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THE ENTHALPIES OF FORMATION OF $CH_3Mn(CO)_5$ AND OF $CH_3Re(CO)_5$, AND THE STRENGTHS OF THE CH_3—Mn AND CH_3—Re BONDS

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Summary

From measurements of the heats of iodination of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$ at elevated temperatures using the 'drop' microcalorimeter method, values were determined for the standard enthalpies of formation at 25° of the crystalline compounds: $\Delta H_f^0[CH_3Mn(CO)_5, c] = -189.0 \pm 2$ kcal mol^{-1} (−790.8 ± 8 kJ mol^{-1}), $\Delta H_f^0[CH_3Re(CO)_5, c] = -198.0 \pm 2$ kcal mol^{-1} (−828.4 ± 8 kJ mol^{-1}). In conjunction with available enthalpies of sublimation, and with literature values for the dissociation energies of the Mn—Mn and Re—Re bonds in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, values are derived for the dissociation energies: $D(CH_3—Mn(CO)_5) = 27.9 \pm 2.3$ or 30.9 ± 2.3 kcal mol^{-1} and $D(CH_3—Re(CO)_5) = 53.2 \pm 2.5$ kcal mol^{-1}. In general, irrespective of the value accepted for D(M—M) in $M_2(CO)_{10}$, the present results require that, $D(CH_3—Mn) = \frac{1}{2}D(Mn—Mn) + 18.5$ kcal mol^{-1} and $D(CH_3—Re) = \frac{1}{2}D(Re—Re) + 30.8$ kcal mol^{-1}.

Introduction

Satisfactory methods for the preparation of binary transition metal alkyls have been developed only in recent years [1]; previously, the view had persisted [2] that the transition metals are either incapable of forming σ-bonds to carbon, or can form only weak bonds of this type. Evidence is accumulating against this view, e.g., the dissociation energies in the diatomic gaseous molecules RuC, RhC, IrC and PtC have been reported [3-5] to lie in the range 140 to 152 kcal mol^{-1}, and in the gaseous dicarbides [6] of Ti, V, Cr, Hf and Zr the dissociation energies $D(M—C_2)$ range from 106 to 159 kcal mol^{-1}; the considerable magnitude of these binding energies is hardly consistent with inherently "weak" metal—carbon bonding, although in these particular molecules the bonding is probably multiple, and otherwise more complex than in a normal M—alkyl σ-bond.

Very few measurements leading directly to M—alkyl bond energies (M =

transition metal) are available. Egger [7] studied the kinetics of thermal decomposition of $(C_5H_5)Pt(CH_3)_3$ in the gas-phase, and concluded that the rate-determining step is the disruption of a $Pt{-}CH_3$ bond; the identification of the activation energy with this bond dissociation energy gave $D[CH_3{-}Pt(C_5H_5)(CH_3)_2$ = 39 ± 5 kcal mol^{-1}. Similar kinetic studies by Fushman, Potyagalio and Chirkov [8] indicated $D[C_2H_5{-}TiCl(C_5H_5)_2]$ = 36 kcal mol^{-1}. Thermochemical evidence is very limited [9, 10], and indecisive, but has implied bond-energy values of the order 60 kcal mol^{-1} for bonds of the type $Pt{-}C_6H_5$ and $Ti{-}C_6H_5$. By comparison the mean bond dissociation energies [11], $\bar{D}(M{-}CH_3)$, in the binary methyls of the Group II, III and IV metals range from 32 kcal mol^{-1} in $Hg(CH_3)_2$ to 69 kcal mol^{-1} in $Al(CH_3)_3$. The present work reports measurements of the enthalpies of formation of $CH_3Mn(CO)_5$ and $CH_3Re(CO)_5$, from which values are obtained for the $CH_3{-}Mn$ and $CH_3{-}Re$ bond energies in these molecules.

Experimental

Calorimeter

The Calvet twin-cell microcalorimeter (Setaram, Lyon) and the drop calorimetric technique have been described previously [12]. Each calorimetric experiment involved two measurements: a sample (10-15 mg) of crystalline iodine (I_2, c) was dropped into the argon filled 'live' cell of the microcalorimeter, and the resultant thermogram recorded. This thermogram area, relating to the vaporization process I_2 (c, 298) → I_2 (g, T_2) of known enthalpy change [13], served to calibrate the calorimeter at T_2. On completion of the vaporization trace, a sample (a few mg) of methyl metal carbonyl was dropped into the same cell (now containing excess iodine vapour), and the reaction thermogram recorded. The extent of the iodination was determined from analysis of the unused iodine, and of the iodine content of the solid metallic iodide formed.

Compounds

$CH_3M(CO)_5$ (M = Mn, Re) were prepared [14, 15] by the reaction between $Na[M(CO)_5]$ and CH_3I in THF. The compounds were purified by sublimation and characterised by microanalysis, infrared, NMR and mass spectroscopy. Normal precautions regarding inert atmospheres were adopted in handling the solid compounds.

Auxiliary data

All heat quantities are given in calories (or in kcal); 1 cal = 4.1840 J. The following auxiliary heat of formation data (in kcal mol^{-1}) were used in evaluating the results:

ΔH_f^0(CO, g) [16] = −26.416 ± 0.04;
ΔH_f^0(MnI_2, c) [12] = −59.4 ± 1.0;
ΔH_f^0(I_2, g) [16] = 14.92 ± 0.01;
ΔH_f^0($Mn_2(CO)_{10}$, c) [12, 16] = −401.0 ± 1;
ΔH_f^0(Mn, g) [16] = 67.1 ± 1;
ΔH_f^0(CH_3, g) [17] = 34.8 ± 0.1;
ΔH_f^0(ReI_3, c) [18] = −10 ± 5;
ΔH_f^0(CH_3I, g) [19] = 3.4 ± 0.3;
ΔH_f^0($Re_2(CO)_{10}$, c) [18] = −395 ± 5;
ΔH_f^0(Re, g) [16] = 184.0 ± 1.5

To reduce values of ΔH measured at elevated temperature to 298 K, the $(H_T - H_{298})$ data (in cal mol^{-1}) of Table 1 were accepted.

TABLE 1

(H_T-H_{298}) DATA (cal mol^{-1})

	$H_{495}-H_{298}$	$H_{533}-H_{298}$	Ref.
CO(g)	1.38	1.65	13
CH_3(g)	1.97	2.39	13
CH_3I(g)	2.42	2.98	13
I_2(g)	1.75	2.09	13
Mn(c)	1.34		20
Re(c)		1.47	20
MnI_2(c)	3.67		20

Results

Methylmanganese pentacarbonyl

$CH_3Mn(CO)_5$ reacted readily with excess iodine vapour at 222°, giving MnI_2 as the solid product. The iodine balance indicated that the main product formed by the released CH_3 radicals was CH_3I, but the analysis was insufficiently thorough to detect possible side-products (e.g. HI, C_2H_6, C_2H_4). The calorimetrically measured enthalpies of reaction, Δh, were evaluated from the individually recorded thermograms; the values Δh, and the molar enthalpies, ΔH_{obs}, referring to the reaction process 1 are listed in Table 2. The values $\Delta H^\star$ refer to the thermal

$$CH_3Mn(CO)_5(c, 248) + 3/2\ I_2(g, 495) \rightarrow MnI_2(c, 495) + CH_3I(g, 495) + 5CO(g, 495) \qquad (1)$$

decomposition per se (eqn. 2), and were obtained by combining ΔH_{obs} and eqn. 1

$$CH_3Mn(CO)_5(c, 298) \rightarrow CH_3(g, 495) + Mn(c, 495) + 5CO(g, 495) \qquad (2)$$

with the iodination reactions 3 and 4.

$$Mn(c, 495) + I_2(g, 495) \rightarrow MnI_2(g, 495);\ \Delta H_3 = -73.7 \pm 1.0 \text{ kcal mol}^{-1} \qquad (3)$$

$$CH_3(g, 495) + \tfrac{1}{2}I_2(g, 495) \rightarrow CH_3I(g, 495);\ \Delta H_4 = -39.3 \pm 0.3 \text{ kcal mol}^{-1} \qquad (4)$$

The values ΔH_3, ΔH_4 derive from the auxiliary data listed above. The values $\Delta H^\star_{298}$, which refer to the isothermal decomposition at 298 K (eqn. 5), were

$$CH_3Mn(CO)_5(c, 298) \rightarrow CH_3(g, 298) + Mn(c, 298) + 5CO(g, 298) \qquad (5)$$

obtained on reducing $\Delta H^\star$ to 298K.

TABLE 2

IODINATION OF $CH_3Mn(CO)_5$ AT 495 K

Expt.	$CH_3Mn(CO)_5$ (mg)	I_2 (mg)	Δh (cal)	ΔH_{obs} (kcal mol^{-1})	$\Delta H^\star$ (kcal mol^{-1})	$\Delta H^\star_{298}$ (kcal mol^{-1})
1	1.590	7.830	−0.090	−11.9	101.1	90.0
2	1.645	8.005	−0.078	− 9.9	103.1	92.9
3	1.850	8.460	−0.106	−12.0	101.0	90.8
4	1.810	8.355	−0.093	−10.8	102.2	92.0
		Mean $\Delta H^\star_{298}$ = 91.7 kcal mol^{-1}				

TABLE 3

IODINATION OF $CH_3Re(CO)_5$ AT 533 K

Expt.	$CH_3Re(CO)_5$ (mg)	I_2 (mg)	Δh (cal)	ΔH_{obs} (kcal mol^{-1})	n	ΔH^* (kcal mol^{-1})	ΔH^*_{298} (kcal mo
1	2.530	7.500	0.344	46.4	2.73	114.9	102.8
2	3.415	10.600	0.409	40.9	2.75	109.6	97.5
3	2.465	7.880	0.329	45.5	2.80	114.8	102.7
4	2.580	7.610	0.346	45.8	2.50	111.8	99.8
		Mean ΔH^*_{298} = 100.7 kcal mol^{-1}					

The uncertainty attached to the mean $\Delta H^\bigstar_{298}$, taking into account the spread in the experimental results and uncertainties in auxiliary data used, is estimated at ± 2 kcal mol^{-1}.

Methylrhenium pentacarbonyl

The iodination reaction was studied at 260°, giving the results summarized in Table 3. The solid product, ReI_n, analysed as predominantly the triiodide admixed with small amounts of lower iodides. The iodine balance indicated that the released CH_3 radicals reacted mainly to form CH_3I, and the values ΔH_{obs} given in Table 3 are accordingly taken to refer to the process 6. The values $\Delta H^\bigstar$ refer to the thermal decomposition according to eqn. 7, and were obtained by

$$CH_3Re(CO)_5(c, 298) - \frac{n+1}{2} I_2(g, 533) \rightarrow ReI_n(c, 533) + CH_3I(g, 533)$$

$$+ 5CO(g, 533) \tag{6}$$

$$CH_3Re(CO)_5(c, 298) \rightarrow CH_3(g, 533) + Re(c, 533) + 5CO(g, 533) \tag{7}$$

removing the exothermic contributions to ΔH_{obs} from the iodination of CH_3 radicals (eqn. 4), and Re metal. For the latter, ReI_n was regarded as a mixture of ReI_3 and Re metal, $[ReI_n \equiv \frac{n}{3} ReI_3 + (1 - \frac{n}{3})Re]$, and an estimated value [18] $\Delta H_8 \approx -32$ kcal mol^{-1} was used for the enthalpy of the process (eqn. 8). (The same estimate was made in similar studies [18] on $Re_2(CO)_{10}$).

$$Re(c, 533) + \tfrac{3}{2}I_2(g, 533) \rightarrow ReI_3(c, 533) \tag{8}$$

The spread in the experimental results attaches an uncertainty of the order ± 2 kcal mol^{-1} to the mean $\Delta H^\bigstar_{298}$ value; the overall uncertainty may be larger because of the use of an estimated value for ΔH_8, but for purposes of comparison of bond energies in $CH_3Re(CO)_5$ and $Re_2(CO)_{10}$, this absolute uncertainty is common to both, and does not affect bond-energy differences.

Discussion

The mean $\Delta H^\bigstar_{298}$ values (Tables 2, 3), in conjunction with the listed values for $\Delta H_f^0(CO, g)$ and $\Delta H_f^0(CH_3, g)$, lead directly to the standard enthalpies of formation, $\Delta H_f^0[CH_3Mn(CO)_5, c] = -189.0 \pm 2$ kcal mol^{-1} (-790.8 ± 8 kJ mol^{-1}) and $\Delta H_f^0[CH_3Re(CO)_5, c] = -198.0 \pm 2$ kcal mol^{-1} (-828.4 ± 8 kJ mol^{-1}). The enthalpies of sublimation of both compounds have been derived from static vapour pressure measurements over the range 20-130° [for $CH_3Mn(CO)_5$] [14], and 40-110° [for $CH_3Re(CO)_5$] [15], at 14.4 kcal mol^{-1} and 15.6 kcal mol^{-1} respectively. Combining these with the standard enthalpies of formation, the values $\Delta H_f[CH_3Mn(CO)_5, g] = -174.6 \pm 2$ kcal mol^{-1} and $\Delta H_f[CH_3Re(CO)_5, g] = -182.4 \pm 2$ kcal mol^{-1} are obtained.

The bond dissociation energy, $D[CH_3\text{—}Mn(CO)_5]$, is identified with the enthalpy change for the dissociation process 9 (at 298 K) and 10. The values

$$CH_3M(CO)_5, g \rightarrow CH_3, g + M(CO)_5, g \qquad (9)$$

$$\Delta H_9 = \Delta H_f^0[CH_3, g] + \Delta H_f^0[M(CO)_5, g] - \Delta H_f^0[CH_3M(CO)_5, g] \qquad (10)$$

$\Delta H_f^0[M(CO)_5, g]$ may be derived, given that values are available for $D[(CO)_5M\text{—}M(CO)_5]$ and $\Delta H_f^0[M_2(CO)_{10}, g]$, from eqn. 11.

$$D[(CO)_5M\text{—}M(CO)_5] = 2\Delta H_f^0[M(CO)_5, g] - \Delta H_f^0[M_2(CO)_{10}, g] \qquad (11)$$

The standard enthalpies of formation of crystalline $Mn_2(CO)_{10}$ and $Re_2(CO)_1$ are listed auxiliary data above, and values for the enthalpies of sublimation have been reported by Baev et al. [21], as $\Delta H_{sub}[Mn_2(CO)_{10}] = 15.7 \pm 0.5$, and $\Delta H_{sub}[Re_2(CO)_{10}] = 18.5 \pm 0.1$ kcal mol^{-1}. These were derived from vapour pressure measurements over the range 78-155° [for $Mn_2(CO)_{10}$], and 90-181° [$(Re_2(CO)_{10}$]. Recently, however, Lemoine et al. [22] have observed solid transitions in both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, and report $\Delta H_{trans}[Mn_2(CO)_{10}] = 3.5$ kcal mol^{-1} at 68°, and $\Delta H_{trans}[Re_2(CO)_{10}] = 3.8$ kcal mol^{-1} at 98°. Accordingly, we adopt modified values for $\Delta H_{sub}^{298}[Mn_2(CO)_{10}] = 19.2 \pm 0.5$ kcal mol^{-1} and $\Delta H_{sub}^{298}[Re_2(CO)_{10}] = 22.3 \pm 0.1$ kcal mol^{-1}, leading to $\Delta H_f^0[Mn_2(CO)_{10}, g] = -381.8 \pm 1.1$ kcal mol^{-1}, and $\Delta H_f^0[Re_2(CO)_{10}, g] = -372.7 \pm 5$ kcal mol^{-1}.

Electron impact studies on $Mn_2(CO)_{10}$ and on the radical $\cdot Mn(CO)_5$ have been made by Bidinosti and McIntyre [23], from which they obtained $D[(CO)_5Mn\text{—}Mn(CO)_5] = 18.9 \pm 1.4$ kcal mol^{-1}. Similar, somewhat less direct studies by Junk and Svec [24] led them to a higher value, $D = 24.9$ kcal mol^{-1}. Junk and Svec have also reported $D[(CO)_5Re\text{—}Re(CO)_5] = 44.7$ kcal mol^{-1}, based on the measured appearance potential of $Re(CO)_5^+$ from $Re_2(CO)_{10}$, and an assumed value for the ionization potential of the radical $\cdot Re(CO)_5$. These values (in kcal mol^{-1}) when substituted into eqns. 11 and 10 are summarized in Table 4.

These results place $D(CH_3\text{—}Mn)$ in the range 28-31 kcal mol^{-1}, and at either extreme we may note that $D(CH_3\text{—}Mn) > D(Mn\text{—}Mn)$. By combining eqns. 10 and 11, and substituting the present values for the ΔH_f^0 terms, eqns. 12 and 13 follow, so that $D(CH_3\text{—}Mn) > D(Mn\text{—}Mn)$ for all values of $D(Mn\text{—}Mn)$

$$D(CH_3\text{—}Mn) = \tfrac{1}{2}D(Mn\text{—}Mn) + 18.5 \text{ kcal mol}^{-1} \qquad (12)$$

$$D(CH_3\text{—}Re) = \tfrac{1}{2}D(Re\text{—}Re) + 30.8 \text{ kcal mol}^{-1} \qquad (13)$$

below 37 kcal mol^{-1}, and $D(CH_3\text{—}Re) > D(Re\text{—}Re)$ for all values of $D(Re\text{—}Re)$ below 62 kcal mol^{-1}.

From studies on polynuclear carbonyls of Fe and Co, it was concluded

TABLE 4

DATA (kcal mol^{-1}) CALCULATED IN EQNS. 10 AND 11 FROM LIT. D[(CO)$_5$M—M(CO)$_5$] VALUES

	B and M[a]	J and S[b]
D(Mn—Mn) in $Mn_2(CO)_{10}$	18.9 ± 1.4	24.9 ± 1.4
D(CH_3—Mn) in $CH_3Mn(CO)_5$	27.9 ± 2.3	30.9 ± 2.3
$\bar{D}$(Mn—CO) in $Mn(CO)_5$	23.3 ± 0.3	22.7 ± 0.3
ΔH_f^0[$Mn(CO)_5$, g]	−181.5 ± 1	−178.5 ± 1
D(Re—Re) in $Re_2(CO)_{10}$		44.7 ± 2.2
D(CH_3—Re) in $CH_3Re(CO)_5$		53.2 ± 2.5
$\bar{D}$(Re—CO) in $Re(CO)_5$		43.2 ± 0.4
ΔH_f^0[$Re(CO)_5$, g]		−164.0 ± 1.5

[a] See ref. 23. [b] The error limits quoted by Junk and Svec refer only to error in appearance potentials of $M(CO)_5^+$; the limits given here are doubled with respect to the authors' values [24]

[18] that the average bond enthalpy contribution, $\bar{M}$, from an M—M bond is less than that from a terminal M—CO bond ($\bar{T}$), and that $\bar{M} \approx 0.68\ \bar{T}$. If this same ratio should apply to $M_2(CO)_{10}$, the total enthalpy of disruption, $M_2(CO)_{10}$ g → 2M, g + 10 CO(g), is given by $\Delta H_{\text{disrupt}} \approx 10.68\ \bar{T}$; for $Mn_2(CO)_{10}$, $\Delta H_{\text{disrupt}} \approx 251.8$ kcal mol^{-1}, $\bar{T} \approx 23.6$ kcal mol^{-1} and $\bar{M} \approx 16.0$ kcal mol^{-1}; for $Re_2(CO)_{10}$ $\Delta H_{\text{disrupt}} \approx 476.5$ kcal mol^{-1}, $\bar{T} \approx 44.6$ kcal mol^{-1} and $\bar{M} \approx 30.4$ kcal mol^{-1}. Replacing D(M—M) in eqns. 12 and 13 by $\bar{M}$, the bond enthalpy contributions from CH_3—Mn and CH_3—Re are 26.5 and 46.0 kcal mol^{-1} respectively. There is no necessary identity, however, between bond enthalpy term values and the corresponding bond dissociation energies [e.g. there may be some reorganization energy in $\cdot M(CO)_5$ relative to $M_2(CO)_{10}$, in respect of the M—CO bond energies]. Taken with the results discussed earlier, it may be concluded that $D(CH_3\text{—}M) \geqslant \bar{T}(M\text{—}CO)$.

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