Journal of Organometallic Chemistry, 260 (1984) 189–197
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THERMOCHEMISTRY OF ARENETRICARBONYLCHROMIUM COMPLEXES CONTAINING TOLUENE, ANISOLE, *N*,*N*-DIMETHYLANILINE, ACETOPHENONE AND METHYLBENZOATE

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(Received August 15th, 1983)

Summary

Microcalorimetric measurements at elevated temperatures were made to determine the enthalpies of sublimation, of thermal decomposition, and of bromination of hexacarbonylchromium and of several (η-arene)tricarbonylchromium complexes. The standard enthalpies of formation (in kJ mol^{-1}) of the crystalline and vapour states respectively of the $[Cr(CO)_3(\eta\text{-ArX})]$ complexes were derived as $X = CH_3$, $-(473 \pm 4)$, $-(380 \pm 5)$; $X = OMe$, $-(593 \pm 8)$, $-(489 \pm 8)$; $X = NMe_2$, $-(522 \pm 8)$, $-(404 \pm 13)$; $X = COMe$, $-(585 \pm 13)$, $-(478 \pm 13)$; $X = C(O)OMe$, $-(772 \pm 8)$, $-(659 \pm 10)$. Values of the enthalpy of disruption reflect the weaker binding of η-arene ligands containing electron-accepting substituents.

Introduction

The enthalpies of formation of several (η-arene)tricarbonylchromium complexes have been reported [1], obtained mainly from microcalorimetric studies of the thermal decomposition and iodination of the complexes at elevated temperatures [2,3]. More recently, the results of calorimetric measurements in solution have been reported [4]. Iodination at high temperature (ca. 480 K) is less advantageous for the study of complexes in which the η-arene ligand itself is reactive with halogen at that temperature, so that accurate analysis of the mixture of reaction products is difficult. Thermal decomposition is preferable in this respect; in practice, however, measured enthalpies of thermal decomposition are subject to correction arising from the exothermic adsorption and chemisorption of carbon monoxide on the active chromium metal surface which is deposited on the walls of the reaction vessel following decomposition. The thermal corrections arising from adsorption amount to 40–50 kJ mol^{-1} for thermal decomposition of $[Cr(CO)_6]$ and $[Cr(CO)_3(\eta\text{-}C_6H_5Me)]$; if similar corrections apply generally to complexes of substituted benzenes, the thermal decomposition measurements provide approximate values for the enthalpies of formation of these complexes.

The 'drop' microcalorimetric method which has been used for iodination studies was adapted to bromination. This procedure has the advantage that it can be applied at less elevated temperatures than are required for satisfactory iodination of metal carbonyl complexes [5]. Studies on the bromination of $[Cr(CO)_6]$, $[Cr(CO)_3(\eta\text{-}C_6H_5Me)]$ and $[Cr(CO)_3(\eta\text{-}C_6H_5CO_2Me)]$ proved to be straightforward and are now reported: in each case the free ligands are not noticeably reactive with bromine vapour at the temperatures used. Attempts were also made to study the bromination of $[Cr(CO)_3(\eta\text{-}C_6H_5OMe)]$ and $[Cr(CO)_3(\eta\text{-}C_6H_5COMe)]$: in each case the arene ligand is rapidly attacked by bromine vapour at the temperature used. Corrections can be made for the Br_2/ligand side-reactions but these are both large and imprecise, so that the derived enthalpy values are also subject to large error limits. For complexes of this type, the 'corrected' thermal decomposition results are probably to be preferred.

Experimental

Calorimeter. The thermal measurements were made using a Calvet twin-cell high-temperature microcalorimeter (Setaram), adapted to the drop calorimetric technique. The thermopile output was amplified (NV 724A nanovoltmeter amplifier) and the thermograms recorded (Rikadenki, DBE 2). The thermogram areas were simultaneously evaluated by the ITC integrator and printer. The calorimeter was calibrated at different temperatures from the sublimation thermograms for naphthalene, benzoic acid, and iodine.

Materials. Hexacarbonylchromium was a commercial sample (Pressure Chemical) which was purified by resublimation. The complexes $[Cr(CO)_3(\eta\text{-}ArX)]$ were prepared by the method of Mahaffy and Pauson [6].

Auxiliary data. The following standard enthalpies of formation at 298 K were used in evaluating the present results (values in kJ mol^{-1}): CO(g) $-(110.53 \pm 0.17)$ [7]; Br_2(g) (30.91 ± 0.05) [7]; $C_6H_5CH_3$(g) (50.1 ± 0.3) [8]; $C_6H_5OCH_3$(g) $-(68.0 \pm 1.1)$ [8]; $C_6H_5COCH_3$(g) $-(86.6 \pm 1.5)$ [8]; $C_6H_5CO_2CH_3$(g) $-(287.9 \pm 6.8)$ [8]; $C_6H_5N(CH_3)_2$(g) (33.5 ± 6) [8]; $CrBr_2$(c) $-(298.3 \pm 6)$ [9]; $CrBr_3$ $-(400.4 \pm 16)$ [9]; Cr(g) (396.6 ± 4) [10].

Measured reaction heats, ΔH^T, at elevated temperatures were converted to room-temperature values, ΔH^{298}, using $(H^T - H^{298})$ data tabulated by Stull, Westrum and Sinke [11] (for organic compounds) and by Barin and Knacke [12] (for metals and inorganic compounds).

Results

Hexacarbonylchromium. The vacuum-sublimation microcalorimetric technique was applied to $[Cr(CO)_6]$ at temperatures in the range 380–408 K, to measure the enthalpy change, ΔH^T, for the process shown in eq. 1.

$$[Cr(CO)_6\ (c, 298)] \rightarrow Cr(CO)_6\ (g, T) \qquad (1)$$

Δ^{298}_{sub} values were obtained from ΔH^T by subtracting the heat content $(H^T - H^{298})$ of the vapour * at temperature T. Results are summarized in Table 1, together with those from thermal decomposition studies over the range 503–613 K, where ΔH^T refers to the process shown in eq. 2.

$$[\mathrm{Cr(CO)_6(c,298)}] \rightarrow \mathrm{Cr}(c,T) + 6\mathrm{CO}(g,T) \qquad (2)$$

The bromination of $Cr(CO)_6$ was studied over the range 410–412 K by dropping samples into the hot reaction zone, charged with Br_2/argon. The solid residue after reaction ($CrBr_n$) was analysed for bromine content, values of n ranging from 2.3–2.5. The measured heats of reaction, ΔH_3^T, refer to the process shown in eq. 3

$$[\mathrm{Cr(CO)_6(c,298)}] + \frac{n}{2}\mathrm{Br_2}(g,T) \rightarrow \mathrm{CrBr}_n(c,T) + 6\mathrm{CO}(g,T) \qquad (3)$$

and are listed in Table 2.

The values $\Delta H_f^0[\mathrm{Cr(CO)_6,c}]$ were obtained from ΔH_3^{298}, assuming the product $CrBr_n$ to be a mixture in the appropriate quantities of $CrBr_2$ and $CrBr_3$. The mean value, $\Delta H_f^0(\mathrm{Cr(CO)_6(c)}) = -(976.6 \pm 4)$ kJ mol^{-1} confirms the recommended literature value [9], based on combustion and iodination studies. It corresponds to $\Delta H^{298} = (316.4 \pm 4)$ kJ mol^{-1} for thermal decomposition; the directly measured value is thus too small by ca. 50 kJ mol^{-1}.

η^6-Toluene(tricarbonyl)chromium. Vacuum-sublimation measurements over the range 398–413 K, and thermal decomposition results over the range 550–570 K are summarized in Table 3. Bromination measurements from 413–432 K are given in Table 4, where ΔH_4^T refers to the cell reaction, shown in eq. 4.

TABLE 1

SUBLIMATION (V.S.) AND THERMAL DECOMPOSITION (T.D.) OF $Cr(CO)_6$

Method	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
V.S.	380	2.110	84.6	16.5	68.1
	408	2.151	90.3	22.1	68.2
	408	2.543	92.6	22.1	70.5
			Mean ΔH_{sub}^{298} (68.9 ± 2) kJ mol^{-1}		
T.D.	503	2.296	310.4	41.3	269.1
	503	2.434	307.7	41.3	266.4
	613	1.988	326.7	64.1	262.6
			Mean ΔH^{298} (266 ± 4) kJ mol^{-1}		

TABLE 2

BROMINATION OF $Cr(CO)_6$

T (K)	Mass (mg)	ΔH_3^T (kJ mol^{-1})	n in ($CrBr_n$)	ΔH_3^{298} (kJ mol^{-1})	$\Delta H_f^0[\mathrm{Cr(CO)_6(c)}]$ (kJ mol^{-1})
412	2.385	−28.1	2.31	−55.1	−973.6
412	2.900	−26.5	2.36	−53.5	−981.2
412	2.505	−30.3	2.36	−57.3	−977.4
410	2.041	−31.0	2.40	−57.5	−981.9
410	1.926	−42.1	2.51	−68.7	−983.7

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* Estimated by using $(H^T - H^{298}) \sim \Sigma(H^T - H^{298})$ for 6CO + Cr(g).

TABLE 3

SUBLIMATION AND THERMAL DECOMPOSITION OF $[Cr(CO)_3(\eta\text{-}C_6H_5Me)]$

Method	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
V.S.	398	2.778	116.0	23.5	92.5
	398	2.726	117.6	23.5	94.1
	398	2.366	113.5	23.5	90.0
	413	3.092	123.4	27.4	96.0
	413	1.851	119.9	27.4	92.5
			Mean ΔH^{298}_{sub} (93.0 ± 2) kJ mol^{-1}		
T.D.	549	1.666	222.8	65.7	157.1
	570	2.259	227.5	72.0	155.5
	570	1.407	213.9	72.0	141.9
	570	1.519	226.9	72.0	154.9
	570	1.782	217.4	72.0	145.4
			Mean ΔH^{298} (151 ± 6) kJ mol^{-1}		

TABLE 4

BROMINATION OF $[Cr(CO)_3(\eta\text{-}C_6H_5Me)]$

T (K)	Mass (mg)	ΔH_4^T (kJ mol^{-1})	n in ($CrBr_n$)	ΔH_4^{298} (kJ mol^{-1})	$\Delta H_f^0[Cr(CO)_3(C_7H_8)]$ (kJ mol^{-1})
413	2.036	−166.1	2.55	−195	−480.2
413	2.073	−165.1	2.50	−194	−475.5
426	2.080	−195.9	2.73	−228.5	−468.1
431	1.859	−211.1	2.88	−245.1	−469.2
431	1.828	−191.4	2.75	−225.4	−473.4
435	2.142	−194.3	2.75	−229.4	−469.4

$$[(C_6H_5CH_3)Cr(CO)_3(c,298)] + \frac{n}{2}Br_2(g,T) \rightarrow$$
$$CrBr_n(c,T) + C_6H_5CH_3(g,T) + 3CO(g,T) \qquad (4)$$

The mean value, $\Delta H_f^0[(C_7H_8)Cr(CO)_3(c)] = -(472.6 \pm 4)$ kJ mol^{-1}, derived from the measured ΔH_4^{298} values, is in good agreement with earlier measurements [2,3] on the iodination of this complex and corresponds to $\Delta H^{298} = (191.1 \pm 4)$ for thermal decomposition of the crystalline compound. As with chromium hexacarbonyl, the directly measured value is too small, in this case by ca. 40 kJ mol^{-1}.

η^6-Methylbenzoate(tricarbonyl)chromium. Vacuum-sublimation measurements from 358–388 K, and thermal decomposition results at 570 K are summarized in Table 5. The bromination reaction was studied over the range 393–422 K, and the measured heats of reaction, ΔH_5^T (Table 6), refer to the cell process shown in eq. 5.

$$[(PhCO_2Me)Cr(CO)_3(c, 298)] + \frac{n}{2}Br_2(g,T) \rightarrow$$
$$CrBr_n(c,T) + 3CO(g,T) + PhCO_2Me(g,T) \qquad (5)$$

Measurements were also made of the enthalpy of vaporization of methylbenzoate by dropping samples into the argon-filled hot-zone at temperatures in the range 388–422 K; in other measurements, samples were dropped into the same reaction

TABLE 5

SUBLIMATION AND THERMAL DECOMPOSITION OF $[Cr(CO_3(\eta\text{-}C_6H_5CO_2Me)]$

Method	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
V.S.	358	2.390	129	15.5	113.5
	363	9.090	126	16.8	109.2
	388	5.840	141	23.2	117.8
			Mean ΔH^{298}_{sub} (113.5 ± 5) kJ mol^{-1}		
T.D.	570	1.607	195.1	79.8	115.3
	570	1.409	186.9	79.8	107.1
	570	1.552	199.7	79.8	119.9
			Mean ΔH^{298} (114 ± 8) kJ mol^{-1}		

TABLE 6

BROMINATION OF $[Cr(CO)_3(\eta\text{-}C_6H_5CO_2Me)]$

T (K)	Mass (mg)	ΔH_5^T (kJ mol^{-1})	n in ($CrBr_n$)	ΔH_5^{298} (kJ mol^{-1})	$\Delta H_f^0[Cr(CO)_3(C_8H_8O_2)]$ (kJ mol^{-1})
393	2.245	−146	2.0	−171.6	−777
408	2.140	−151	2.1	−181	−779
412	2.275	−161	2.01	−192	−758
422	2.480	−140	2.03	−174	−778
422	2.775	−121	1.84	−155	−767

vessel, which now contained bromine vapour. The results indicated no more than a slight effect from the mixing of methylbenzoate and bromine vapours at these temperatures ($\Delta H^{298}_{vap} = (56.2 \pm 1)$ kJ mol^{-1} in argon; $\Delta H^{298}_{vap} = (55.5 \pm 2)$ kJ mol^{-1} in bromine/argon).

The mean ΔH_f^0 value for $[(C_8H_8O_2)Cr(CO)_3$ (c)] from bromination ($-(722 \pm 8)$ kJ mol^{-1}) corresponds to $\Delta H^{298} = (152.5 \pm 8)$ kJ mol^{-1} for the enthalpy of thermal decomposition; the directly measured value, as in the case of $[(toluene)Cr(CO)_3]$, is too low by ca. 40 kJ mol^{-1}.

η^6-Anisole(tricarbonyl)chromium. Vacuum-sublimation (363–388 K) and thermal decomposition (525–613 K) measurements on $[(anisole)Cr(CO)_3]$ are summarized in Table 7. The thermal decomposition values, 'corrected' to allow for the exothermic contribution from adsorption of CO on the metal surface (by adding ca. 40 kJ mol^{-1} to ΔH^{298} as measured), lead to $\Delta H_f^0[(C_6H_5OCH_3)Cr(CO)_3](c) \sim -(592 \pm 6)$ kJ mol^{-1}.

Bromination studies were made over the temperature range 399–421 K. The measured heats of bromination include the exothermic contribution from bromination of the ligand *; this was evaluated from separate measurements (drop anisole samples into Br_2/argon in the hot reaction vessel) at temperatures near to 400 K. The bromination heats ΔH_6^T, in Table 8, refer to the idealized reaction (eq. 6).

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* At temperatures near to 400 K the reaction:

$C_6H_5OMe(l) + \text{excess } Br_2(g,400) \rightarrow \text{products } (400)$

has $\Delta H_r \sim -105$ kJ mol^{-1}. The product is mainly $C_6H_2Br_3(OMe)$.

TABEL 7

SUBLIMATION AND THERMAL DECOMPOSITION OF [$Cr(CO)_3(\eta\text{-}C_6H_5OMe)$]

Method	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
V.S.	363	2.514	120.6	16.3	104.3
	373	2.862	125.9	18.8	107.1
	379	2.415	120.9	20.3	100.6
	381	2.626	125.6	20.8	104.8
	388	3.280	126.9	22.6	104.3
			Mean ΔH_{sub}^{298} (104.2 ± 2) kJ mol^{-1}		
T.D.	525	2.220	220.7	62.0	158.7
	525	2.240	208.6	62.0	146.6
	570	1.809	234.3	76.3	158.0
	613	1.199	237.2	90.3	146.9
			Mean ΔH^{298} (152.6 ± 6) kJ mol^{-1}		

TABLE 8

BROMINATION OF [$Cr(CO)_3(\eta\text{-}C_6H_5OMe)$]

T (K)	Mass (mg)	ΔH_6^T (kJ mol^{-1})	n in ($CrBr_n$)	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH_6^{298} (kJ mol^{-1})	ΔH_f^0(c) (kJ mol^{-1})
399	1.441	−105	2.0	26.5	−131.5	−597.3
410	1.984	−125	2.1	29.8	−154.8	−585.8
415	2.129	−153	2.5	31.3	−184.3	−602.2
421	1.831	−102	2.0	33.0	−135.0	−593.8
421	1.813	−136	2.3	33.0	−169.0	−593

$$[(C_6H_5OCH_3)Cr(CO)_3](c,298) + \frac{n}{2}Br_2(g,T) \rightarrow$$

$$CrBr_n(c,T) + 3CO(g,T) + C_6H_5OCH_3(g,T) \qquad (6)$$

The analysis of the bromine content in the solid residue (the value of n in $CrBr_n$) was not decisive, due to some slight contamination of the residue with involatile brominated products from the anisole ligand. The derived enthalpy of formation, ΔH_f^0[(anisole)$Cr(CO)_3$(c)] = −(595 ± 5) kJ mol^{-1}, is in agreement with that from thermal decomposition, but is in reality subject to larger overall experimental uncertainty than indicated in Table 8. The value ΔH_f^0(c) ~ −(593 ± 8) kJ mol^{-1} is proposed.

η^6-Acetophenone(tricarbonyl)chromium. Vacuum-sublimation measurements at 391–395 K, and thermal decomposition results at 570 K are given in Table 9. The 'corrected' enthalpy of thermal decomposition (ΔH^{298} ~ (123.5 ± 11) + 40 kJ mol^{-1}) corresponds to $\Delta H_f^0[(C_6H_5COCH_3)Cr(CO)_3(c)]$ ~ −(582 ± 11) kJ mol^{-1}.

Bromination measurements at 431 K are summarized in Table 10. As with the anisole complex, allowance for the exothermal bromination of the ligand was made, based on separate measurements for the addition of acetophenone * to excess

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* These measurements gave ΔH_r^T ~ −38 kJ mol^{-1} for the reaction:

$C_6H_5COMe(l,298)$ + excess Br_2(g, 395) → products (395)

corresponding to ΔH^T for bromination of C_6H_5COMe (g,398) of ca. −108 kJ mol^{-1}.

TABLE 9

SUBLIMATION AND THERMAL DECOMPOSITION OF $[Cr(CO)_3(\eta\text{-}C_6H_5COMe)]$

Method	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
V.S.	391	1.988	130.7	24.0	106.7
	395	1.558	132.3	25.0	107.3
			Mean ΔH^{298}_{sub} (107 ± 0.6) kJ mol^{-1}		
T.D.	570	0.923	207.9	79.7	128.2
	570	1.113	192.2	79.7	112.5
	570	1.651	209.6	79.7	129.9
			Mean ΔH^{298} (123.5 ± 11) kJ mol^{-1}		

TABLE 10

BROMINATION OF $[Cr(CO)_3(\eta\text{-}C_6H_5COMe)]$

T (K)	Mass (mg)	ΔH_7^T (kJ mol^{-1})	n in ($CrBr_n$)	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH_7^{298} (kJ mol^{-1})	ΔH_f^0(c) (kJ mol^{-1})
431	1.447	−122.5	2.0	37.5	−160	−587
431	1.656	−120	2.0	37.5	−158	−589
431	1.663	−144.5	2.2	37.5	−182	−589

Br_2/argon vapour in the hot zone (ca. 395 K). The values ΔH_7^T refer to the idealized bromination reaction (eq. 7).

$$[(C_6H_5COCH_3)Cr(CO)_3(c,298)] + \frac{n}{2}Br_2(g,T) \rightarrow$$

$$CrBr_n(c,T) + C_6H_5COCH_3(g,T) + 3CO(g,T) \qquad (7)$$

The derived mean value of the enthalpy of formation, $\Delta H_f^0(c) = -(588 \pm 1.4)$ kJ mol^{-1} is subject to considerably larger uncertainty than indicated by the results of Table 10. (There is some uncertainty in the correction made for bromination of ligand, and in the analysis of $CrBr_n$ formed). The bromination result is in good agreement with that from thermal decomposition, and the intermediate value $\Delta H_f^0 \sim -(585 \pm 13)$ kJ mol^{-1} is proposed.

η^6-N,N-Dimethylaniline(tricarbonyl)chromium. The vacuum-sublimation of $[(C_6H_5N(CH_3)_2)Cr(CO)_3]$ was examined by the microcalorimetric technique at 411–413 K, and thermal decomposition measurements were made at 525 K. The

TABLE 11

SUBLIMATION AND THERMAL DECOMPOSITION OF $[Cr(CO)_3(\eta\text{-}C_6H_5NMe_2)]$

Method	T (K)	Mass (mg)	ΔH^T (kJ mol^{-1})	$\Sigma(H^T - H^{298})$ (kJ mol^{-1})	ΔH^{298} (kJ mol^{-1})
V.S.	411	1.433	155.5	32.1	123.4
	413	2.034	156.3	32.8	123.5
	413	1.523	141.0	32.8	108.2
			Mean ΔH^{298}_{sub} (118.4 ± 10) kJ mol^{-1}		
T.D.	525	1.541	247.5	70.4	177.1
	525	1.612	254.2	70.4	183.8
	525	1.885	260.7	70.4	190.3
			Mean ΔH^{298} (183.7 ± 8) kJ mol^{-1}		

TABLE 12

DISRUPTION ENTHALPIES OF [Cr(CO)$_3$(η-arene)] COMPLEXES

Complex	ΔH_f^0(c) (kJ mol^{-1})	ΔH_f^0(g) (kJ mol^{-1})	$\Delta H^{298}_{\text{disrupt}}$ (kJ mol^{-1})
$(C_6Me_6)Cr(CO)_3$	$-(671 \pm 8)$	$-(548 \pm 9)$	526 ± 9
$(C_6H_3Me_3)Cr(CO)_3$	$-(571 \pm 8)$	$-(463 \pm 9)$	512 ± 9
$(C_6H_5NMe_2)Cr(CO)_3$	$-(522 \pm 8)$	$-(404 \pm 13)$	503 ± 13
$(C_6H_6)Cr(CO)_3$	$-(443 \pm 8)$	$-(352 \pm 9)$	500 ± 9
$(C_6H_5Me)Cr(CO)_3$	$-(473 \pm 4)$	$-(380 \pm 5)$	496 ± 5
$(C_6H_5OMe)Cr(CO)_3$	$-(593 \pm 8)$	$-(489 \pm 8)$	486 ± 8
$(C_6H_5Cl)Cr(CO)_3$	$-(467 \pm 21)$	$-(365 \pm 21)$	481 ± 21
$(C_{10}H_8)Cr(CO)_3$	$-(365 \pm 7)$	$-(258 \pm 8)$	474 ± 8
$(C_6H_5COMe)Cr(CO)_3$	$-(585 \pm 13)$	$-(478 \pm 13)$	456 ± 13
$(C_6H_5CO_2Me)Cr(CO)_3$	$-(772 \pm 8)$	$-(659 \pm 10)$	436 ± 10

TABLE 13

CALCULATED ENTHALPY OF LIGAND (L) DISPLACEMENT BY BENZENE FROM [Cr(CO)$_3$L]

Ligand, L	ΔH_g^{298}(kJ mol^{-1})
Hexamethylbenzene	+26
Mesitylene	+12
N,N-Dimethylaniline	+3
Benzene	0
Toluene	−4
Anisole	−14
Chlorobenzene	−19
Naphthalene	−26
Acetophenone	−44
Methylbenzoate	−64

results are given in Table 11; the 'corrected' enthalpy of thermal decomposition ($\Delta H^{298} = (183.7 \pm 8) + 40$) kJ mol^{-1} leads to $\Delta H_f^0[(C_6H_5N(CH_3)_2)Cr(CO)_3(c)] \sim -(521.8 \pm 8)$ kJ mol^{-1}. Bromination studies were not made with this compound.

Discussion

The present results are included in Table 12, in which the available data on the enthalpies of formation of arene(tricarbonyl)chromium complexes are collected together. The table lists ΔH_f^0(c), ΔH_f^0(g), and the $\Delta H^0_{\text{disrupt}}$ values, where the latter refer to the dissociation reaction (at 298 K) (eq. 8).

$$[LCr(CO)_3(g)] \rightarrow Cr(g) + L(g) + 3CO(g) \tag{8}$$

The range of 90 kJ mol^{-1} from the highest (526 kJ mol^{-1}) to the lowest (436 kJ mol^{-1})$\Delta H_{\text{disrupt}}$ value in Table 12 reflects the differences in the (η-arene)–metal bond enthalpy contribution. The order is clearly shown by the calculated enthalpies of the gas-phase ligand displacement reactions (eq. 9) given in Table 13.

$$[LCr(CO)_3(g)] + C_6H_6(g) \rightarrow [(C_6H_6)Cr(CO)_3(g)] + L(g) \tag{9}$$

The relative ease of displacement of methylbenzoate and of acetophenone from their respective complexes is consistent with electron withdrawal from the benzene ring by the substituent CO_2CH_3 and $COCH_3$ groups. In both these groups, inductive and mesomeric effects act in the same direction. In chlorobenzene and in anisole, the mesomeric and inductive effects oppose one another and the metal–ligand bond enthalpy contribution is reduced, but to a lesser degree. At the other extreme, in the highly methyl-substituted ligands, mesitylene and hexamethylbenzene, the metal–ligand bond enthalpy is increased as a consequence of electron donation to the benzene ring. The position of *N,N*-dimethylaniline relative to toluene and chlorobenzene in the sequence indicates that the dimethylamido group acts as a strong donor, which causes an increase in the metal–ligand bond enthalpy contribution. Our earlier work suggested an empirical correlation between the enthalpy of formation of the $[Cr(CO)_3(\eta\text{-arene})]$ complex and that of the arene ligand [1]. The results reported here reinforce the conclusion and lead to a revision of the linear equation 10 with a correlation coefficient of 0.98 for ten complexes.

$$\Delta H_f^0([Cr(CO)_3(\eta\text{-arene})(g)] = 0.91\ \Delta H_f^0(\text{arene}(g)) - 423 \qquad (10)$$

Acknowledgment

We thank Professor P.L. Pauson for the generous provision of some of the materials used in this work, and the Science and Engineering Research Council for a grant to purchase the microcalorimeter.

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