

Thermochemistry of pentacarbonyl(2-propenyl)manganese and tetracarbonyl(η^3 -2-propenyl)manganese. Thermochemical considerations in alkenyl isomerisation reactions

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Abstract

Microcalorimetric measurements at elevated temperatures of the enthalpies of sublimation, thermal decomposition and iodination of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$ and $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ have been made to obtain the standard enthalpies of formation $\Delta_f H_m^\circ(\text{cr})$ and $\Delta_f H_m^\circ(\text{g})$ (in that order) as follows (values in kilojoules per mole): $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$ $-(727 \pm 20)$, $-(679 \pm 25)$; $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ $-(651 \pm 12)$, $-(570 \pm 15)$. The values of $\Delta_f H_m^\circ(\text{g})$ are used to derive enthalpy contributions for the (propenyl-Mn) bonds in these molecules, and thus to provide thermochemical information on the irreversible $\eta^1 \rightarrow \eta^3$ isomerisation reaction involved. © 1997 Elsevier Science S.A. © 1997 Elsevier Science S.A.

Keywords: Manganese; Calorimetry; Alkenyl; Isomerisation

1. Introduction

An earlier study reported microcalorimetric measurements of the thermal decomposition and iodination of tricarbonyliodo(η^3 -prop-2-enyl)iron and tricarbonyl(η^4 -cyclooctatetraene)iron from which estimates for the enthalpy contributions of the bonds between iron and the organic ligand in these complexes were derived [1]. The present work considers the mechanistically important $\eta^1 \leftrightarrow \eta^3$ isomerisation reaction [2] on manganese which involves intramolecular displacement of a bound CO ligand [3].

2. Experimental

The thermal measurements were made using a Calvet twin-cell microcalorimeter (Setaram, Lyon), adapted to the drop calorimetric technique [4]. Heats of sublimation were measured by using the microcalorimetric vacuum sublimation method [5]. All measurements were made in an argon atmosphere. Measurements of the initial temperature of the sample, that is to say the

temperature reached by the sample on falling from the entrance to the chute into the cell of the microcalorimeter using diiodine as calibrant, indicated that this was in the range 318–321 K for an operating (cell) temperature of 470–500 K.

2.1. Materials

Samples of pentacarbonyl(2-propenyl)manganese, a pale yellow liquid, and tetracarbonyl(η^3 -2-propenyl)manganese, a yellow crystalline solid, were prepared by standard methods [3,6]. The purity of each compound was established by element microanalysis, and by spectroscopic measurements (IR, NMR, mass) which were in agreement with published values. Although many of the published preparations of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$ indicate [6,7] that it is often contaminated with small but significant amounts of $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$, we have found that by taking particular care in the preparation, purification and manipulation of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$, this compound can be obtained with negligible (much less than 1%) $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ as indicated by IR spectra in the 2150–1900 cm^{-1} region. The purified samples were stored in an atmosphere of argon at ca. 250 K. Care was

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taken to shield the samples from direct light at all times. All glassware was oven-dried and cooled in a dinitrogen atmosphere. 3-Iodo-prop-1-ene (BDH Merck) and decacarbonyldimanganese (Strem) were purified by distillation/sublimation in the usual manner.

2.2. Auxiliary data

The following auxiliary heat of formation data (in kilojoules per mole) were used in evaluating the calorimetric results.

$\text{CO}(\text{g}) = -(110.52 \pm 0.17)$ [8]; $\text{I}_2(\text{g}) = (62.44 \pm 0.04)$ [8]; $\text{MnI}_2(\text{c}) = -(246.5 \pm 3)$ [9]; $\text{Mn}(\text{g}) = (283.5 \pm 0.2)$ [10]; $\text{I}(\text{g}) = (106.76 \pm 0.04)$ [9]; $\text{C}_3\text{H}_5\text{I}(\text{g}) = (95.4 \pm 4)$ [11]; hexa-1,5-diene(g) = (84.1 ± 1.2) [11]; $\text{Mn}(\text{CO})_5(\text{g}) = -(713 \pm 11)$ [12]; $\text{C}_3\text{H}_5(\text{g}) = (166.9 \pm 2)$ [13]; $\text{C}_6\text{H}_5\text{CH}_2(\text{g}) = (200 \pm 6)$ [12]; $\text{CH}_3(\text{g}) = (146.9 \pm 0.6)$ [12]. The value of $\Delta_f H_m^\circ(\text{MnI}_n, (n < 2), \text{c})$ was assumed equal to $0.5n [\Delta_f H_m^\circ(\text{MnI}_2, \text{c})]$ in agreement with previous practice [4,14]. $\Delta_f H_m^T(\text{C}_6\text{H}_{10}\text{I}_2, \text{g}) \sim (98 \pm 7)$ was estimated assuming that the enthalpy of addition of $\text{I}_2(\text{g})$ to hexa-1,5-diene(g) is the same as for the addition of $\text{I}_2(\text{g})$ to but-1-ene for which $\Delta H(\text{iodination}) = -(50.2 \pm 6.3) \text{ kJ mol}^{-1}$ [1,11]. The enthalpies of reaction, ΔH^T , measured at temperature T were adjusted to refer to 298 K by using $(H_T - H_{298})$ data for organic compounds from Stull et al. [15] and calculations based on Benson [16], and for inorganic compounds from Barin [9] and the JANAF tables [17]. The specific heat of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)](\text{l})$ was approximated to that of $\text{Fe}(\text{CO})_5(\text{l})$ [18].

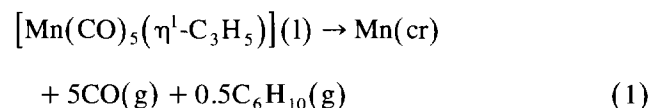
3. Results

3.1. Pentacarbonyl(2-propenyl)manganese

Attempts to measure the enthalpy of vaporisation at 350 K using the vacuum sublimation microcalorimetric technique [5] were unsuccessful because some decarbonylation occurred and $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ was identified as a product. The same problem was encoun-

tered, albeit less significantly, when the microcalorimeter was operated at ambient temperature and the applied vacuum was increased from 0.1 to 0.005 Torr. Under these conditions, the problem of reproducibility also increased.

Thermal decomposition of the liquid compound at 470–500 K was rapid and complete within the hot zone. Hexa-1,5-diene, C_6H_{10} , was identified as the major organic product. Variability in the measured enthalpy of the reaction



for which we found $\Delta H(298) = 180\text{--}220 \text{ kJ mol}^{-1}$, and its low value, indicated that exothermic reactions of carbon monoxide and the diene on the surface of the freshly-formed metal films were likely to be responsible, as we have noticed in previous studies [1,4,14]. To inhibit transformation of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$ to $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ in passing through a temperature gradient into the hot zone, experiments were also made in a mixed argon/carbon monoxide gas atmosphere in the calorimeter. The value of $\Delta H(298)$ obtained was in the same range.

Iodination of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$ was studied in the same 470–500 K temperature range in a mixed argon/CO atmosphere. Carefully weighed samples of the liquid complex in glass capillary tubes were dropped into a known excess of diiodine vapour in the hot reaction cell. The ensuing reaction was both rapid and complete within the hot zone. Following the end of reaction, indicated by return to the base line, the excess of diiodine was removed by evacuation and condensation; the amount of diiodine was determined titrimetrically. The volatile liquid products were identified (GCMS) as 3-iodo-prop-1-ene and hexa-1,5-diene. The involatile solid residues (MnI_n) were analysed for iodine content separately. The iodine balance provides only a rough measure of diiodine consumed in the

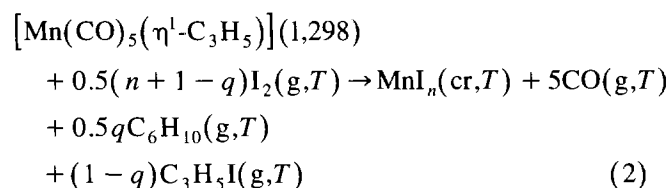
Table 1
Iodination of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$, $M = 236.061 \text{ g mol}^{-1}$

T (K)	[Mn] (mg)	I_2 (mg)	n	q	$\Delta H_m^T(2) \text{ kJ mol}^{-1}$	$\Delta H_m^{298}(2) \text{ kJ mol}^{-1}$	$\Delta_f H_m^\circ \text{ kJ mol}^{-1}$	
							(a)	(b)
473	2.416	10.800	1.79	0.8	-18.8	-57.4	-727	-736
473	3.422	8.944	1.83	0.8	-33.8	-72.6	-718	-727
493	2.698	8.211	1.88	0.7	-12.3	-57.2	-739	-753
493	2.035	9.600	1.80	0.6	-23.0	-68.6	-713	-732
493	2.341	9.035	1.94	0.7	-31.2	-76.4	-729	-743
Mean value							-725	-738

Table 2
Sublimation of $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ at 373 K

[Mn] (mg)	$\Delta_{\text{sub}} H_{\text{m}}^{\text{T}}$ (kJ mol ⁻¹)	$\Delta_{\text{sub}} H_{\text{m}}^{298}$ (kJ mol ⁻¹)
2.636	97.1	80.9
2.350	98.6	82.4
3.092	99.4	83.2
2.335	94.5	78.3
Mean value	(81.2 ± 1.9)	

reaction because of manipulation losses. Overall the iodination reaction was assumed to be described by the equation



the values of n and q being obtained from iodine analysis and the iodine balance. The term $(1-q)\text{C}_3\text{H}_5\text{I}$ includes both 3-iodo-prop-1-ene and 5,6-diiodohex-1-ene. The results of the iodination experiments are summarised in Table 1, in which $\Delta H_{\text{m}}^{\text{T}}(2)$ is the measured enthalpy of reaction (2) at temperature T and $\Delta H_{\text{m}}^{298}(2)$ refers to the same reaction carried out isothermally at 298 K. The $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ values for $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)](1)$ listed in column a are derived assuming that the iodoalkene product is exclusively 3-iodo-prop-1-ene, that is

$$\begin{aligned}
 \Delta_{\text{f}} H_{\text{m}}^{\circ} = &(-488.4 - 22.1q - 155.5n \\
 &- \Delta H_{\text{m}}^{298}(2)) \text{ kJ mol}^{-1} \quad (3)
 \end{aligned}$$

The values listed in column b are based on the extreme assumption that the iodoalkene product is exclusively 5,6-diiodohex-1-ene, for which

$$\begin{aligned}
 \Delta_{\text{f}} H_{\text{m}}^{\circ} = &(-534.8 + 24.3q - 155.5n \\
 &- \Delta H_{\text{m}}^{298}(2)) \text{ kJ mol}^{-1} \quad (4)
 \end{aligned}$$

We choose a value of $\Delta_{\text{f}} H_{\text{m}}^{\circ}$ which is weighted towards the mean value of column a, and thus

$$\begin{aligned}
 \Delta_{\text{f}} H_{\text{m}}^{\circ}([\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)](1)) \\
 = &-(727 \pm 20) \text{ kJ mol}^{-1}
 \end{aligned}$$

Table 4
Enthalpies of formation, $\Delta_{\text{f}} H$, and bond dissociation enthalpy contributions in $\text{Mn}_2(\text{CO})_{10}$ and derivatives

Complex	$\Delta_{\text{f}} H(\text{cr}/1)$ (kJ mol ⁻¹)	$\Delta_{\text{f}} H(\text{g})$ (kJ mol ⁻¹)	$D(\text{R-Mn})^a$ (kJ mol ⁻¹)	Ref.
$\text{Mn}_2(\text{CO})_{10}$	-1677 ± 4	-1585 ± 5	159 ± 21	[12]
$\text{Mn}(\text{CO})_5\text{CH}_3$	-813 ± 4	-753 ± 4	187 ± 4	[12]
$\text{Mn}(\text{CO})_5\text{CH}_2\text{C}_6\text{H}_5$	-726 ± 8	-642 ± 8	129 ± 10	[12]
$\text{Mn}(\text{CO})_5\text{CH}_2\text{CH}=\text{CH}_2$	-727 ± 20	-679 ± 25	133 ± 25	^b
$\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)$	-651 ± 12	-570 ± 15	305 ± 15	^b

^a Based on $\Delta_{\text{f}} H([\text{Mn}(\text{CO})_5]_2\text{g}) = -713 \pm 11 \text{ kJ mol}^{-1}$.

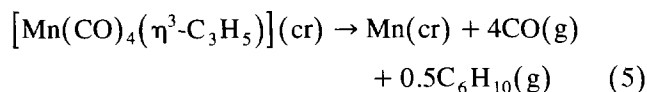
^b This work.

Table 3
Iodination of $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$, $M = 208.051 \text{ g mol}^{-1}$

T (K)	[Mn] (mg)	I_2 (mg)	n	q	$\Delta H(6)$	$\Delta H^{98}(6)$	$\Delta_{\text{f}} H$
473	2.259	9.069	1.81	0.8	-8.9	-24.6	-652
473	1.970	9.039	1.89	0.9	-20.1	-52.9	-639
493	3.145	11.258	1.92	0.8	-2.1	-36.3	-658
493	2.426	9.448	1.96	0.8	-11.8	-50.4	-650
493	2.686	10.218	1.93	0.9	-7.2	-44.6	-653
Mean value							-651

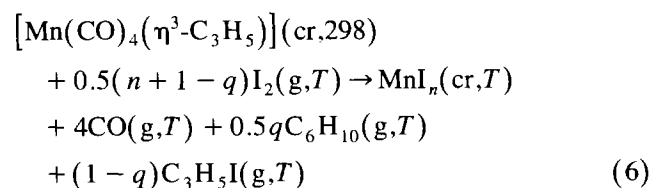
3.2. Tetracarbonyl (η^3 -2-propenyl)manganese

Vacuum sublimation studies were made at 373 K with results shown in Table 2. Thermal decomposition in argon at 493 K was rapid and apparently complete within the hot zone giving a black solid and some bright metallic film together with a liquid. Mass spectrometry was used to show that the liquid is hexa-1,5-diene. Variability in the measured enthalpy, $\Delta H(298)$, of the reaction



for which we found $\Delta H^{298} = 130\text{--}170 \text{ kJ mol}^{-1}$, together with its value being lower than expected, indicated that exothermic reactions of CO and of the diene on the surface of the metal film were likely to be responsible. This approach was discontinued.

Iodination of $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$ was studied in the temperature range 460–500 K and, using carefully weighed samples of the crystalline solid complex, the experiments were carried out in the manner already described for $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$. The iodination reaction was assumed to be described by the equation



The results from the iodination experiments are summarised in Table 3, where $\Delta H_{\text{m}}^{\text{T}}(6)$ is the measured

enthalpy of reaction (6) at temperature T , and $\Delta H_m^{298}(6)$ refers to the same reaction carried out isothermally at 298 K. The values of $\Delta_f H_m^\circ[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)](\text{cr})$ are derived assuming that the iodoalkene product is exclusively 3-iodo-prop-1-ene, that is

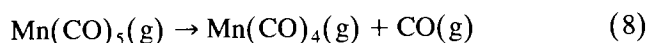
$$\Delta_f H_m^\circ = (-377.9 - 22.1q - 155.5n - \Delta H^{298}(6)) \text{ kJ mol}^{-1} \quad (7)$$

A value for $\Delta_f H_m^\circ$ can also be calculated on the assumption that 5,6-diiiodohexene is formed exclusively which leads to a mean value of $-(659 \pm 20) \text{ kJ mol}^{-1}$. We choose a value of $\Delta_f H_m^\circ$ which is weighted towards the lower value in Table 3, thus

$$\Delta_f H_m^\circ([\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)](\text{cr})) = -(651 \pm 12) \text{ kJ mol}^{-1}$$

4. Discussion

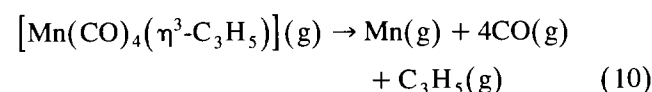
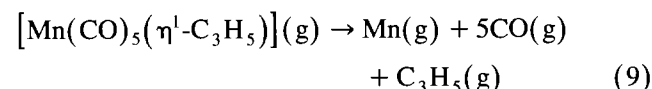
The enthalpies of formation of various derivatives of $\text{Mn}_2(\text{CO})_{10}$ from the present study and previous reports are collected in Table 4. The enthalpy of vaporisation of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)](\text{l}) \sim 48 \text{ kJ mol}^{-1}$ is based on the known value of $\Delta_{\text{vap}} H_m[\text{Fe}(\text{CO})_5](\text{l}) = 40.2 \text{ kJ mol}^{-1}$ [18]. The values of $D(\text{R}-\text{Mn}(\text{CO})_5)$ show that the $\eta^1\text{-C}_3\text{H}_5\text{-Mn}$ bond enthalpy contribution is similar to that of the $\text{C}_6\text{H}_5\text{CH}_2\text{-Mn}$ bond, and both are smaller than the simple σ -alkyl bond enthalpy contribution in $[(\text{CO})_5\text{Mn}-\text{CH}_3]$. Like the prop-2-enyl group, the benzyl group also has the capacity to bind to a metal in both η^1 and η^3 modes [19]. Measurements of the rate of thermal decarbonylation of $[\text{Mn}(\text{CO})_5(\eta^1\text{-C}_3\text{H}_5)]$ in decalin solvent have been reported [20], from which values of the activation parameters $\Delta H^\ddagger = (107.1 \pm 5.9) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = (-13.0 \pm 1.7) \text{ J K}^{-1} \text{ mol}^{-1}$ have been calculated. It was concluded that the irreversible $\eta^1 \rightarrow \eta^3$ conversion proceeds by a dissociative loss of CO to produce coordinatively unsaturated (16 electron) $[\text{Mn}(\text{CO})_4(\eta^1\text{-C}_3\text{H}_5)]$ which then isomerizes to the coordinatively saturated (18 electron) $[\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_5)]$. Collision induced dissociation (CID) threshold energies measured in a flowing after-glow-triple quadrupole apparatus and an estimate of the electron affinity, $EA[\text{Mn}(\text{CO})_4] \sim 2.4 \text{ eV}$ (231 kJ mol^{-1}) [21], provide an estimate of the dissociation energy



$D[(\text{CO})_4\text{Mn}-\text{CO}] = (168 \pm 20) \text{ kJ mol}^{-1}$ which is close to the measured value $(170 \pm 16) \text{ kJ mol}^{-1}$ for the corresponding reaction of the $[\text{Mn}(\text{CO})_5]^-$ ion [21]. Using this information enables us to calculate the bond enthalpy contribution $D[(\text{CO})_4\text{Mn}-(\eta^3\text{-C}_3\text{H}_5)] = 305 \text{ kJ mol}^{-1}$. This increase in the (prop-2-enyl)-Mn

bond enthalpy contribution from η^1 -coordination to η^3 -coordination is assisted by the gain of stabilisation energy of prop-2-enyl which has been estimated as $56 \pm 3 \text{ kJ mol}^{-1}$ [13] and the energy gain from the release of coordinated CO (translational entropy $\Delta S \sim 150 \text{ J K}^{-1} \text{ mol}^{-1}$) of $\sim 30 \text{ kJ mol}^{-1}$ at 493 K with reference to 298 K. This may be used to provide an estimate of the enthalpy contribution of the (η^2 -vinyl-Mn) bond enthalpy contribution $\sim 90 \text{ kJ mol}^{-1}$.

An alternative interpretation of the enthalpy of formation can be made by assuming total disruption of the complex. In the compounds under consideration the processes involved are:



giving, after substitution of the appropriate enthalpies of formation, $\Delta_f H_{m,\text{tot},\text{dis}}^\circ(9) = 576.8 \text{ kJ mol}^{-1}$ and $\Delta_f H_{m,\text{tot},\text{dis}}^\circ(10) = 578.3 \text{ kJ mol}^{-1}$. These enthalpies of total disruption can be divided between the enthalpy contributions of the bonds being broken, where a standard value for $D(\text{Mn}-\text{CO})$ in $[\text{Mn}(\text{CO})_5(\text{g})] = 88.9 \text{ kJ mol}^{-1}$ [12] is used, giving $D(\eta^1\text{-C}_3\text{H}_5\text{-Mn}) = 132 \text{ kJ mol}^{-1}$ and $D(\eta^3\text{-C}_3\text{H}_5\text{-Mn}) = (223 \pm 20) \text{ kJ mol}^{-1}$. The latter may be compared with the estimate of $D(\eta^3\text{-C}_3\text{H}_5\text{-Fe}) = (176 \pm 11) \text{ kJ mol}^{-1}$ in $[\text{Fe}(\text{CO})_3(\eta^3\text{-C}_3\text{H}_5)]$ [1].

Acknowledgements

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