THE ENTHALPIES OF THERMAL DECOMPOSITION OF IRON—OLEFIN COMPLEXES, AND THE STRENGTHS OF IRON—OLEFIN BONDS *

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Summary

From microcalorimetric studies at elevated temperatures, values were ob-tained for the enthalpies of thermal decomposition of [(ethylene)Fe(CO)$_4$] and of selected [(diene)Fe(CO)$_3$] and [(diene)$_2$Fe(CO)] compounds. Dibutadiene-iron carbonyl was found to decompose thermally on melting, and to give dimers and trimers of butadiene as products of decomposition. Dicyclohexa-dieneiron carbonyl gave dimeric cyclohexadiene as a product of decomposition. [(Butadiene)Fe(CO)$_3$] appeared to be thermally more stable than the [(buta-diene)$_2$Fe(CO)] complex. Measurements were also made of the enthalpies of sublimation (or of vaporization) of the complexes studied.

The thermal decomposition data yield values for the C$_2$H$_4$—Fe bond enthalpy contribution in [(C$_2$H$_4$)Fe(CO)$_4$] (23.1 kcal mol^{-1}, 96.7 kJ mol^{-1}), and for the average diene—Fe bond enthalpy contribution in selected [(diene)Fe(CO)$_3$] and [(diene)$_2$Fe(CO)] compounds (ca. 44 kcal mol^{-1}, 184 kJ mol^{-1}).

Introduction

Although numerous transition metal olefin complexes have been prepared and characterized, little is known of the thermochemistry of these compounds, or of the strengths of the olefin—metal bonds in them. Pettit and Barnes [1], and also Hartley [2] have reviewed the available data on the thermodynamics of forma-tion of olefin— and acetylene—metal complexes, most of which relate to equi-libria involved in the formation of complexes in solution. Direct calorimetric measurements were made by Partenheimer [3] in studies of a series of PdCl$_2$ complexes with bidentate olefin ligands, from which the relative strengths of different olefin—PdCl$_2$ bonds were obtained, but again these values refer to complexes in solution. Mortimer et al. [4,5] used differential scanning calori-metry to measure the heats of thermal dissociation of C$_2$F$_4$ from solid com-plexes of the type [ClIr(CO)(PPh$_3$)$_2$(C$_2$F$_4$)] and [ClPtCH$_3$(Me$_3$As)$_2$(C$_2$F$_4$)].

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* No reprints available.

The measured ΔH identify with C_2F_4—metal bond dissociation energies only in so far as the heats of sublimation of the solid reactants and solid products are identical, but no information is yet available in this regard. A study by Cramer [6] of the gas-phase pyrolysis of $[(C_5H_5)Rh(C_2H_4)_2]$ indicated that the bond strength of Rh—C_2H_4 is <31 kcal mol^{-1}, and a value of 33 kcal mol^{-1} was obtained by Tolman [7] for the bond strength of Ni—C_2H_4, from equilibrium studies of the reaction of ethylene with $[Ni(P(O-tol)_3]$ in solution. The present work reports on measurements of the enthalpies of formation of selected iron—olefin carbonyls, from which thermochemical bond-energy term values have been derived.

Experimental

Calorimeter

The Calvet twin-cell microcalorimeter (Setaram, Lyon), the drop calorimetric technique [8] and the calibration method [9] have been described previously.

Compounds

[(Ethylene)Fe(CO)$_4$] was prepared as described by Murdoch and Weiss [10]. We are indebted to the late Prof. Dr. E. Koerner von Gustorf for supplying pure samples of each of the following compounds, specifically for the present studies: (buta-1,3-diene)iron tricarbonyl, $[(C_4H_6)Fe(CO)_3]$, dibuta-1,3-diene-iron carbonyl, $[(C_4H_6)_2Fe(CO)]$, dicyclohexa-1,3-dieneiron carbonyl, $[(C_6H_8)_2Fe(CO)]$, (buta-1,3-diene)(diethylmuconate)iron carbonyl, $[(C_4H_6)$-$(C_{10}H_{14}O_4)Fe(CO)]$, (methylsorbate)iron tricarbonyl, $[(C_7H_{10}O_2)Fe(CO)_3]$, bis(methylsorbate)iron carbonyl, $[(C_7H_{10}O_2)_2Fe(CO)]$.

Auxiliary data

Heat quantities are given in calories, (or in kcal); 1 cal = 4.1840 J. The following heat of formation data (kcal mol^{-1}) were used in evaluating the results:
ΔH_f^0 (CO, g) [11] = -26.416 ± 0.4; ΔH_f^0 (C$_2$H$_4$,g) [12] = 12.45 ± 0.10;
ΔH_f^0 (buta-1,3-diene,g) [12] = 26.11 ± 0.15;
ΔH_f^0 (cyclohexa-1,3-diene,g) [12] = 25.38 ± 0.19;
ΔH_f^0 (I$_2$,g) [11] = 14.92 ± 0.01; ΔH_f^0 (Fe,g) [11] = 99.5 ± 1;
ΔH_f^0 (FeI$_2$,c) [11] = -27.0 ± 1.

To reduce ΔH values measured at elevated temperatures to 298 K, tabulated $(H_T - H_{298})$ data were taken from the JANAF Thermochemical Tables [13], from Stull, Westrum and Sinke [14], and from Hultgren, Orr, Anderson and Kelley [15].
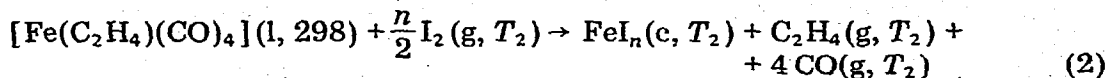
Results

(Ethylene)iron tetracarbonyl

The thermal decomposition in argon gas at 500 K appeared to be a very clean reaction, leading to the deposition of a bright metallic mirror on the walls of the reaction vessel. The measured ΔH_{500} values for the decomposition process (eq. 1) ranged from 53—55 kcal mol^{-1}; for the isothermal decomposition at

$$[Fe(C_2H_4)(CO)_4](l, 298) \rightarrow Fe(c, 500) + C_2H_4(g, 500) + 4\,CO(g, 500) \qquad (1)$$
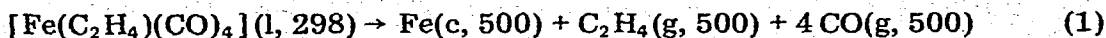
298 K, the mean value reduced to $\Delta H_{298} = 44.3$ kcal mol^{-1}.

Iodination studies were made over the temperature range 491—500 K, giving the results summarized in Table 1. The values ΔH are the measured enthalpy changes (evaluated from the recorded thermogram areas), corresponding to the molar enthalpies, ΔH_{obs}, for the reaction process

$$[Fe(C_2H_4)(CO)_4](l, 298) + \frac{n}{2}I_2(g, T_2) \rightarrow FeI_n(c, T_2) + C_2H_4(g, T_2) +$$
$$+ 4\,CO(g, T_2) \qquad (2)$$

where T_2 = calorimeter temperature. The solid product, FeI_n, consisted of FeI_2 admixed with small amounts of metal (deposited mainly on the inner walls of the capillary container). The gas-phase equilibrium in the $(C_2H_4 + I_2)$ system has been studied by Benson and Amano [16], from which it was shown that $C_2H_4I_2$ is almost completely dissociated at temperatures approaching 500 K. The values ΔH^* were obtained from ΔH_{obs} by removing the exothermic contribution due to the iodination reaction

$$Fe(c, T_2) + \frac{n}{2}I_2(g, T_2) \rightarrow FeI_n(c, T_2) \qquad (3)$$

where $FeI_n \equiv \frac{n}{2}FeI_2 + (1 - \frac{n}{2})Fe$. Using the given auxiliary data, these adjustments were $\Delta H^* = \Delta H_{obs} + 20.51\,n$ ($T_2 = 491$ K) and $\Delta H^* = \Delta H_{obs} + 20.49\,n$ ($T_2 = 500$ K). The values ΔH_{298}^* relate to the isothermal decomposition process at 25°C, i.e.

$$[Fe(C_2H_4)(CO)_4](l, 298) \rightarrow Fe(c, 298) + 4\,CO(g, 298) + C_2H_4(g, 298) \qquad (4)$$
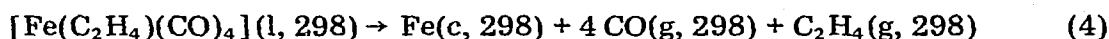
The uncertainty attached to the mean value, $\Delta H_{298}^* = 46.0$ kcal mol^{-1} is estimated at ±2 kcal mol^{-1}.

Dibutadieneiron carbonyl

Dibutadieneiron carbonyl decomposes rapidly at temperatures above the melting point (ca. 130°C), depositing iron in the form of a fine black powder. Figure 1 shows a typical decomposition thermogram, obtained by dropping a sample (4.36 mg) into the hot reaction cell (argon-filled) at 145°C. The initial endotherm (recording the heating and melting of the sample) is seen to turn sharply to become a pronounced exotherm, thereafter returning gradually to the baseline.

TABLE 1

IODINATION OF $[Fe(C_2H_4)(CO)_4]$

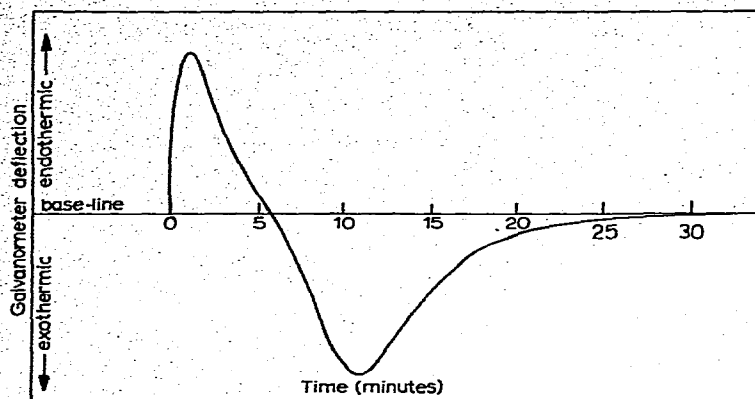| Expt.	$[Fe(C_2H_4)(CO)_4]$ (mg)	I_2 (mg)	Δh (cal)	T_2 (K)	n	ΔH_{obs} (kcal mol^{-1})	ΔH^* (kcal mol^{-1})	ΔH_{298}^* [a] (kcal mol^{-1})
1	3.120	8.90	0.344	491	1.55	21.6	53.4	44.3
2	5.405	8.61	0.558	500	1.70	20.2	55.0	45.4
3	4.040	9.25	0.483	500	1.65	23.4	57.2	47.6
4	3.210	8.93	0.347	500	1.77	21.2	57.4	47.8
5	1.235	10.83	0.100	491	1.85	15.9	53.8	44.7

[a] Mean $\Delta H_{298}^* = 46.0$ kcal mol^{-1}.

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Fig. 1. Thermal decomposition of [Fe(C$_4$H$_6$)$_2${CO)] at 418 K.

Visual examination of the reaction vessel after removal from the calorimeter showed a black powder deposited within the capillary tube container, and on the wall near to the neck of capillary, but there was no formation of a metallic mirror. Liquid droplets had condensed on the walls within the reaction vessel, and in the inlet tube. Mass spectroscopic analysis of the liquid product indicated the presence of oligomers of butadiene including dimer (C$_8$H$_{12}$), trimer (C$_{12}$H$_{18}$), and (possibly) traces of tetramer (C$_{16}$H$_{24}$). Thermal decomposition apparently occurs in the liquid phase, and is probably assisted by the dimerization (and trimerization) of butadiene ligands as they detach from the iron. The exotherm in Fig. 1 reflects the fact that polymerization of butadiene occurs, following melting of the sample. At temperatures just below the melting-point, thermal decomposition was not observed and it was possible to vacuum sublime the entire sample from the reaction vessel at 399—400 K without any visible signs of decomposition. A typical vacuum-sublimation thermogram is shown in Fig. 2. The thermal decomposition and vacuum sublimation results over the range 399—439 K are summarized in Table 2.

TABLE 2

THERMAL DECOMPOSITION OF [Fe(C$_4$H$_6$)$_2$CO]

Expt.	mass [Fe(C$_4$H$_5$)$_2$-CO] (mg)	T (K)	ΔH_{obs} (kcal mol^{-1})	ΔH_{298} (kcal mol^{-1})
1 [a]	3.920	399	24.6	18.6
2 [a]	4.120	400	23.6	17.8
				Mean=18.2
3	3.900	418	— 9.6	—16.5
4	4.360	418	—13.9	—20.8
5	3.975	418	—13.6	—20.5
6	4.200	423	—13.3	—20.5
7	3.790	439	— 8.6	—16.9
				Mean = —19.0

[a] Vacuum sublimation: no thermal decomposition observed.
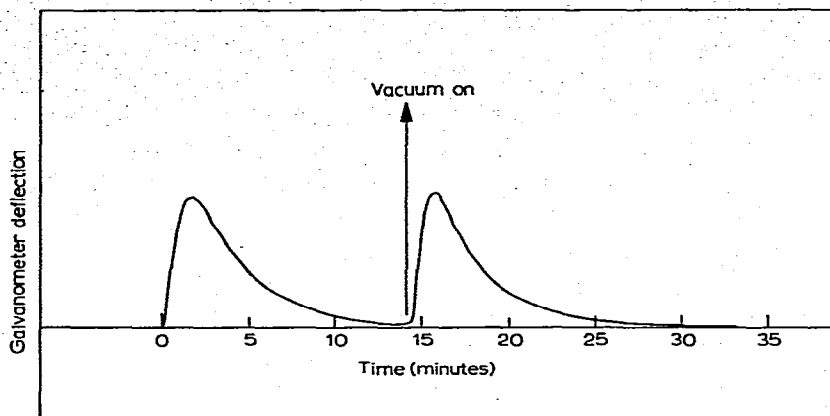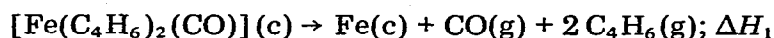
Fig. 2. Sublimation of $[Fe(C_4H_6)_2(CO)]$ at 400 K.

The mean ΔH_{298} (Table 2) for overall decomposition may be regarded as the sum of an endothermic contribution, ΔH_1, from the idealized decomposition:

$$[Fe(C_4H_6)_2(CO)](c) \rightarrow Fe(c) + CO(g) + 2\,C_4H_6(g); \Delta H_1$$

and an exothermic contribution, ΔH_2, from polymerization of butadiene, $2\,C_4H_6(g) \rightarrow polymer(g)$. Dimerization reactions, (e.g. $2\,C_4H_6(g) \rightarrow$ cyclooctadiene(g), and $2\,C_4H_6(g) \rightarrow$ vinylcyclohexene(g)), require that $\Delta H_2 \approx -36$ kcal mol^{-1} of dimer formed. Trimerization reactions could lead to significantly more negative values for ΔH_2, (e.g. for the trimerization $3\,C_4H_6(g) \rightarrow$ bicyclohexenyl-(g), ΔH may be estimated * at ~ -84 kcal, corresponding to $\Delta H_2 \sim -56$ kcal for the reaction $3\,C_4H_6(g) \rightarrow C_{12}H_{18}(g)$), but others (e.g. $3\,C_4H_6(g) \rightarrow$ cyclododecatriene(g)) have ΔH_2 values near to -36 kcal. Higher oligomer formation would give more negative values ($\Delta H_2 < -36$ kcal) since the high boiling-point products remain in condensed states at the calorimeter temperature used. Product analysis indicated both dimers and trimers in appreciable quantities, with some evidence for the presence of higher oligomers. For dimers as the sole product ($\Delta H_2 \sim -36$ kcal), the measured $\Delta H_{298} = -19 \pm 2$ kcal mol^{-1} would require $\Delta H_1 = 17$ kcal mol^{-1}. For trimers as sole product ($\Delta H_2 \leqslant -56$ kcal), ΔH_1 increases and may reach values as high as 37 kcal mol^{-1}.

The catalytic oligomerization of butadiene by $[Fe(C_4H_6)_2(CO)]$ in solution at 100°C has been investigated by Buchkremer [17]. The products included dimers (4-vinylcyclohexene, cyclooctadiene), trimers, and higher oligomers. In cyclohexane solvent, the higher oligomer fraction (average mol. wt. 616, corresponding to $(C_4H_6)_{11}$) accounted for 55% of the butadiene converted; the dimer fraction consumed 19% and the trimer fraction 13%. The relative amounts of each fraction varied from solvent to solvent.

Thermograms obtained by dropping $[Fe(C_4H_6)_2(CO)]$ into iodine vapour at temperatures in the range 487—505 K were entirely exothermal. The measured ΔH_{obs} were more negative the larger the excess of iodine used. The products

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* Using H_f^0(cyclohexylcyclohexane, l) $= -78.7$ kcal mol^{-1} [12], and assuming that the enthalpy of hydrogenation of bicyclohexyl is twice that of cyclohexene.

of reaction were a black powder (FeI$_2$), some metallic iron (mirror), and droplets of brown-red liquid (butadiene polymer + dissolved iodine). It seems probable that the initial thermal disruption leads to formation of butadiene dimer, and that this may add on iodine, or polymerize further, in the presence of a sufficient excess of iodine vapour. Measurements made with a limited excess iodine (possibly thereby reducing the polymerization of butadiene beyond the dimer stage) led to values $\Delta H_{298}^{\star} \sim -4$ kcal mol^{-1} (after correction for formation of FeI$_2$); assuming dimer formation ($\Delta H_2 = -36$ kcal), this gives $\Delta H_1 \sim 32$ kcal mol^{-1}, corresponding to $\Delta H_f^{\circ}[Fe(C_4H_6)_2(CO),c] \sim -6.2$ kcal mol^{-1}. Preliminary results obtained by Dr. G. Pilcher for the heat of combustion of $[Fe(C_4H_6)_2(CO)]$ indicate that the enthalpy of formation is less negative than -12 kcal mol^{-1}, and near to -9 kcal mol^{-1}.

Butadieneiron tricarbonyl

Thermal decomposition studies over the range 485—534 K gave endothermic thermograms, showing only slight exothermic tailing. Metal deposited as a diffuse grey film on the walls of the reaction vessel, often extending into the exit tube. The measured ΔH_{obs} ranged from 25—30 kcal mol^{-1}, corresponding to $\Delta H_{298} = 15$—18 kcal mol^{-1}; this is almost certainly less than the true value for the clean decomposition, $[Fe(C_4H_6)(CO)_3](l) \rightarrow Fe(c) + 3\ CO(g) + C_4H_6(g)$, due to surface side-reactions, including polymerization, of the liberated butadiene on the active metal deposits.

Iodination studies over the range 450—520 K gave thermograms which frequently showed extensive exothermic tailing following the initial endotherm. Tailing was significantly reduced by limiting the excess of iodine present ($I_2/C_4H_6 > 2$, but < 3). The tailing was primarily due to polymerization and/or iodination of liberated butadiene, as evidenced by the occasional formation of sticky film on the capillaries and wall of the reaction vessel. A measured ΔH_{obs} (Table 3) is accordingly based on the endothermal part of the total thermogram, presumed to refer to the primary reaction,

$$[Fe(C_4H_6)(CO)_3](l, 298) + \frac{n}{2}I_2(g, T_2) \rightarrow FeI_n(c, T_2) + 3\ CO(g, T_2) + C_4H_6 - (g, T_2) \quad (5)$$
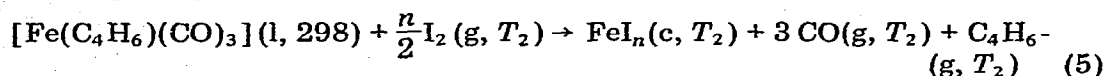
The asterisked experiments listed in Table 3 gave essentially endothermic thermograms, for which the corrections for 'tailing' were small.

TABLE 3

IODINATION OF [(C$_4$H$_6$)Fe(CO)$_3$]

Expt.	I$_2$ mass (mg)	[(C$_4$H$_6$)Fe-(CO)$_3$] (mg)	T (K)	n	ΔH_{obs} (kcal mol^{-1})	$\Delta H^{\star}$ (kcal mol^{-1})	$\Delta H_{298}^{\star a}$ (kcal mol^{-1})
1	10.29	2.965	502	2.0	12.3	53.3	42.8
2	10.70	3.855	502	1.98	14.4	55.0	44.5
3*	10.90	5.365	503	1.97	15.9	56.3	45.8
4*	7.275	3.205	503	2.0	16.0	57.0	46.5
5	9.96	4.32	503	1.93	15.8	55.3	44.8
6	9.165	1.960	507	1.95	13.0	53.0	42.3

a Mean $\Delta H_{298}^{\star} = 44.5$ kcal mol^{-1}.

Vacuum sublimation measurements [18] on [Fe(C$_4$H$_6$)(CO)$_3$] were made at 391 K and 432 K; the liquid evaporated without decomposition at these temperatures. From the mean of three measurements, corrected to 298 K, ΔH_{vap} = 11.7 ± 0.5 kcal mol^{-1}.

Dicyclohexa-1,3-dieneiron carbonyl

Vacuum sublimation measurements were made at 402 K and at 414 K. The crystals sublimed without decomposition at the lower temperature, but at 414 K some decomposition occurred and a metallic mirror formed in the capillary tube container, although the majority of the sample managed to sublime unchanged. From the measurements at 402 K, corrected to 298 K, ΔH_{sub} = 22.7 ± 0.5 kcal mol^{-1}.

Thermal decomposition measurements were made at 417 K and at 505 K; the thermograms were entirely endothermal, without significant tailing. Metal was deposited mainly as a grey film on the walls of reaction vessel, and some black powder remained in, and near to the capillary tube container. Oily drops of liquid condensed in the exit tube, and on the walls of the reaction vessel; mass spectroscopic analysis of the liquid indicated products based on the dimer of cyclohexadiene (m/e = 162, 160, 156), but there was little or no evidence of trimeric species.

The measurements at 505 K gave values ΔH ~26 kcal mol^{-1}, corresponding to ΔH_{298} ~11 kcal mol^{-1}, for the decomposition process at 25°C. The enthalpy of the dimerization reaction 2 C$_6$H$_8$(g) → C$_{12}$H$_{16}$(g) may be estimated from available thermochemical data *, ΔH ~—30.5 kcal mol^{-1}; assuming dicyclohexadiene to be the major product of thermal decomposition, the measured ΔH_{298} ~11 kcal mol^{-1} corresponds to ΔH_{298} ~41.5 kcal mol^{-1} for the direct disruption process

$$[Fe(C_6H_8)_2 CO] (c) \rightarrow Fe(c) + CO(g) + 2 C_6H_8(g) \qquad (6)$$
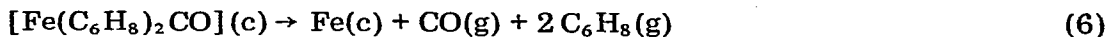
Iodination studies, at 503 K gave rise to entirely exothermal thermograms. The iodine balance indicated appreciable attack by iodine on the liberated cyclohexadiene. A typical iodination gave solid product analysing as FeI$_{1.44}$, and the iodine balance was consistent with formation of C$_{12}$H$_{16}$I$_2$; the measured ΔH_{503} ~—13 kcal mol^{-1}, corrected for the exothermic contributions from the formation of FeI$_2$, dimerization of C$_6$H$_8$ and iodination of dimer, led to ΔH_{298} ~44 kcal mol^{-1} for the disruption process (eq. 6).

(Butadiene)(diethylmuconate)iron carbonyl

Thermal decomposition measurements at 473 K gave rise to entirely endothermic thermograms. There was no formation of metallic mirror; the iron depositing as a black powder in the capillary tube container, and on the wall of the reaction vessel near the neck of the capillary. Oily liquid droplets condensed on the walls of the reaction vessel and in the exit tube. Mass spectral analysis of the liquid indicated the presence of butadiene dimer; there was also evidence (m/e = 254, 282, 310) for [(diethylmuconate)Fe(CO)$_3$], suggesting that thermal decomposition was not complete at 473 K. At higher temperatures

* $\Delta H_f^°$(dicyclohexadiene, l) = 6.3 ± 1.7 kcal mol^{-1} [12], and ΔH_{vap} ~14 kcal mol^{-1} (estimate).

(527—533 K), the decomposition thermograms showed pronounced exothermal tailing, following the initial endothermal peak.

The measurements at 473 K gave $\Delta H_{obs} = 21.7 \pm 1$ kcal mol^{-1}; on reduction (approximate only) to 298 K, $\Delta H_{298} \sim 3.3$ kcal mol^{-1}. This value is probably low, in view of the incomplete decomposition at 473 K. The higher temperature thermograms, interpreted in terms of their endothermal parts only, gave $\Delta H_{obs} = 34 \pm 2$ kcal mol^{-1}, reducing to $\Delta H_{298} \sim 8$ kcal mol^{-1}. Assuming this to apply to a primary thermal decomposition yielding dimeric products (e.g. butadiene dimer), the idealized decomposition (eq. 7) is estimated to have $\Delta H_{298} \sim 44$ kcal mol^{-1}.

$$[(C_{10}H_{14}O_4)(C_4H_6)Fe(CO)](c) \rightarrow C_{10}H_{14}O_4(g) + C_4H_6(g) + CO(g) + Fe(c) \quad (7)$$
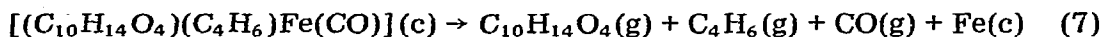
Vacuum sublimation measurements were made at 391 K and at 403 K; the mean value, $\Delta H_{391} = 35.0$ kcal mol^{-1} reduces (approximate only) to ΔH_{298}(sub) $\sim 26.0 \pm 1$ kcal mol^{-1}.

Bis(methylsorbate)iron carbonyl

Thermal decomposition studies at 473 K gave rise to endothermic thermograms; metal, which deposited on the wall of the reaction vessel and in the capillary tube container, resembled black paint, and there was no mirror formation. Oily liquid drops condensed in the exit tube and in the reaction vessel. Mass spectral analysis of the liquid indicated methyl sorbate; other peaks ($m/e = 266, 238, 210, 182$) can be attributed to $[Fe(C_7H_{10}O_2)(CO)_3]$, so that normal thermal decomposition was not complete at 473 K. Peaks at m/e 238, 220 and 208 can be ascribed to products arising from methylsorbate dimer, but the parent peak ($m/e = 252$) was very weak. The mean ΔH_{obs} (6 measurements) was 22.7 ± 1 kcal mol^{-1}; on reduction (approximate only) to 298 K, ΔH_{298} ~ 6.2 kcal mol^{-1}, but this value is too low, thermal decomposition being incomplete. Thermal decomposition studies at higher temperatures (513 K, 521 K) gave endothermic thermograms with slight exothermic tailing. The mean ΔH_{obs} at 513 K (30.7 ± 0.5 kcal mol^{-1}) corresponds to ΔH_{298} ~ 9.5 kcal mol^{-1}. Assuming dimerization of the methyl sorbate to take place on thermal decomposition, and that the enthalpy of dimerization is the same as for dimerization of butadiene, the idealized decomposition (eq. 8) has ΔH_{298} ~ 45.5 kcal mol^{-1}.

$$[(C_7H_{10}O_2)_2FeCO](c) \rightarrow 2\,C_7H_{10}O_2(g) + CO(g) + Fe(c) \quad (8)$$
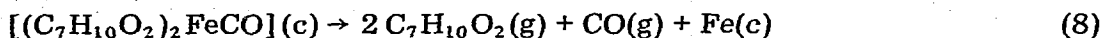
Vacuum sublimation measurements were made at 414 K, $\Delta H_{414} = 38.4 \pm 0.5$ kcal mol^{-1}, reducing to ΔH_{298}(sub) ~ 28.2 kcal mol^{-1} at 298 K.

(Methylsorbate)iron tricarbonyl

Thermal decomposition studies at 474 K gave endothermic thermograms, which returned only slowly to the base-line. At 512 K, the thermograms were entirely endothermic, showing no tailing, and gave ΔH_{512} ~ 45 kcal mol^{-1} for the thermal decomposition reaction. The metal was deposited as a black powder, no mirror being formed; some liquid drops condensed on the walls of the reaction vessel.

Iodination studies were made over the range 489—512 K. The thermograms resembled those given on iodination of butadieneiron tricarbonyl, each show-

TABLE 4

IODINATION OF (METHYLSORBATE)IRON TRICARBONYL

Expt.	$[(C_7H_{10}O_2)\text{-}Fe(CO)_3]$ (mg)	I_2 (mg)	T (K)	n	ΔH_{obs} (kcal mol^{-1})	ΔH^{*} (kcal mol^{-1})	ΔH^{*}_{298} ^{a} (kcal mol^{-1})
1	4.870	6.770	489	1.39	23.0	51.5	38.3
2	5.055	8.895	489	1.58	23.2	55.6	42.4
3*	4.755	6.660	502	1.29	31.3	57.8	43.6
4	5.195	6.935	512	1.20	29.8	54.4	39.4

^{a} Mean ΔH^{*}_{298} = 40.9 kcal mol^{-1}.

ing an initial endotherm, followed by an exothermic tail. They were interpreted by rejecting the tailing as due to side-reactions (iodination, polymerization) of the liberated methylsorbate. Results are summarized in Table 4; in one case (asterisked) the tailing correction was small, and much less than in the others. Vacuum sublimation measurements at 395 K gave ΔH_{395} ~23.3 kcal mol^{-1}, reducing to ΔH_{298}(vap) ~17.3 kcal mol^{-1}.

Discussion

The thermal decomposition studies have revealed significant differences in the decomposition patterns of olefin-iron-carbonyl complexes. Only one of the compounds studied (ethylene iron tetracarbonyl) decomposed cleanly, depositing a bright metallic mirror on the walls of the reaction vessel. Diffuse mirrors were deposited from [(butadiene)Fe(CO)$_3$] and some mirror formation was also seen on decomposition of [(cyclohexadiene)$_2$Fe(CO)]. The other compounds studied deposited iron as a black powder, and/or a sticky paint. The bis(diene)iron monocarbonyls appeared to decompose (on melting) in the liquid state, and the products included dimers and higher oligomers of the dienes. On the other hand, (butadiene)- and (methylsorbate)-iron tricarbonyls melt without decomposition near room temperature, and remain stable as liquids at temperatures below ca. 500 K.

The interpretation of the measured heats of thermal decomposition, ΔH_{obs}, is straightforward for [Fe(C$_2$H$_4$)(CO)$_4$], but less so for the other compounds. The difficulties arise from side-reactions, including polymerization, of the dienes following disruption of the iron—ligand bonds. The important assumption made here is that the thermal decomposition of bis(diene) complexes is assisted by the cooperative dimerization of the dienes in the primary disruption process; the same assumption was made in interpreting the heats of iodination of [(diene)$_2$Fe(CO)] (diene = butadiene, cyclohexa-1,3-diene).

The results of the present studies are summarized in Table 5. The values $\Delta H^{298}_{dec.}$ refer to the reactions 9a and 9b where L = diene. The values $\Delta H^{298}_{disrupt}$ refer

$$FeL(CO)_3(l) \rightarrow Fe(c) + L(g) + 3\,CO(g) \tag{9a}$$
$$FeL_2(CO)(c) \rightarrow Fe(c) + 2\,L(g) + CO(g) \tag{9b}$$

to the corresponding gaseous reactions 10a and 10b and measure the sum total

TABLE 5

OLEFIN—IRON BOND ENTHALPY CONTRIBUTIONS

Compound	ΔH_{sub}^{298} (kcal mol^{-1})	$\Delta H_{dec.}^{298}$ (kcal mol^{-1})		$\Delta H_{disrupt.}^{298}$ (kcal mol^{-1})	ΔH^{298} (per diene—Fe (kcal mol^{-1})
[(C$_2$H$_4$)Fe(CO)$_4$] liq.	[10.0 ^{a}]e	T.D.	44.3		
		Iod.	46.0	135.5	23.1 ^{c}
[(C$_4$H$_6$)Fe(CO)$_3$] liq.	11.7 ^{a}	T.D.	18		
		Iod.	44.5	132.3	48.0
[(C$_7$H$_{10}$O$_2$)Fe(CO)$_3$] liq.	17.3 ^{a}	T.D.	>30		
		Iod.	40.9	123.1	38.8
[(C$_6$H$_8$)$_2$FeCO] c.	22.7	T.D.	41.5	118.3	45.1
		Iod.	44	120.8	46.3
[(C$_{10}$H$_{14}$O$_4$)(C$_4$H$_6$)FeCO] c.	26.0	T.D.	44	117.5	44.6
[(C$_7$H$_{10}$O$_2$)$_2$FeCO] c.	28.2	T.D.	45.5	116.8	44.4
[(C$_4$H$_6$)$_2$FeCO] c.	18.2	T.D.	>17 <37	<118.3	<45.0
		Iod.	32	113.3	42.6
		Comb.	35 ^{b}	116.3	44.0

^{a} ΔH_{vap}^{298} : e = estimate. ^{b} Preliminary value. ^{c} Olefin—Fe bond enthalpy contribution.

$$FeL(CO)_3(g) \rightarrow Fe(g) + L(g) + 3\,CO(g) \qquad (10a)$$
$$FeL_2(CO)(g) \rightarrow Fe(g) + 2\,L(g) + CO(g) \qquad (10b)$$

of the binding enthalpy contributions from the iron—ligand bonds in the molecules concerned. The bond enthalpy contribution of Fe—CO has been previously evaluated [19] at 28.1 kcal mol^{-1}, and this same value was used in obtaining the bond enthalpy contributions listed in the final column of Table 5.

The value $\Delta H_{dec.}^{298}$ = 46.0 ± 2 kcal mol^{-1} (Table 1) for [(C$_2$H$_4$)Fe(CO)$_4$] (l) corresponds to ΔH_f^o = —139.2 ± 2 kcal mol^{-1} (—528.4 ± 9 kJ mol^{-1}) for the standard heat of formation at 298 K of the liquid. The $\Delta H_{dec.}^{298}$ values for the (diene)iron carbonyls listed in Table 5 are subject to experimental uncertainty of similar order (2—3 kcal mol^{-1}), and to additional uncertainty arising from assumptions made in interpretation of the thermograms. Using selected $H_{dec.}^{298}$ values from Table 5, 44.5 kcal mol^{-1} (for [(C$_4$H$_6$)Fe(CO)$_3$] (l)); 32 kcal mol^{-1} (for [(C$_4$H$_6$)$_2$Fe(CO)] (c)); and 42 kcal mol^{-1} (for [(C$_6$H$_8$)$_2$Fe(CO)] (c)); the derived ΔH_f^o values at 298 K are —8.6 kcal mol^{-1} (—36.1 kJ mol^{-1}), —6.2 kcal mol^{-1} (—25.9 kJ mol^{-1}), and —17.65 kcal mol^{-1} (—73.9 kJ mol^{-1}) respectively.

The average value of the diene—Fe bond enthalpy contribution (Table 5) is ca. 44 kcal mol^{-1}, which is slightly less than double that of ethylene—Fe in [Fe(C$_2$H$_4$)(CO)$_4$]. The conjugated dienes thus appear to bond to iron as if the two C=C bonds were largely independent of one another. The C$_2$H$_4$—Fe bond enthalpy contribution is smaller than that from Fe—CO (Fe—C$_2$H$_4$/Fe—CO ~0.82), and compares in this respect with Rh—C$_2$H$_4$ (Rh—C$_2$H$_4$/Rh—CO ~0.72 [6.20]) and with Ni—C$_2$H$_4$ (Ni—C$_2$H$_4$/Ni—CO ~0.94 [7]). The diene—Fe bond enthalpy contribution may be compared with the value of 71 kcal mol^{-1} recently reported by Tel'noi et al. [21] for the C$_5$H$_5$—Fe bond enthalpy contribution in ferrocene. The same authors report [21] 68 kcal mol^{-1} for the (C$_5$H$_5$—Cr) contribution in chromocene, which may be compared with the (C$_6$H$_6$—Cr) bond enthalpy contribution in [Cr(C$_6$H$_6$)$_2$] which has been evaluated at 39 kcal mol^{-1} [8,18,22].

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