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ENTHALPIES OF FORMATION OF DECACARBONYLDIRHENIUM AND SOME PENTACARBONYLRHENIUM DERIVATIVES

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Summary

Microcalorimetric measurements were made at elevated temperatures to determine the enthalpies of sublimation, thermal decomposition and bromination of $[Re_2(CO)_{10}]$ and of $[Re(CO)_5X]$ ($X = CH_3$, Cl, Br), from which the standard enthalpies of formation, ΔH_f° (c), ΔH_f° (g), were derived as follows (values in kJ mol^{-1}): $[Re_2(CO)_{10}]$ $-(1660 \pm 11)$, $-(1559 \pm 11)$; $[Re(CO)_5CH_3]$ $-(830 \pm 6)$, $-(760 \pm 6)$; $[Re(CO)_5Cl]$ $-(986 \pm 18)$, $-(877 \pm 18)$; $[Re(CO)_5Br]$ $-(950 \pm 8)$, $-(858 \pm 8)$. The bond dissociation enthalpies $D(X\text{–}Re(CO)_5)$ are derived as 220 ($X = CH_3$), 314 ($X = Cl$), 283 ($X = Br$) kJ mol^{-1} relative to the value 187 kJ mol^{-1} for D(Re–Re) in $[Re_2(CO)_{10}]$.

Introduction

Enthalpies of formation of decacarbonyldirhenium [1] and of methylpentacarbonylrhenium [2] have been obtained from measurements of enthalpies of iodination at elevated temperatures, forming ReI_3 as the metal-containing product. The derived heats of formation depend, however, on an estimated value for the enthalpy of formation of ReI_3(c), which was obtained by extrapolation from known values for $ReCl_3$(c) and $ReBr_3$(c) [3]. Following the adaption of the high temperature microcalorimetric technique by Zafarani-Moattar [4] to measurements of the heats of bromination of metal carbonyls, we have examined the bromination of some pentacarbonylrhenium derivatives, to obtain enthalpy values which relate directly to the known value for $\Delta H_f^\circ[ReBr_3,c]$. Measurements by the vacuum sublimation microcalorimetric technique [5] have also been made on these compounds to obtain enthalpies of sublimation, and enthalpies of formation of the gaseous molecules.

Experimental

Calorimeter. The Calvet twin-cell microcalorimeter (Setaram) and the drop-calorimetric technique have already been described [6,7].

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Materials. Decacarbonyldirhenium (Strem) was resublimed prior to use. $[Re(CO)_5CH_3]$ was prepared as described by Hieber, Braun and Beck [8]; $[Re(CO)_5Cl]$ and $[Re(CO)_5Br]$ were prepared by a standard method [9]. The purity of these materials was established by microanalysis and spectroscopy (infrared, mass).

Auxiliary data. The following auxiliary heat of formation data (kJ mol^{-1}) were used in evaluating the calorimetric results:

$CO(g) = -(110.524 \pm 0.17)$ [10]; $Br_2(g) = (30.907 \pm 0.11)$ [10];
$I_2(g) = (62.42 \pm 0.08)$ [10]; $ReCl_3(c) = -(272.4 \pm 4.2)$ [3];
$ReBr_3(c) = -(175.7 \pm 5)$ [3]; $CH_3Br(g) = -(37.2 \pm 0.9)$ [11];
$Re(g) = (775.7 \pm 6.3)$ [3]; $CH_3(g) = (146.2 \pm 1.0)$ [12,13];
$Cl(g) = (121.30 \pm 0.01)$ [10]; $Br(g) = (111.84 \pm 0.12)$ [10].

The enthalpies of reaction, ΔH^T, measured at elevated temperatures, T, were adjusted to 298 K using heat content data, $(H_T - H_{298})$, for CO(g), $Br_2(g)$, $I_2(g)$ and $CH_3Br(g)$ from Stull, Westrum and Sinke [14]. The $(H_T - H_{298})$ values for $ReCl_3(c)$ and $ReBr_3(c)$ were estimated, assuming these to be of similar magnitude to the known values for $TaCl_3$, $TaBr_3$, $ZrCl_3$ and $ZrBr_3$, as given by Barin and Knacke [15]; $(H_T - H_{298})$ for Re(c) was taken from Barin and Knacke [15].

Results

Enthalpies of sublimation of crystalline samples of $[Re_2(CO)_{10}]$, $[Re(CO)_5CH_3]$, $[Re(CO)_5Cl]$ and $[Re(CO)_5Br]$ were measured by the vacuum-sublimation microcalorimetric technique [5]. The results are summarized in Table 1, where ΔH^T refers

TABLE 1

SUBLIMATION OF $[Re_2(CO)_{10}]$, $[Re(CO)_5CH_3]$, $[Re(CO)_5Br]$ AND $[Re(CO)_5Cl]$

Compound	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$(H_T - H_{298})$ (kJ mol^{-1})	ΔH_{sub}^{298} (kJ mol^{-1})	mean ΔH_{sub}^{298} (kJ mol^{-1})
$Cr(CO)_6$ [a]	408	2.151	91.0	22.1	68.9	70.0
	408	2.543	93.3	22.1	71.2	
$[Re_2(CO)_{10}]$	386	2.700	132.4	30.5	101.9	100.9
	386	2.383	129.7	30.5	99.2	
	397	2.510	135.8	34.3	101.5	
$[Re(CO)_5CH_3]$	386	2.000	84.2	17.8	66.4	70.0
	386	2.278	88.1	17.8	70.3	
	397	2.181	92.9	20.0	72.9	
	397	2.084	90.4	20.0	70.4	
$[Re(CO)_5Br]$	401	4.289	109.1	19.9	89.2	92.1
	381	2.805	107.8	16.1	91.7	
	366	5.875	107.5	13.2	94.3	
	363	2.240	106.2	12.6	93.6	
	358	4.000	103.6	11.7	91.9	
$[Re(CO)_5Cl]$	386	2.803	128.8	17.2	111.6	110.9
	386	2.252	125.9	17.2	108.7	
	397	2.204	131.8	19.3	112.5	
	397	2.001	130.0	19.3	110.7	

[a] Test substance.

TABLE 2

BROMINATION OF DECACARBONYLDIRHENIUM

T (K)	Mass (mg)	ΔH_2^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_2^{298} (kJ mol^{-1})
529	2.141	199.5	88.6	110.9
538	2.805	193.1	92.2	100.9
538	3.663	206.4	92.2	114.2
538	3.415	219.5	92.2	127.3
538	2.141	194.7	92.2	102.5

to the measured enthalpy change for the cell-process

$$[(CO)_5Re\ R)](c, 298) \rightarrow [(CO)_5Re\ R](g, T) \qquad (1)$$

ΔH_{sub}^{298} values were obtained from ΔH^T by subtraction of the heat content $(H_T - H_{298})$ of the vapour; these corrections were estimated using an approximation which treats the ligands (R + 5CO) as separate entities, and adding their individual contributions. For example, for $[Re(CO)_5CH_3]$, $[H_T - H_{298}] = \Sigma(H_T - H_{298})$ for CH_3, 5CO [14] + Re(c) [15]. This procedure gives a reasonably good fit for the hexacarbonyls of chromium, molybdenum and tungsten, for which experimental data are available for comparison [16].

Decacarbonyldirhenium, $[Re_2(CO)_{10}]$

Bromination measurements were made by dropping samples into excess Br_2/N_2 gas in the hot reaction vessel at temperatures in the range 530–540 K. Reaction was rapid, giving a dark almost black powder of $ReBr_3$, and traces of a blue deposit (probably $ReBr_5$) near the exit from the reaction tube. The measured heats of reaction, ΔH_2^T, referring to the cell-reaction:

$$[Re_2(CO)_{10}](c, 298) + 3Br_2(g, T) \rightarrow 2ReBr_3(c, T) + 10CO(g, T) \qquad (2)$$

are listed in Table 2. The mean value, $\Delta H_2^{298} = (111.2 \pm 10)$ kJ mol^{-1} corresponds to ΔH_f° $[Re_2(CO)_{10},c] = -(1660.6 \pm 11)$ kJ mol^{-1}, in fair agreement with the earlier value of $-(1652.7 \pm 21)$ kJ mol^{-1} from iodination [1], and with ~ -1666 kJ mol^{-1} as reported [3] from measurements of the heat of combustion by Chernova, Sheiman, Rabinovitch and Syrkin [17].

Samples of $[Re_2(CO)_{10}]$ dropped into the N_2-filled hot-zone at 626 K decomposed readily, forming a bright metallic mirror deposit on the walls of the reaction vessel. The measured enthalpies of thermal decomposition, ΔH_3^T, refer to the

TABLE 3

THERMAL DECOMPOSITION OF DECACARBONYLDIRHENIUM

T (K)	Mass (mg)	ΔH_3^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_3^{298} (kJ mol^{-1})
626	3.380	650.8	114.8	536.0
626	4.032	627.6	114.8	512.8
626	3.460	634.4	114.8	519.6

TABLE 4

BROMINATION OF METHYLPENTACARBONYLRHENIUM

T (K)	Mass (mg)	ΔH_4^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_4^{298} (kJ mol^{-1})
488	2.366	43.6	42.3	1.3
488	2.231	47.0	42.3	4.7
488	1.600	43.7	42.3	1.4

process:

$$[\mathrm{Re_2(CO)_{10}}](\mathrm{c}, 298) \rightarrow \mathrm{Re}(\mathrm{c}, T) + 10\mathrm{CO}(\mathrm{g}, T) \qquad (3)$$

and include 'spurious' exothermic effects arising from adsorption of CO on the metal deposit, for which corrections can rarely be made. Typical results are given in Table 3. The mean $\Delta H_3^{298} = (522.9 \pm 14)$ kJ mol^{-1} leads to $\Delta H_f^\circ[\mathrm{Re_2(CO)_{10}},\mathrm{c}] = -(1628.3 \pm 14)$ kJ mol^{-1}, and (as expected) is numerically less exothermic than from bromination or iodination studies.

Methylpentacarbonylrhenium, [Re(CO)$_5$CH$_3$]

The bromination of [Re(CO)$_5$CH$_3$] was studied at 488 K; reaction was rapid, giving a dark residue of ReBr$_3$, with traces of the more volatile, blue pentabromide. The measured reaction heats, ΔH_4^T, referring to the cell-reaction:

$$[\mathrm{Re(CO)_5CH_3}](\mathrm{c}, 298) + 2\mathrm{Br_2}(\mathrm{g}, T) \rightarrow \mathrm{CH_3Br}(\mathrm{g}, T) + 5\mathrm{CO}(\mathrm{g}, T) + \mathrm{ReBr_3}(\mathrm{c}, T) \qquad (4)$$

are listed in Table 4. Combined with given auxiliary data, the mean $\Delta H_4^{298} = 2.5 \pm 2.4$ kJ mol^{-1} leads to ΔH_f° [Re(CO)$_5$CH$_3$,c] $= -(829.7 \pm 6)$ kJ mol^{-1}, in good agreement with that obtained previously [2] from iodination studies.

Thermal decomposition in N$_2$-gas was studied at 626 K. The metal deposited as a mirror on the walls of the reaction vessel, but no attempt was made to identify the hydrocarbon products of decomposition. The measured enthalpy of decomposition, $\Delta H^{626} \sim 280$ kJ mol^{-1}, reduces to ~ 210 kJ mol^{-1} at 298 K, and leads to ΔH_f°[Re(CO)$_5$CH$_3$,c] ~ -805 kJ mol^{-1}, assuming that ethane is the hydrocarbon product formed. This is again less than from bromination, possibly due to the reduction of ΔH^{626} from its true value from absorption of CO on the metal deposit.

TABLE 5

BROMINATION OF BROMOPENTACARBONYLRHENIUM

T (K)	Mass (mg)	ΔH_5^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_5^{298} (kJ mol^{-1})
460	2.397	223.0	33.9	189.1
460	1.975	231.7	33.9	197.8
538	3.105	236.2	50.5	185.7
538	3.395	246.7	50.5	196.2
538	1.801	232.9	50.5	182.4

TABLE 6

THERMAL DECOMPOSITION OF BROMOPENTACARBONYLRHENIUM

T (K)	Mass (mg)	ΔH_6^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_6^{298} (kJ mol^{-1})
626	3.070	383.5	64.2	319.3
626	3.307	407.8	64.2	343.6
626	2.535	422.6	64.2	358.4

Bromopentacarbonylrhenium, [Re(CO)$_5$Br]

Bromination of [Re(CO)$_5$Br] was studied over the temperature range 460–540 K and the results are summarised in Table 5, where ΔH_5^T refers to the cell-reaction:

$$[\mathrm{Re(CO)_5Br}](\mathrm{c}, 298) + \mathrm{Br_2}(\mathrm{g}, T) \rightarrow \mathrm{ReBr_3}(\mathrm{c}, T) + 5\mathrm{CO}(\mathrm{g}, T) \qquad (5)$$

The mean value of $\Delta H_5^{298} = (190.2 \pm 5)$ kJ mol^{-1} corresponds to ΔH_f°[Re(CO)$_5$Br,c] = $-(949.4 \pm 8)$ kJ mol^{-1}.

Measurements were also made of thermal decomposition of [Re(CO)$_5$Br] at 626 K, which gave a deposit on the walls of the reaction vessel, presumably of the monobromide, ReBr:

$$[\mathrm{Re(CO)_5Br}](\mathrm{c}, 298) \rightarrow \mathrm{ReBr}(\mathrm{c}, T) + 5\mathrm{CO}(\mathrm{g}, T) \qquad (6)$$

Measured values of ΔH_6^T are given in Table 6. The enthalpy of formation of ReBr is not known: the simple assumption that ΔH_f°[ReBr,c] ~ $\frac{1}{3}\Delta H_f^\circ$[ReBr$_3$,c], taken with the mean value $\Delta H_6^{298} = (340.4 \pm 23)$ kJ mol^{-1} leads to ΔH_f°[Re(CO)$_5$Br,c] ~ $-(952 \pm 23)$ kJ mol^{-1} which is in fair agreement with the value derived from direct bromination.

Chloropentacarbonylrhenium

The bromination of [Re(CO)$_5$Cl] was studied over the temperature range 488–538 K. The measured enthalpies of reaction, ΔH_7^T, relating to the process

$$[\mathrm{Re(CO)_5Cl}](\mathrm{c}, 298) + \mathrm{Br_2}(\mathrm{g}, T) \rightarrow \mathrm{ReBr_2Cl}(\mathrm{c}, T) + 5\mathrm{CO}(\mathrm{g}, T) \qquad (7)$$

are given in Table 7. The mean value, $\Delta H_7^{298} = (177.1 \pm 10)$ kJ mol^{-1} leads to ΔH_f°[Re(CO)$_5$Cl,c] = $\{-(760.7 \pm 10) + \Delta H_f^\circ[\mathrm{ReBr_2Cl,c}]\}$ kJ mol^{-1}.

No value is yet available for the enthalpy of formation of the mixed trihalide ReBr$_2$Cl. The crystal structures of ReX$_3$ (X = Cl, Br) show that these molecules

TABLE 7

BROMINATION OF CHLOROPENTACARBONYLRHENIUM

T (K)	Mass (mg)	ΔH_7^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_7^{298} (kJ mol^{-1})
488	2.008	209.5	39.8	169.7
488	2.176	213.6	39.8	173.8
538	2.921	240.7	50.3	190.4
538	2.609	215.9	50.3	165.6
538	3.161	236.2	50.3	185.9

TABLE 8

ENTHALPIES OF ATOMIZATION OF RHENIUM HALIDES

Halide	$\Delta H_f^\circ(g)$ (kJ mol^{-1})	ΔH_{atom}^{298} (kJ mol^{-1})	Bonds
$ReCl_5$	-306.7 ± 11 [21]	1689 ± 13	5(ReCl)
$ReBr_5$	-193.7 ± 10 [22]	1529 ± 10	5(ReBr)
Re_3Cl_9	-600 ± 11	4019 ± 16	6(ReCl) + 6(μ_2-ClRe) + 3(Re–Re)
Re_3Br_9	-318 ± 20	2981 ± 23	6(ReBr) + 6(μ_2-BrRe) + 3(Re–Re)

contain Re_3 clusters in Re_3X_9 units [18]. These molecules are also trimeric in the vapour phase. Enthalpies of formation of $[Re_3Cl_9,g]$ and $[Re_3Br_9,g]$ can be derived from the measured enthalpies of sublimation [19,20] of $ReCl_3$ and $ReBr_3$. Values of $\Delta H_f^\circ[ReCl_5,g]$ [3,21] and $\Delta H_f^\circ[ReBr_5,g]$ [22] are also available. These data are presented in Table 8 together with the enthalpies of atomization, ΔH_{atom}^{298}, of these rhenium halides.

In the ReX_5 molecules, all the Re–X bonds are ‘terminal’, whereas in $[Re_3X_9]$, there are six terminal Re–X bonds and six ‘bridging’, μ_2-XRe bonds in the $[Re_3X_3]$ cluster. The mean bond enthalpy contributions of the terminal bonds are $\bar{D}(Re{-}Cl) = (337.8 \pm 3)$ kJ mol^{-1} in $ReCl_5$ and $\bar{D}(Re{-}Br) = (305.8 \pm 2.5)$ kJ mol^{-1} in $ReBr_5$; transfer of these values to $[Re_3Cl_9]$ and $[Re_3Br_9]$ then leaves a contribution of 1992.2 kJ mol^{-1} from the $[Re_3Cl_3]$ cluster, and of 1146.2 kJ mol^{-1} from the $[Re_3Br_3]$ cluster. In the ‘mixed’ halide, $[Re_3Cl_3Br_6]$, the most stable structure is calculated to have $\Delta H_{atom} = 3827$ kJ mol^{-1}, and is based on the $[Re_3Cl_3]$ cluster with six terminal ReBr bonds. The calculated ΔH_{atom} value corresponds to $\Delta H_f^\circ[Re_3Br_6Cl_3,g] = -465$ kJ mol^{-1}, and since the enthalpy of the sublimation process

$$3[ReBr_2Cl,c] \rightarrow [Re_3Br_6Cl_3,g] \tag{8}$$

should not differ significantly from that for $3[ReBr_3,c]$, ($\Delta H_8 \sim 209$ kJ), the estimated $\Delta H_f^\circ[ReBr_2Cl,c] = -(225 \pm 15)$ kJ mol^{-1}. This compares with $-(208 \pm 5)$ kJ mol^{-1} on the basis of the simple assumption that $\Delta H_f^\circ[ReBr_2Cl,c] \sim 1/3\Delta H_f^\circ[ReCl_3,c] + 2/3\, \Delta H_f^\circ[ReBr_3,c]$. Combined with $\Delta H_7^{298} = (177.1 \pm 10)$ kJ mol^{-1}, the estimated $\Delta H_f^\circ[ReBr_2Cl,c] = -(225 \pm 15)$ kJ mol^{-1} leads to $-(985.7 \pm 18)$ kJ mol^{-1} for $\Delta H_f^\circ[Re(CO)_5Cl,c]$.

Thermal decomposition studies on $[Re(CO)_5Cl]$ were made at 626 K, and results are given in Table 9, where ΔH_9^T refers to

$$[Re(CO)_5Cl](c, 298) \rightarrow ReCl(c, T) + 5CO(g, T) \tag{9}$$

TABLE 9

THERMAL DECOMPOSITION OF CHLOROPENTACARBONYLRHENIUM

T (K)	Mass (mg)	ΔH_9^T (kJ mol^{-1})	$\Sigma(H_T - H_{298})$ (kJ mol^{-1})	ΔH_9^{298} (kJ mol^{-1})
626	3.088	401.6	64.2	337.4
626	3.351	394.5	64.2	330.3
626	2.576	392.5	64.2	328.2

TABLE 10

BOND DISSOCIATION ENTHALPIES, $D(\mathrm{R{-}Re(CO)_5})$

Compound	$\Delta H_f^\circ(\mathrm{c})$ (kJ mol^{-1})	$\Delta H_{\mathrm{sub}}^\circ$ (kJ mol^{-1})	$\Delta H_f^\circ(\mathrm{g})$ (kJ mol^{-1})	$D[\mathrm{R{-}Re(CO)_5}]$ (kJ mol^{-1})
$\mathrm{(OC)_5Re{-}Re(CO)_5}$	-1660 ± 11	101 ± 2	-1559 ± 11	187
$\mathrm{CH_3{-}Re(CO)_5}$	-830 ± 6	70 ± 2	-760 ± 6	220 ± 8
$\mathrm{Br{-}Re(CO)_5}$	-950 ± 8	92 ± 2	-858 ± 8	283 ± 11
$\mathrm{Cl{-}Re(CO)_5}$	-986 ± 18	111 ± 2	-877 ± 18	314 ± 19

The enthalpy of formation of ReCl is not known. If we assume that it approximates to 1/3 $\Delta H_f^\circ[\mathrm{ReCl_3,c}]$, the mean $\Delta H_9^{298} = (332 \pm 6)$ kJ mol^{-1} then leads to a value of ca. -975 kJ mol^{-1} for $\Delta H_f^\circ[\mathrm{Re(CO)_5Cl,c}]$.

Discussion

The crucial problem in interpretation of these thermochemical results is provided by the decision on the value to be assigned to the dissociation energy of the Re–Re bond in $[\mathrm{Re_2(CO)_{10}}]$. The ionization potential of $[\mathrm{Re_2(CO)_{10}}]$ $(8.36 \pm 0.03$ eV) is used as the basis for an estimate of $IP[(\mathrm{Re(CO)_5})]$ 8.40 eV. The measured value of $AP[(\mathrm{Re(CO)_5}^+)]$ 10.34 eV, so that $D(\mathrm{Re{-}Re})$ in $[\mathrm{Re_2(CO)_{10}}] = (1.94 \pm 0.05)$ eV $(187 \pm 5$ kJ mol^{-1}) [23]. Measurement of the kinetics of reaction between $\mathrm{Re_2(CO)_{10}}$ and $\mathrm{PPh_3}$ in decalin solution were interpreted [24] in terms of initial dissociation of the metal–metal bond and subsequent substitution, so that the activation energy was equated with the metal–metal bond energy and $D(\mathrm{Re{-}Re}) = (165.5 \pm 0.8)$ kJ mol^{-1}. Recently, it has been shown that this substitution proceeds by a CO dissociation mechanism without detectable rupture of the metal–metal bond [25]. This is then consistent with the higher value of $D(\mathrm{Re{-}Re})$ obtained from electron impact studies.

On this basis and with $\Delta H_f^\circ[\mathrm{Re_2(CO)_{10},g}] = -1559.7 \pm 11$ kJ mol^{-1}, we calculate $\Delta H_f^\circ[\mathrm{Re(CO)_5,g}] = -686.4 \pm 6$ kJ mol^{-1}, and the bond dissociation energies shown in Table 10. The values of $D(\mathrm{R{-}Re(CO)_5})$ may be compared with those obtained for analogous manganese complexes [26]. The trend $D(\mathrm{M{-}Cl}) > D(\mathrm{M{-}Br}) > D(\mathrm{M{-}CH_3}) > D(\mathrm{M{-}M})$ is the same for both metals (M = Mn, Re) but the changes are larger for manganese than for rhenium, irrespective of the value chosen for enthalpy of formation of the $[\mathrm{M(CO)_5}]$ radical [27].

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