THERMOCHEMISTRY OF THIOLATO DERIVATIVES OF MANGANESE CARBONYL. THE STRENGTH OF MANGANESE–SULPHUR BONDS

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Abstract—Calorimetric measurements of the thermal decomposition of $[Mn_2(CO)_8(SR)_2]$ ($R = CH_3$, C_2H_5) have been made in the temperature range $T = 450–550$ K. Analyses of the decomposition reactions indicate that the products include the sulphide, R_2S, and manganese(II) sulphide. Using drop microcalorimetric methods, values were determined for the standard molar enthalpies of formation at 298 K of the crystalline compounds: $\Delta_f H_m^\circ([Mn_2(CO)_8(SCH_3)_2], cr) = -(1521 \pm 30)$ kJ mol^{-1}, $\Delta_f H_m^\circ([Mn_2(CO)_8(SC_2H_5)_2], cr) = -(1555 \pm 30)$ kJ mol^{-1}. These are combined with molar enthalpies of sublimation and other standard enthalpy contributions to provide an estimate of the Mn—S bond enthalpy contribution $D(Mn—SR) = (162 \pm 5)$ kJ mol^{-1}. A group disruption model is also considered.

Information on enthalpies of formation of simple derivatives of the *d*-transition metals containing phosphorus and sulphur donor ligands is scarce. Although a small amount of information has accumulated[1] concerning relative enthalpy changes in reactions of complexes in solution, standard enthalpy of formation measurements have not been made. We report the results of a microcalorimetric study of the thermal decomposition of the simplest sulphur-containing derivatives of decacarbonyldimanganese. These compounds were first reported more than 30 years ago by Stone and co-workers;[2] since then these simple compounds have been objects of interest for their spectroscopic properties[3] and their photochemical and electrochemical reactivity.[4]

EXPERIMENTAL

The Calvet twin-cell high temperature microcalorimeter (Setaram, Lyon), the drop calorimetric technique and the iodine calibration method have been described previously.[5] The ΔH measurements

may spread over $\pm 2\%$ from the mean of several. All thermal decompositions were made under argon. The compounds $[Mn_2(CO)_8(SR)_2]$ ($R = CH_3$, C_2H_5) were prepared from the reaction[2] between $[MnH(CO)_5]$ and R_2S_2, purified by recrystallization and characterized by microanalysis, IR, NMR (^1H and ^{13}C) and mass spectroscopy. The results were in close agreement with values in the literature.[2,3] Normal precautions regarding inert atmospheres were adopted in handling the solid compounds. The enthalpy of sublimation of $[Mn_2(CO)_8(SCH_3)_2]$ was measured using the microcalorimetric vacuum sublimation technique reported earlier.[6]

Auxiliary data

The following values of $\Delta_f H_m^\circ$ (kJ mol^{-1}), where $\Delta_f H_m^\circ$ denotes standard molar enthalpy of formation, were used in evaluating the results: $CO(g) = -110.52$;[7] C_2H_6 (g) $= -83.86$;[7] C_2H_4 (g) $= +52.5$;[8] $(CH_3)_2S(g) = -37.5$;[8] $(C_2H_5)_2S$ (g) $= -83.6$;[8] $MnS(c) = -273.8$;[7] $Mn(g) = +280.7$;[9] $S(g) = +278.8$;[9] $CH_3S(g) = 124.6$.[10] To reduce $\Delta_f H_m^\circ(T)$ measured at an elevated temperature, T, to 298 K, the values of $\Delta_{298} H_m^\circ$
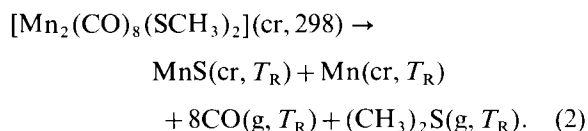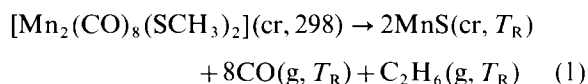
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in the following sources were used $CO(g)$,[7] $Mn(c)$,[7] $MnS(c)$,[11] $C_2H_6(g)$,[8] $C_2H_4(g)$,[8] $(CH_3)_2S(g)$,[8] $(C_2H_5)_2S(g)$.[8] To reduce $\Delta H_m^\circ(T)$ of the sample the following values of $C_p(298)/JK^{-1} mol^{-1}$ are estimated on the basis of known values of $C_p[Fe(CO)_5, 1]$[9] and other organic and inorganic compounds: $[Mn_2(CO)_8(SCH_3)_2] \sim 510$; $[Mn_2(CO)_8(SC_2H_5)_2] \sim 560$. These values are assumed to be independent of temperature in the range used.

RESULTS

Bis(μ-methanethiolato)octacarbonyldimanganese

Thermal decomposition was studied at 471 and 524 K, hereafter referred to as T_R. Analysis of the solid residues from decomposition and of the volatile products showed that the decomposition products are the same at both temperatures. The solid residue contains both manganese(II) sulphide and manganese. The solid residue is air sensitive and consequently difficult to manipulate and to analyse; quantitative analyses were poorly reproducible, but all indicated that manganese(II) sulphide is the principal solid product. The volatile products were collected and analysed by GC-MS which showed that the ratio of $(CH_3)_2S$ to C_2H_6 is approximately 3. Consequently we may describe the decomposition of this compound as follows:

$$[Mn_2(CO)_8(SCH_3)_2](cr, 298) \rightarrow 2MnS(cr, T_R)$$
$$+ 8CO(g, T_R) + C_2H_6(g, T_R) \quad (1)$$

$$[Mn_2(CO)_8(SCH_3)_2](cr, 298) \rightarrow$$
$$MnS(cr, T_R) + Mn(cr, T_R)$$
$$+ 8CO(g, T_R) + (CH_3)_2S(g, T_R). \quad (2)$$

The results of quantitative analyses show that the two decomposition processes (1 and 2) occur in the ratio 3. The results are summarized in Table 1.

Table 2. Enthalpy of sublimation $\Delta_{sub}H_m(T)(kJ\ mol^{-1})$ of mass m of $[Mn_2(CO)_8(SCH_3)_2]$ at calorimeter temperature $T(K)$

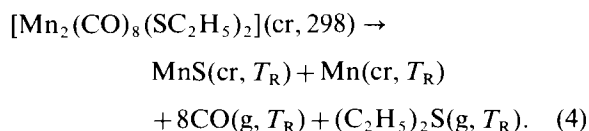| m (mg)	T (K)	$\Delta_{sub} H_m\ (T)$ (kJ mol^{-1})	$\Delta_{sub} H_m$ (298 K) (kJ mol^{-1})
6.242	340	106.3	113.8
6.793	340	107.1	114.6
5.822	340	106.1	113.7

$\langle \Delta_{sub}H_m(298\ K) \rangle = 114.2\ kJ\ mol^{-1}$.

These values lead to $\Delta_f H_m^\circ([Mn_2(CO)_8(SCH_3)_2], cr) = -(1521 \pm 30)\ kJ\ mol^{-1}$. The complex sublimes with only very slight decomposition at 360–380 K in the microcalorimeter. The value of $\Delta H_{sub}(298)$ was obtained by subtracting $(H_T - H_{298})$ from ΔH_{obs} for the complex; values of $(H_T - H_{298})$ were estimated using the approximation $\{H(T) - H(298)\}\{Mn_2(CO)_8(SR)_2(cr)\} \approx \Sigma(H_T - H_{298})$ $[Me_2S_2(g) + 8CO(g) + 2Mn(cr)]$. Values of $\Delta H_{sub}(T)$ were calculated directly from the area of the sublimation thermograms in the usual way.[6] The results are shown in Table 2.

Bis(μ-ethanethiolato)octacarbonyldimanganese

Analysis of the solid residues [manganese(II) sulphide, manganese, trace quantities of carbon] and of the volatile products (ethane, ethene, diethylsulphide) of thermal decomposition indicates that two parallel decomposition paths are in operation at 471 and 524 K (T_R):

$$[Mn_2(CO)_8(SC_2H_5)_2](cr, 298) \rightarrow 2MnS(cr, T_R)$$
$$+ 8CO(g, T_R) + C_2H_4(g, T_R) + C_2H_6(g, T_R) \quad (3)$$

Table 1. Thermal decomposition of a mass m of $[Mn_2(CO)_8(SCH_3)_2]$ at calorimeter temperature $T(K)$. $M = 341.192\ g\ mol^{-1}$

m (mg)	T (K)	ΔH_m° (kJ mol^{-1})	
4.314	471	256.6	
3.885	471	258.7	$\langle \Delta H_m^\circ(471\ K) \rangle = 256.3\ kJ\ mol^{-1}$
4.365	471	253.6	
4.131	524	267.5	
3.996	524	269.8	$\langle \Delta H_m^\circ(524\ K) \rangle = 259.4\ kJ\ mol^{-1}$
4.090	524	270.9	

$\langle \Delta H_m^\circ(298\ K) \rangle$ (process 1) $= 190.4\ kJ\ mol^{-1}$.
$\langle \Delta H_m^\circ(298\ K) \rangle$(process 2) $= 190.8\ kJ\ mol^{-1}$.

$[Mn_2(CO)_8(SC_2H_5)_2](cr, 298) \rightarrow$

$$MnS(cr, T_R) + Mn(cr, T_R)$$
$$+ 8CO(g, T_R) + (C_2H_5)_2S(g, T_R). \quad (4)$$

Quantitative analysis indicated that these two decomposition processes (3 and 4) occur in the ratio 9 : 1. The results are summarized in Table 3. These values lead to $\Delta_f H_m^\circ([Mn_2(CO)_8(SC_2H_5)_2], cr) = -(1555 \pm 30)$ kJ mol^{-1}.

DISCUSSION

Although the structures of the $[Mn_2(CO)_8SR]$ (R $= CH_3$, C_2H_5) complexes have not been determined, the structure of the iron complex $[Fe_2(CO)_6 (SCH_3)_2]$ is known.[12] The spectroscopic and physical properties[2,3] of $[Mn_2(CO)_8(SCH_3)_2]$ lend strong support to the structure:
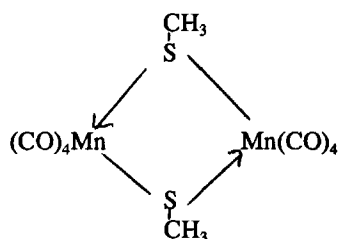
in which there is no direct manganese–manganese bond, all the CO ligands are terminally bound and the two CH_3S groups provide bridges between the two $\{Mn(CO)_4\}$ groups.

The enthalpies of formation of the two compounds we have measured (Table 4) can be interpreted in terms of a total disruption model. Taking $[Mn_2(CO)_8(SCH_3)_2]$ as an example, the total disruption enthalpy $\Delta_f H_{m,tot.dis.}^\circ$ can be expressed as

$$[Mn_2(CO)_8(SCH_3)_2](g) = 2Mn(g) +$$
$$8CO(g) + 2SCH_3(g) \quad (5)$$
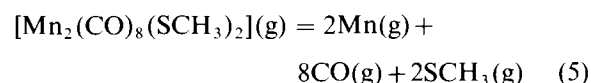
for which $\Delta_f H_{m,tot.dis.}^\circ = 1334$ kJ mol^{-1}. This, in turn, can be divided between the enthalpy contributions of the bonds being broken

$$\Delta_f H_{m,tot.dis.}^\circ = 8Q(Mn—CO_{terminal})$$
$$+ 4Q(Mn—SCH_3).$$

Using the value[13] of $Q(Mn—CO_{terminal}) = 85$ kJ mol^{-1} in $\{Mn(CO)_5\}$ leads to an estimate of $Q(Mn—SCH_3) = 164$ kJ mol^{-1}. The enthalpy of sublimation of $[Mn_2(CO)_8(SC_2H_5)_2]$ is assumed to be the same as that of the methyl analogue. Proceeding in the same way to estimate $\Delta_f H_{m,tot.dis.}^\circ = 1350$ kJ mol^{-1} leads to $Q(Mn—SC_2H_5) = 160$ kJ mol^{-1}.

An alternative interpretation of the enthalpy of formation is provided by the group disruption model. In this case, disruption of the compound can be expressed by

$$[Mn_2(CO)_8(SCH_3)_2](g) = 2\{Mn(CO)_4\}(g)$$
$$+ 2(SCH_3)(g). \quad (6)$$
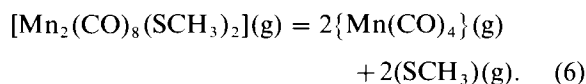
It is possible to estimate[14] $\Delta_f H[Mn(CO)_4] = -(435 \pm 40)$ kJ mol^{-1}, since recent measurements[15] of the electron affinity of $Mn(CO)_5$, $Fe(CO)_4$ and $Co(CO)_4$ indicate that they are all ~ 2.4 eV, so that the value of EA $[Mn(CO)_4]$ is likely to be similar, say (2.4 ± 0.2) eV. The enthalpy change of the process (eq. 6), $\Delta_f H_m^\circ$ (grp.diss.) $= 786$ kJ mol^{-1}. Distribution of this between the enthalpy contributions of the four Mn—S bonds being broken leads to an estimate of $D(Mn—SCH_3) = 196$ kJ mol^{-1}. The large experimental uncertainties make it difficult to have a strictly meaningful comparison of bond enthalpies in detail.

Recently we have also determined[16] the standard molar enthalpies of formation of the iron complexes $[Fe_2(CO)_6(SR)_2]$ (R $= CH_3$, C_2H_5). From the results, the enthalpy contributions of the (Fe—SR)

Table 3. Thermal decomposition of a mass m of $[Mn_2(CO)_8(SC_2H_5)_2]$ at calorimeter temperature T(K). $M = 369.246$ g mol^{-1}

m (mg)	T (K)	ΔH_m° (kJ mol^{-1})	
4.148	471	299.9	
3.552	471	296.6	$\langle \Delta H_m^\circ (471\ K) \rangle = 298.1$ kJ mol^{-1}
3.987	471	207.8	
3.925	524	316.9	
3.713	524	322.0	$\langle \Delta H_m^\circ (524\ K) \rangle = 318.9$ kJ mol^{-1}
3.983	524	317.8	

$\langle \Delta H_m^\circ (298\ K) \rangle$(process 3) $= 227.2$ kJ mol^{-1}.
$\langle \Delta H_m^\circ (298\ K) \rangle$(process 4) $= 226.8$ kJ mol^{-1}.

Table 4. Summary of results. All values in kJ mol^{-1}

Compound	$\Delta_f H_m$ (cr)	$\Delta_{sub} H_m$	$\Delta_f H_m^\circ$ (g)	D (Mn—SR)
[Mn$_2$(CO)$_8$(SCH$_3$)$_2$]	-1521 ± 30	114.2 ± 4	-1407	164
[Mn$_2$(CO)$_8$(SC$_2$H$_5$)$_2$]	-1555 ± 30	114[a]	-1441	160

[a] Estimated value.

bonds has been estimated as $Q(\text{Fe—SR}) = (178 \pm 5)$ kJ mol^{-1}.

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