{12}$] and suggests that there is no dramatic change (in terms of bond energies) as replacement progresses.

There are two methods which have been used for the calculation of the bond enthalpy contributions in these molecules [11], the one derives from a simple electron-pair bond model and takes no account of bond length [9], the other relates bond enthalpy logarithmically to bond length [12]. The crystal structures of $Fe_2(CO)_9$ [13], $Fe_3(CO)_{12}$ [14] and of $Ru_3(CO)_{12}$ [15] have been redetermined recently. $Fe_3(CO)_{12}$, in which there are two long (2.677(2), 2.683(1) Å) and one short (2.558(1) Å) iron—iron bonds, is known to contain two semi-bridging carbonyl ligands across the shorter Fe—Fe distance [14], whereas all the carbonyl groups in $Ru_3(CO)_{12}$ are terminal, although the metal—metal bonds (2.8595, 2.8515 Å) are not strictly equivalent [15].

The structures of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$ have not been determined. However, the infrared spectrum of $Fe_2Ru(CO)_{12}$ in solution [16] contains weak absorptions on the region 1870—1800 cm^{-1} which are similar to those observed in the infrared spectrum of $Fe_3(CO)_{12}$, suggesting that there are edge-bridging carbonyl ligands present. The ^{13}C NMR spectrum of $Fe_2Ru(CO)_{12}$ recorded at various temperatures [17] is consistent with rapid scrambling of CO ligands over the [Fe_2Ru] cluster, in the manner proposed [14] for $Fe_3(CO)_{12}$. There is no evidence for edge-bridging CO ligands in $FeRu_2(CO)_{12}$ which is therefore presumed [16] to have a similar structure to $Ru_3(CO)_{12}$.

At room temperature and atmospheric pressure, iron has a body centered cubic structure (a = 2.866 Å [18]) with eight nearest neighbour contacts (2.482 Å); under the same conditions, ruthenium has a hexagonal close packed structure (a = 2.705, c = 4.281 Å [18]) with six nearest neighbours at 2.65 Å

TABLE 4

ENTHALPY OF FORMATION AND DISRUPTION OF [$Fe_xRu_y(CO)_{12}$]

	ΔH_f^0(g) (kJ mol^{-1})	$\Delta H_{disrupt}$ (kJ mol^{-1})
$Fe(CO)_5$	—(723.8 ± 8)	(588.2 ± 8)
$Fe_2(CO)_9$	—(1334.7 ± 25)	(1174 ± 25)
$Fe_3(CO)_{12}$	—(1753.1 ± 30)	(1678 ± 30)
$Fe_2Ru(CO)_{12}$	—(1721 ± 24)	(1884 ± 25)
$FeRu_2(CO)_{12}$	—(1789 ± 25)	(2193 ± 28)
$Ru_3(CO)_{12}$	—(1798 ± 27)	(2443 ± 32)

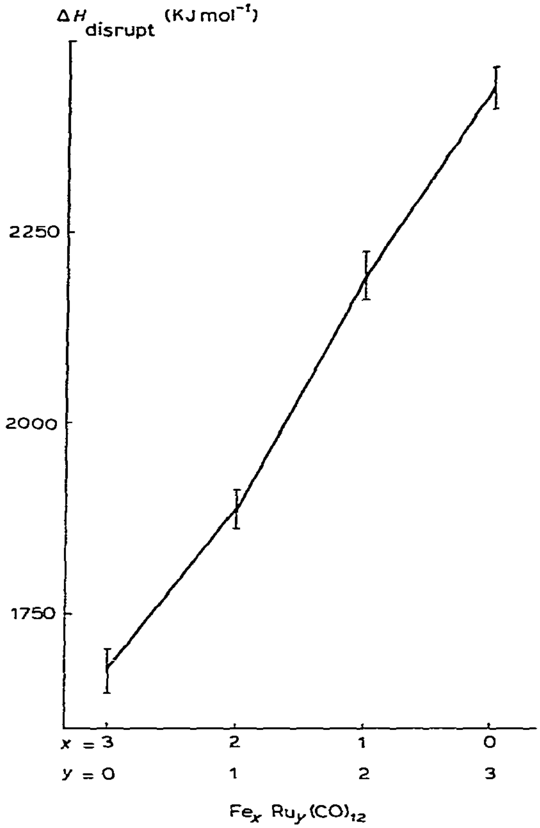

Fig. 1. Variation of $\Delta H_{\text{disrupt}}$ (kJ mol^{-1}) with ruthenium content in $Fe_xRu_y(CO)_{12}$.

and six at 2.71 Å, with an average Ru—Ru distance 2.68 Å.

Using the electron-pair bond model [11] to evaluate bond enthalpy contributions to $\Delta H_{\text{disrupt}}$, the bonds can be described as follows for $FeRu_2(CO)_{12}$,

$$\Delta H_{\text{disrupt}} = 8\,T(\text{Ru}) + 4\,T(\text{Fe}) + E(\text{Ru—Ru}) + 2\,E(\text{Fe—Ru})$$

where T is the terminal M—CO bond enthalpy. Using a similar equation for the description $Fe_2Ru(CO)_{12}$, we calculate E(Fe—Ru) = (117 ± 12) kJ mol^{-1} in $FeRu_2(CO)_{12}$ and E(Fe—Ru) = (90 ± 15) kJ mol^{-1} in $Fe_2Ru(CO)_{12}$.

The bond length-bond enthalpy relation [12] gives E(Ru—Ru) = 78 kJ mol^{-1} in $Ru_3(CO)_{12}$ and E(Fe—Fe) = 52 (at 2.68 Å) and 65 kJ mol^{-1} (at 2.56 Å). Using these values together with appropriate values of T(Ru) and T(Fe) gives E(Fe—Ru) = 94 kJ mol^{-1}, if the Ru—Ru bond length is unchanged in $FeRu_2(CO)_{12}$. When applied to $Fe_2Ru(CO)_{12}$ with the assumption that the Fe—Fe bond length is similar to the longer (2.68 Å) distance in $Fe_3(CO)_{12}$, this method gives E(Fe—Ru) = 80 kJ mol^{-1}.

The results obtained by the two methods of calculation are not in close agreement, but are dependent on upon important assumptions about the structures of the compounds. We note, however, that the derived E(Fe—Ru) in $FeRu_2(CO)_{12}$ is greater than in $Fe_2Ru(CO)_{12}$ and that the average value in both systems (95 ± 20) kJ mol^{-1} is markedly greater than the mean of E(Ru—Ru) and E(Fe—Fe). In this context it is pertinent to point out that calculations of the dissociation energy of the diatomic molecule FeRu suggest [12] that D(FeRu) (214 kJ mol^{-1}) lies between $D(Fe_2)$ (100 kJ mol^{-1}) and $D(Ru_2)$ (327 kJ mol^{-1}). In the only case where the experimental data is available for a *3d*/*4d* system D(RhV) (360 ± 29) kJ mol^{-1} is greater than $D(V_2)$ (238 ± 21) kJ mol^{-1} and $D(Rh_2)$ (281.6 ± 20.9) kJ mol^{-1} [1].

Acknowledgements

We thank Professor G.L. Geoffroy for his gift of $Fe_2Ru(CO)_{12}$ and $FeRu_2(CO)_{12}$, the Science Research Council for support, and the British Council for a travel grant (to A.K.B.).

References

1 K.A. Gingerich, Faraday Symp. Chem. Soc., 14 (1980) 109.
2 J.A. Connor and H.A. Skinner, Adv. Chem. Ser., (1981) in press.
3 P. Chini, J. Organometal. Chem. 200 (1980) 37.
4 A. Fumagalli, G. Longoni, P. Chini, A. Albinati and S. Brückner, J. Organometal. Chem., 202 (1980) 329.
5 M. Tachikawa and E.L. Muetterties, J. Amer. Chem. Soc., 102 (1980) 4541.
6 J.A. Connor, H.A. Skinner and Y. Virmani, J. Chem. Soc. Faraday 1, 68 (1972) 1754.
7 D.D. Wagman, W.H. Evans, V.B. Parker, I. Halow, S.M. Bailey and R.H. Schumm, Nat. Bur. Stand. Tech. Notes. 1—4 (1969) Washington D.C.
8 V.P. Glyshko and V.A. Medvedev, Thermal Constants of Compounds (Transition Metals) Vol. 6,., Akad. Nauk. SSSR, Moscow, 1974.
9 J.A. Connor, H.A. Skinner and Y. Virmani, Faraday Symp. Chem. Soc., 8 (1973) 18.
10 F.A. Adedeji, D.L.S. Brown, J.A. Connor, M.L. Leung, M.I. Paz Andrade and H.A. Skinner, J. Organometal. Chem., 97 (1975) 221.
11 J.A. Connor in B.F.G. Johnson (Ed.), Transition Metal Clusters, Wiley, London, 1980, p. 345.
12 C.E. Housecroft, K. Wade and B.C. Smith, J. Chem. Soc. Chem. Commun., (1978) 765; idem, J. Organometal. Chem., 170 (1979) C1.
13 F.A. Cotton and J.M. Troup, J. Chem. Soc. Dalton, (1974) 800.
14 F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 4155.
15 M.R. Churchill, F.J. Hollander and J.P. Hutchinson, Inorg. Chem., 16 (1977) 2655.
16 D.B.W. Yawney and F.G.A. Stone, J. Chem. Soc. A. (1969) 502; J. Knight and M.J. Mays, Chem. Commun., (1970) 1006.
17 A. Forster, B.F.G. Johnson, J. Lewis, T.W. Matheson, B.H. Robinson, W.G. Jackson, J. Chem. Soc. Chem. Commun., (1974) 1042.
18 J. Donohue, Structures of the Elements, Wiley, London, 1974.
19 A. Miedema, Faraday Symp. Chem. Soc., 14 (1980) 136.