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THERMOCHEMISTRY OF ARENE CHROMIUM TRICARBONYLS AND THE STRENGTHS OF ARENE—CHROMIUM BONDS

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Summary

From microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and of iodination, values of the standard enthalpies of formation of the following arene chromium tricarbonyl compounds were determined: $\Delta H_f^\circ[(\eta\text{-}C_6H_5Me)Cr(CO)_3,c] = -114 \pm 1.5$ kcal mol^{-1} (-476 ± 6 kJ mol^{-1}), $\Delta H_f^\circ[(\eta\text{-}1,3,5\text{-}C_6H_3Me_3)Cr(CO)_3,c] = -136.5 \pm 2$ kcal mol^{-1} (-571 ± 8 kJ mol^{-1}), $\Delta H_f^\circ[(\eta\text{-}C_6H_5Cl)Cr(CO)_3,c] = -111.5 \pm 5$ kcal mol^{-1} (-467 ± 21 kJ mol^{-1}).

A microcalorimetric vacuum sublimation technique is described, from which enthalpies of sublimation, ΔH_{sub} (298°K), were obtained for benzoic acid, 2-, 3- and 4-chlorobenzoic acids, anthracene, $Cr(CO)_6$, $W(CO)_6$, $[C_6H_6Cr(CO)_3]$, $[(C_6H_5Me)Cr(CO)_3]$, $[(1,3,5\text{-}C_6H_3Me_3)Cr(CO)_3]$, $[C_6Me_6Cr(CO)_3]$, $[(C_6H_5Cl)\text{-}Cr(CO)_3]$, and $[(cyclo\text{-}C_7H_8)Cr(CO)_3]$. Values are derived for arene—Cr bond enthalpy contributions in a series of $[(arene)Cr(CO)_3]$ molecules in the gas phase: these decrease along the series $(C_6Me_6\text{—}Cr) \gg (C_6H_3Me_3\text{—}Cr) > (C_6H_5\text{-}Me\text{—}Cr) \approx (C_6H_6\text{—}Cr) > (C_6H_5Cl\text{—}Cr) > [(cyclo\text{-}C_7H_8)\text{—}Cr]$.

Introduction

Measurements of the standard enthalpies of formation, ΔH_f° (c), of a few selected arene chromium tricarbonyls, (arene = benzene, toluene and hexamethylbenzene) have been previously reported [1]. The measured values were combined with estimated heats of sublimation to obtain ΔH_f° (g) values, from which the enthalpies of disruption:

$$(Arene)Cr(CO)_3\ (g) \rightarrow Arene\ (g) + 3\ CO\ (g) + Cr\ (g)$$

were calculated. These studies indicated that hexamethylbenzene is more strongly bonded to the $Cr(CO)_3$ moiety than is either benzene or toluene.

The present studies have extended the earlier investigation to include [(1,3,5-$C_6H_3Me_3$)Cr(CO)$_3$] and [(C_6H_5Cl)Cr(CO)$_3$]. Measurements are also reported of the enthalpies of sublimation of these, and other arene chromium tricarbonyls. The iodination of [C_6H_6Cr(CO)$_3$] and [(C_6H_5Me)Cr(CO)$_3$] was re-examined, confirming the previous value for $\Delta H_f^\circ[C_6H_6Cr(CO)_3, c]$, and slightly modifying that for [($C_6H_5CH_3$)Cr(CO)$_3$].

Experimental

Calorimeter

The thermal measurements were made with the Calvet high temperature twin-microcalorimeter (Setaram, Lyon) using the drop-calorimetric technique [2]. Thermal decomposition and iodination studies followed the same procedure as in previous studies [1,3,4], but the use of the microcalorimeter for measuring enthalpies of sublimation is novel, and is described separately later.

Compounds

Pure samples of 2-, 3-, and 4-chlorobenzoic acids were supplied to us by Prof. H.O. Pritchard. Benzoic acid was "Analar"; resublimed commerical samples of anthracene (Eastman Kodak), chromium and tungsten hexacarbonyls, and (toluene)chromium tricarbonyl (Strem Chemicals, Inc.) were used. Samples of (benzene)chromium tricarbonyl [5], (mesitylene)chromium tricarbonyl [6], (hexamethylbenzene)chromium tricarbonyl [6], (chlorobenzene)chromium tricarbonyl [7] and (cycloheptatriene)chromium tricarbonyl [8] were prepared as described in the given references, purified by fractional sublimation in vacuo, and stored under nitrogen.

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 present results:

$\Delta H_f^\circ(CO,g) = -26.416 \pm 0.04$ [9]; $\Delta H_f^\circ(\text{mesitylene},g) = -3.81 \pm 0.33$ [10]
$\Delta H_f^\circ(I_2,g) = 14.92 \pm 0.01$ [9]; $\Delta H_f^\circ(\text{biphenyl},g) = 43.53 \pm 0.6$ [10]
$\Delta H_f^\circ(Cr,g) = 94.8 \pm 1$ [9]; $\Delta H_f^\circ(\text{chlorobenzene},g) = 12.21 \pm 0.16$ [10]
$\Delta H_f^\circ(CrI_3,c) = -49.0 \pm 1$ [9]; $\Delta H_f^\circ(CrCl_2,c) = -95 \pm 1$ [9]
$\Delta H_f^\circ(CrI_2,c) = -37.5 \pm 1$ [9];

To reduce ΔH_T values to ΔH_{298}, tabulated $(H_T - H_{298})$ data from the following sources were used:
I_2(g) [11]; CO(g) [11]; mesitylene(g) [11]; biphenyl(g) [11]; chlorobenzene(g) [11]; benzoic acid(g) [11]; $CrCl_2$(c) [12]; Cr(c) [13]; Cr(CO)$_6$(g) [14]; W(CO)$_6$(g) [14].

Results

(Mesitylene)chromium tricarbonyl, [$C_9H_{12}Cr(CO)_3$]

The iodination of (mesitylene)Cr(CO)$_3$ was studied in the calorimeter at 235°C. The solid product was a black powder, which analysed as CrI$_n$, with n =

TABLE 1

IODINATION OF (MESITYLENE)CHROMIUM TRICARBONYL AT 508 K

Expt.	$(C_9H_{12})Cr(CO)_3$ (mg)	I_2 (mg)	Δh (cal)	ΔH_{obs} (kcal mol^{-1})	n	ΔH^*_{obs} (kcal mol^{-1})	ΔH^*_{298} (kcal mol^{-1})
1	4.360	12.190	0.032	1.9	2.84	69.5	54.0
2	3.955	11.955	0.035	2.3	2.76	68.4	52.9
3	4.430	11.500	0.042	2.4	2.65	66.5	51.0
4	4.045	11.920	0.121	7.7	2.58	70.4	54.9
5	4.240	12.300	0.067	4.1	2.72	69.5	54.0

Mean $\Delta H^*_{298} = +53.4$ kcal mol^{-1}.

2.5—2.8. The liquid formed appeared to be unchanged mesitylene; separate measurements (made by dropping mesitylene samples into iodine/argon at 240 °C) showed that the mixing of the vapours is virtually thermoneutral. The measured reaction enthalpies, Δh, (determined from the thermogram areas) correspond to molar enthalpies, ΔH_{obs}, for the calorimetric process:

$$C_9H_{12}Cr(CO)_3(c,298\ K) + \frac{n}{2} I_2(g,508\ K) \rightarrow CrI_n(c,508\ K) + 3CO(g,508\ K) + C_9H_{12}(g,508\ K) \quad (1)$$

The experimental results are summarized in Table 1.

The values ΔH^*_{obs} refer to the thermal decomposition process:

$$C_9H_{12}Cr(CO)_3(c,298\ K) \rightarrow Cr(c,508\ K) + 3CO(g,508\ K) + C_9H_{12}(g,508\ K) \quad (2)$$

and were obtained from ΔH_{obs} by removing the exothermic contribution [1] from the iodination $Cr(c,508\ K) + \frac{n}{2} I_2(g,508\ K) \rightarrow CrI_n(c,508\ K)$. The values ΔH^*_{298} for the isothermal decomposition process were obtained by reducing the ΔH^* to 298 K. The overall uncertainty attached to the mean ΔH^*_{298} value is estimated at ± 2 kcal mol^{-1}.

(Chlorobenzene)chromium tricarbonyl, [$(C_6H_5Cl)Cr(CO)_3$]

Thermal decomposition studies were made over the temperature range 214-231°C. The products of decomposition were a black powder (which formed within, and near the neck of the capillary tube container), and a crop of colorless crystals, some of which condensed in the cooler parts of the exit-tube, well removed from the reaction vessel. A few yellow crystals were noticed in the

TABLE 2

THERMAL DECOMPOSITION OF $(C_6H_5Cl)Cr(CO)_3$

Expt.	$(C_6H_5Cl)Cr(CO)_3$ (mg)	Δh (cal)	T (K)	ΔH_{obs} (kcal mol^{-1})	ΔH_{298} (kcal mol^{-1})	ΔH^o_f (kcal mol^{-1})
1	5.681	0.317	487	13.9	2.8	—107.8
2	3.963	0.216	490	13.5	2.3	—107.3
3	3.910	0.191	490	12.2	1.0	—106.0
4	4.595	0.276	503	14.9	2.8	—107.8

exit-tube; no more than traces of liquid products were visible. Mass spectroscopic analysis of the products (dissolved in ether) clearly indicated biphenyl as a main product; other peaks indicated traces of chlorobenzene (*m/e* 112/114) and of $Cr(CO)_6$ (*m/e* 220/108/80).

The thermal decomposition results are summarized in Table 2. To interpret the observed ΔH, it was assumed that the decomposition approximated to:

$$(C_6H_5Cl)Cr(CO)_3(c,298) \rightarrow ½C_6H_5{\cdot}C_6H_5(g,T) + 3CO(g,T) + CrCl(c,T) \qquad (3)$$

and that $CrCl \equiv ½(Cr + CrCl_2)$. The values $\Delta H_f^\circ(c)$ in the final column were calculated from the corresponding thermochemical equation:

$$\Delta H_f^\circ(C_6H_5ClCr(CO)_3,c) = ½\Delta H_f^\circ(C_{12}H_{10},g) + 3\Delta H_f(CO,g) + ½\Delta H_f^\circ(CrCl_2,c) - \Delta H_{298} \qquad (4)$$

where ΔH_{298} derives from ΔH_{obs} on reduction to 298 K.

The iodination of (chlorobenzene)chromium tricarbonyl was studied at 216°C. The iodine content of the black powder (remaining in the reaction vessel) indicated a product $CrI_{2.3} - CrI_{2.5}$, there was some visual evidence for the formation of a colorless crystalline product (admixed with excess iodine), but very much less of this was observed than in the direct thermal decomposition experiments. The thermal results are summarized in Table 3; they are interpreted on the basis of a straightforward iodination reaction:

$$C_6H_5ClCr(CO)_3\,(c,298) + {}^3/_2I_2(g,489) \rightarrow 3CO(g,489) + C_6H_5Cl(g,489) + CrI_3(c,489) \qquad (5)$$

admixed with the thermal decomposition process shown in eqn. 3. The relative amounts of the two processes were evaluated from the analysis, CrI_n, of the iodine content of the solid product. Accordingly, ΔH_{obs} is presumed to relate to the overall calorimeter reaction:

$$(C_6H_5Cl)Cr(CO)_3(c,298) + \frac{n}{2}I_2(g,489) \rightarrow 3CO(g,489) + \frac{n}{3}C_6H_5Cl(g,489) + \left(0.5 - \frac{n}{6}\right)C_{12}H_{10}(g,489) + \frac{n}{3}CrI_3(c,489) + \left(1 - \frac{n}{3}\right)CrCl(c,489) \qquad (6)$$

for which $\Delta H_{obs} = \frac{n}{3}\Delta H_5 + \left(1 - \frac{n}{3}\right)\Delta H_3$ (7)

where ΔH_5 is referred to in eqn. 5 and ΔH_3 in eqn. 3. The values ΔH_5 in Table 3

TABLE 3

IODINATION OF $(C_6H_5Cl)Cr(CO)_3$ AT 489 K

Expt.	$(C_6H_5Cl)Cr(CO)_3$ (mg)	I_2 (mg)	Δh (cal)	ΔH_{obs} (kcal mol^{-1})	n	ΔH_5 (kcal mol^{-1})	$\Delta H_5^\star$	$\Delta H_{298}^\star$
1	4.565	11.375	−0.169	−9.2	2.45	−14.3	56.4	45.5
2	3.865	11.280	−0.145	−9.3	2.40	−15.0	55.7	44.8
3	4.190	9.130	−0.156	−9.3	2.30	−16.2	54.5	43.6

were evaluated from eqn. 7, using the average value of ΔH_3 at 489 K from Table 2, $\Delta H_3 = 13.5$ kcal mol^{-1}. The values ΔH_5^* were obtained from ΔH_5 by removing the contribution $Cr(c) + {}^3/_2I_2(g) \rightarrow CrI_3(c)$, for which [1] $\Delta H = -70.7$ kcal mol^{-1} at 489 K. On reduction to 298 K, ΔH_{298}^* relates to the idealized thermal decomposition at 25°C,

$$C_6H_5ClCr(CO)_3(c) \rightarrow Cr(c) + 3CO(g) + C_6H_5Cl(g) \tag{8}$$

The mean $\Delta H_{298}^* = 44.5$ kcal mol^{-1} (Table 3) corresponds to $\Delta H_f^\circ[(C_6H_5Cl)Cr(CO)_3,c] = -111.5$ kcal mol^{-1}, compared with -107.2 kcal mol^{-1} from the thermal decomposition studies of Table 2. The several assumptions made in interpreting both the thermal decomposition and iodination results make it difficult to assess the error limits to be attached to either value. The iodination result is considered preferable, but should be regarded as provisional and subject to uncertainty of not less than ±5 kcal mol^{-1}.

(Toluene)chromium tricarbonyl, [(C$_7$H$_8$)Cr(CO)$_3$]

The iodination of (toluene)chromium tricarbonyl was studied at 230°C. The mean ΔH_{298}^* (4 measurements) was 46.5 ± 1 kcal mol^{-1}; this compares with 45 ± 2 kcal mol^{-1} reported previously [1], which was based on measurements made at 271°C. The revised value corresponds to $\Delta H_f^\circ[(C_6H_5CH_3)Cr(CO)_3,c] = -113.8 \pm 1.5$ kcal mol^{-1}. The iodination of (benzene)chromium tricarbonyl was also studied at 232°C. The results confirmed the earlier studies (241-271°C), and the value $\Delta H_f^\circ[(C_6H_6)Cr(CO)_3,c] = -106 \pm 2$ kcal mol^{-1}.

Enthalpies of sublimation

The microcalorimeter was set at a temperature T, close to the melting point of the substance under investigation. A weighed sample, contained in a thin capillary tube, was dropped from room temperature via the inlet chute into the argon-filled "live" cell of the microcalorimeter at the same time as an identical (but empty) capillary tube was let fall into the twin "reference" cell. The resulting endotherm (A_1), arising from the thermal change $X(c,298) \rightarrow X(c,T)$ was recorded until the trace had returned almost to the base-line. The exit tubes from both the "live" and the "reference" cells were then connected (cone-joints) to a vacuum system, and both cells evacuated simultaneously. The second endotherm (A_2) was traced through to completion, recording the sublimation process $X(c,T) \rightarrow X(g,T)$. A typical example is shown in Fig. 1, obtained with anthracene

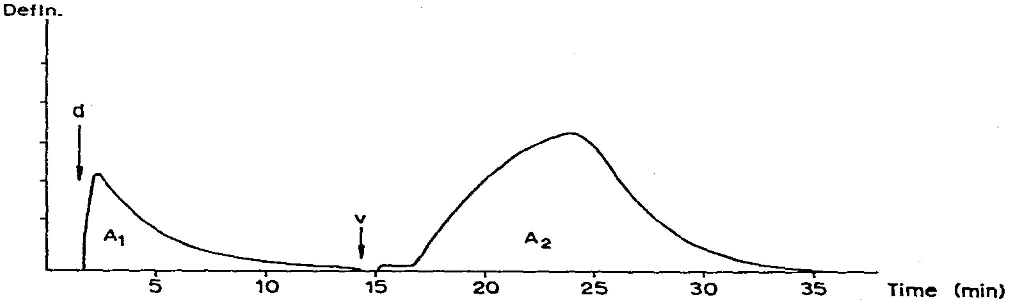

Fig. 1. Thermogram for sublimation of anthracene. $T = 421$ K; m = 3.200 mg; d, sample drop; v, vacuum on; defln, galvanometer deflection.

TABLE 4

ENTHALPIES OF SUBLIMATION, $\Delta H_{\text{sub}}(298)$

Compound	Mass (mg)	T (K)	$\Delta H_{\text{sub}}(T)$ (kcal mol^{-1})	ΔH_{obs} (kcal mol^{-1})	$(H_T - H_{298,\text{g}})$ (kcal mol^{-1})	$\Delta H_{\text{sub}}(298)$ (kcal mol^{-1})
Benzoic acid	3.140	413	(15.6*)	25.7	3.43 [11]	22.25
	3.100	413	(15.4*)	25.6	3.43	22.15
	3.485	413	(15.5*)	25.7	3.43	22.3
						Mean = 22.2
Anthracene	3.200	421	(23.0)	29.5	6.47	23.0
	2.840	421	(22.9)	29.9	6.47	23.4
						Mean = 23.2
$Cr(CO)_6$	6.095	379	(15.8)	21.0	4.14 [14]	16.9
	7.520	394		21.2	4.94 [14]	16.3
						Mean = 16.6
$W(CO)_6$	9.875	275	(16.4)	21.7	4.01 [14]	17.7
	7.390	441		25.0	7.63 [14]	17.4
	12.592	441		25.1	7.63	17.5
						Mean = 17.5
2-Chlorobenzoic acid	4.700	413	(17.2*)	28.0	3.88	24.1
	3.895	413	(17.4*)	28.1	3.88	24.2
						Mean = 24.2
3-Chlorobenzoic acid	5.540	413	(24.1)	28.9	3.88	25.0
	5.400	414	(23.5)	29.5	3.92	25.6
						Mean = 25.3
4-Chlorobenzoic acid	5.610	413	(24.0)	29.6	3.88	25.7
	5.375	413	(24.7)	29.7	3.88	25.8
						Mean = 25.8
(Benzene)$Cr(CO)_3$	5.725	391	(21.9)	26.4	4.62	21.8
	4.214	401	(21.7)	27.1	5.15	22.0
	3.825	401	(22.3)	27.4	5.15	22.3
	3.575	401	(20.9)	26.4	5.15	21.3
						Mean = 21.8
(Toluene)$Cr(CO)_3$	5.365	371	(17.2*)	26.9	4.09	22.8
	5.905	391	(16.5*)	27.6	5.20	22.4
	3.390	401	(16.8*)	28.5	5.77	22.7
	4.500	401	(17.0*)	28.0	5.77	22.3
	5.454	401	(16.8*)	28.8	5.77	23.0
						Mean = 22.6
(Mesitylene)-$Cr(CO)_3$	4.300	393	(24.2)	32.8	6.45	26.4
	5.580	395	(24.5)	32.4	6.59	25.8
	4.395	400	(23.8)	31.5	6.93	24.6
	3.878	401	(25.7)	34.8	7.00	27.8
	5.935	441	(23.5)	34.9	9.95	25.0
						Mean = 25.9
(Hexamethylbenzene)$Cr(CO)_3$	5.710	440	(27.3)	44.2	13.64	30.6
	6.025	440	(26.5)	43.7	13.64	30.0
	3.795	441	(26.4)	42.7	13.73	29.0
	4.670	462	(26.0)	44.1	15.58	28.5
						Mean = 29.5
(Chlorobenzene)-$Cr(CO)_3$	4.93	391	(17.8*)	29.5	5.01	24.5
	5.425	393	(18.2*)	29.5	5.12	24.4
	7.440	393	(17.6*)	29.6	5.12	24.5
						Mean = 24.5
(Cycloheptatriene)-$Cr(CO)_3$	3.545	365	—	26.0	4.00	22.0
	5.135	370	(16.0*)	27.3	4.28	23.0
						Mean = 22.5

at 148°C. The calorimeter was calibrated for sublimation studies over the temperature range 90-150°C by using crystalline iodine as standard substance. Tests of the sublimation technique were made using benzoic acid, anthracene, chromium hexacarbonyl and tungsten hexacarbonyl. Results are summarized in Table 4, and are generally in fair agreement with available literature values [14,15].

Sublimation studies on *o*-, *m*- and *p*-chlorobenzoic acids, and on several arene chromium tricarbonyls, are included in Table 4. The values ΔH_{obs}, determined from the combined thermogram areas ($A_1 + A_2$), refer to the overall change $X(c,298) \rightarrow X(g,T)$. $\Delta H_{\text{sub}}(298)$ values were obtained from ΔH_{obs} by subtracting $(H_T - H_{298})$ for X(g). Values $\Delta H_{\text{sub}}(T)$ were calculated directly from the sublimation thermogram areas (A_2). In cases (asterisked in Table 4) where measurements were made at temperatures $T >$ m.p., the recorded data are $\Delta H_{\text{vap}}(T)$. $(H_T - H_{298})$ values for gaseous benzoic acid [11] and gaseous hexacarbonyls of Cr and W [14] are from the literature. For the chlorobenzoic acids, the $(H_T - H_{298})$ values were estimated by adding to $(H_T - H_{298})$ for benzoic acid an amount equal to the difference between $(H_T - H_{298})$ for C_6H_5Cl and C_6H_6. Experimental $(H_T - H_{298})$ data are not available for the $ArCr(CO)_3$ compounds, and the values used were estimated using the approximation:

$$(H_T - H_{298}) \approx \Sigma(H_T - H_{298}) \qquad \text{for arene(g)} + 3\text{CO(g)} + \text{Cr(c)} \tag{9}$$

A similar additive approximation, applied to $M(CO)_6$ (where M = Cr, Mo, W), and to bis(benzene)chromium [16], holds reasonably well in the range 350-450 K. For anthracene, $(H_T - H_{298})$ was estimated by extrapolation along the series benzene → naphthalene → anthracene.

Discussion

The microcalorimetric vacuum sublimation here described lacks the precision and control of the more elegant Knudsen-cell calorimetric method, developed by Malaspina and coworkers [15,17], but it has the advantage of speed and simplicity. Values obtained for $\Delta H_{\text{sub}}(T)$ by the present method compare with those from the more elaborate technique within limits of ± 5%.

Table 5 summarizes available thermochemical data on arene chromium tricarbonyls. The values $\Delta H(\text{Cr—L})$ refer to the sum total of the Cr—ligand bond

TABLE 5

ARENE—Cr BOND ENTHALPIES[a]

Compound	ΔH_f^0 (c)	ΔH_{sub}^0	ΔH_f^0 (g)	ΔH (Cr—L)	D (Arene—Cr)
$(C_6H_6)Cr(CO)_3$	−106 ± 2	21.8 ± 1	−84.2	120 ± 3	42.5 ± 3
$(C_6H_5CH_3)Cr(CO)_3$	−114 ± 1.5	22.6 ± 1	−91.2	119 ± 3	41.5 ± 3
$[C_6H_3(CH_3)_3]Cr(CO)_3$	−136.5 ± 2	25.9 ± 1	−110.6	122.5 ± 3	45 ± 3
$[C_6(CH_3)_6]Cr(CO)_3$	−166.5 ± 3[b]	29.5 ± 1	−137.0	132 ± 4	55 ± 4
$(C_6H_5Cl)Cr(CO)_3$	−111.5 ± 5	24.5 ± 1	−87	115 ± 5	38 ± 5
$(\text{cyclo-}C_7H_8)Cr(CO)_3$	−74 ± 3	22.5 ± 1	−51.5	111 ± 4	34 ± 4

[a] All values given in kcal mol^{-1}. [b] The ΔH_f^0 (c) value given in ref. 1 (−171 ± 3) was based on $\Delta H_f^0(C_6Me_6,g) = -25.26$ kcal mol^{-1} [11], which appears to be an erroneous entry. The revised value of ΔH_f^0 (c) is based on $\Delta H_f^0(C_6Me_6,g) = -20.75 \pm 0.65$ kcal mol^{-1} [10].

enthalpy contributions in the gaseous [(arene) $Cr(CO)_3$] molecules at 298 K, i.e., to ΔH for the disruption process:

$$(\text{arene})Cr(CO)_3(g) \rightarrow \text{arene}(g) + 3CO(g) + Cr(g)$$

The final column, *D*(arene—Cr) lists each arene—Cr bond enthalpy contribution, calculated by assuming that each Cr—CO bond in the $Cr(CO)_3$ moiety has the same average contribution [18,19] as in $Cr(CO)_6$ — i.e., 25.7 kcal mol^{-1}. From this table, it seems that progressive methyl substitution into the benzene ring effects an increase in the (arene)—Cr bond enthalpy contribution, so that (hexamethylbenzene)—Cr ≫ (mesitylene)—Cr > (toluene)—Cr, whereas chlorine substitution reduces the contribution and (benzene)—Cr > (chlorobenzene)—Cr. Cycloheptatriene is decidedly less strongly bound to chromium than is benzene.

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