Bond Energies in Dicobalt Octacarbonyl and Bromo- and Chloro-methylidynetricobalt Enneacarbonyls

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Using a solution calorimetric method at 298.15 K, the standard enthalpies of formation of crystalline [Co_3(CBr)-$(CO)_9$], [Co_3(CCl)$(CO)_9$], and [$Co_2(CO)_8$] have been determined as −284.3 ± 2.2, −283.5 ± 2.4, and −298.9 ± 1.2 kcal mol^{-1} respectively. The enthalpies of sublimation of the compounds were determined by effusion manometry as 23.8 ± 0.4, 28.1 ± 0.6, and 15.6 ± 0.8 kcal mol^{-1} respectively. Bond energies have been derived from the gas-phase enthalpies of formation and their structural implications are discussed.

HEATS of formation of transition metal compounds are scarce compared with the availability of corresponding data for main-group compounds [1,2] and acutely so for organometallic derivatives.[3] Consequently there is little quantitative information on the strengths of transition-metal–carbon bonds. Static oxygen-bomb calorimetry offers a means of determining these thermodynamic data but the composition of the final products is often uncertain, a problem recognized by Cotton *et al.*[4] in the early calorimetric studies on metal carbonyls. An investigation was therefore initiated with an aim of evaluating the applicability of reaction calorimetry, in particular constant-temperature-environment solution calorimetry, to this area. Halogens were chosen as the general reagents because they usually react rapidly and cleanly with organometallic compounds to give products, for example metal halides, for which ancillary thermodynamic data are available. An allied approach by Connor and his co-workers,[5-7] who monitored high-temperature iodination or decomposition in a Calvet microcalorimeter, has yielded promising results.

Recent work on derivatives of the tricobalt carbon cluster Co_3C has suggested that its unusual stability arises from strong Co–C rather Co–Co interactions.[8] In order to assess the Co–C bond energy it was necessary to study [$Co_4(CO)_{12}$] and [$Co_2(CO)_8$] as well as [Co_3-(CCl)$(CO)_9$] and [Co_3(CBr)$(CO)_9$]. Vapour pressures of the last three compounds were determined over a range of temperature using an effusion manometer and heats of sublimation were derived. A preliminary report of part of this work has appeared.[9]

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EXPERIMENTAL

Materials.—Carbon tetrachloride (Merck, Uvasol) was run slowly down a column (75 × 2.5 cm) of type 4A molecular sieves (B.D.H.) until the water content by a Karl Fischer determination was *ca.* 0.0005 mass %. The purity determined by gas–liquid chromatography was 99.997 mass %. Carbon tetrabromide (B.D.H.) was twice crystallized from absolute ethanol and dried at room temperature at a pressure of 0.1 Torr.* Dicobalt octacarbonyl (Strem Chemicals) was purified by vacuum sublimation as large (*ca.* 1 mm), deep orange, crystals. The purified sample was stored at 253 K. Any decomposition {to $[Co_4(CO)_{12}]$ or Co} was immediately evident by a blackening of the crystal surface. Chloro- and bromomethylidynetricobalt enneacarbonyls were prepared according to Ercoli *et al.*[10] These compounds were purified by three crystallizations from hexane followed by pumping for 12 h at a pressure of 0.1 Torr. Impurities were shown to be absent in the mass spectrum and by thin-layer chromatography [Found: C, 23.2 ± 0.05 (mean ± two standard deviations of the mean; three analyses); Br, 15.25 ± 0.1 (mean ± two s.d.m., eight analyses). Calc. for $C_{10}BrCo_3O_9$: C, 23.05; Br, 15.35. Found: C, 25.15; Cl, 7.35; Co, 37.15. Calc. for $C_{10}ClCo_3O_9$: C, 25.2; Cl, 7.45; Co, 37.1%]. The density of $[Co_2(CO)_8]$ is 1.87 g cm^{-3} (ref. 11) and those of $[Co_3(CBr)(CO)_9]$ and $[Co_3(CCl)(CO)_9]$ were determined at 294 and 298 K as 2.05 and 2.02 g cm^{-3} respectively.

Procedure.—Calorimeter. The reaction vessel (100 cm^3 volume, part no. 8725-1) and stirrer (part no. 8728-1) were the same as those used in the LKB 8700-1 precision calorimetry system. Modifications to limit corrosion of these components are described below. The reaction vessel was screwed *via* the locking ring on to a circular 0.25 in thick aluminium plate. This plate carried the aluminium stirrer bearing housing, three symmetrically placed aluminium support posts to an upper square 0.25 in thick aluminium plate, and a chimney for the heater and thermistor leads. All aluminium parts were anodized. The reaction vessel was air insulated by a flanged glass bell and the system was operated in the isoperibol mode at 25.000 ± 0.008 °C (stability over 24 h). The upper part of the stirrer shaft was of stainless steel running in glass-impregnated polytetrafluoroethylene bearings. A small segment was cut from the O ring above the flange of the reaction vessel so that the latter was vented. This flange was fabricated in stainless steel and corroded markedly in halogen vapour; hence it was given a heavy rhodium plate over a silver plate. The gold stirrer also corroded badly in Br_2–CCl_4 solutions so this was plated directly with rhodium. The equilibration time and leakage modulus were determined by the method of Sunner and Wadsö[12] as 2.5 min and 0.012 min^{-1} respectively. Calibration (reproducible to ±0.02%) was by electrical substitution[13] and timing referenced to a quartz clock standard. The precision and accuracy of the system were checked with two standard reactions: (*i*) the neutralization of *ca.* 40 mass % of aqueous $HClO_4$ in excess of aqueous NaOH which, corrected for the dilution of $HClO_4$, $NaClO_4$, and NaOH, gave −13.38 ± 0.04 kcal mol^{-1} for the enthalpy of ionization of water. (Vanderzee and Swanson[14] obtained −13.336 ± 0.018 kcal mol^{-1} for this function.); and (*ii*) the enthalpy of neutralization of tris[(hydroxymethyl)amino]methane (tham) in excess of 0.1 mol dm^{-3} aqueous HCl gave ΔH (298.15 K, $1\,278 < N < 2\,038$) = −7.113 ± 0.008 kcal mol^{-1}. [Prosen and Kilday,[15] in an exhaustive study of this reaction, obtained ΔH(298.15 K, $N = 1\,345$) = −7.115 ± 0.007 kcal mol^{-1}; N is the mole ratio of water to tham.]

Effusion manometer. The manometer and its operation have been described[16] previously. The method involved weighing at known times a Knudsen cell containing the sample and relating the rate of weight loss to the vapour pressure. Dicobalt octacarbonyl decomposes on heating to $[Co_4(CO)_{12}]$ and/or Co with evolution of CO. Clearly, weight loss due to decomposition must be avoided during the effusion experiments. Accordingly the sample was visually inspected and a portion analyzed gravimetrically for Co as the pyridinethiocyanate complex[17] after each three measurements. Using these analytical results and assuming a decomposition mode to give either $[Co_4(CO)_{12}]$ + CO or Co + CO, the proportional mass loss per measurement was between 0.2 and 0.7 mass % throughout the experimental temperature range (15—25 °C). Evaluation of the vapour pressure from the rate of mass loss required[16] a knowledge of the collision diameters and these were estimated from crystallographic data[11,18] and van der Waals radii as 9.87, 9.43, and 9.13 Å for $[Co_2(CO)_8]$, $[Co_3(CBr)(CO)_9]$, and $[Co_3(CCl)(CO)_9]$ respectively. The sensitivity of the derived enthalpies of sublimation to these choices was also investigated. For reasons mentioned previously[16] the gradient (and hence the enthalpy of sublimation) of the $\log_e p$ against T^{-1} plot is more reliable than the absolute vapour pressures.

Reaction stoicheiometry. Reactions (1)—(3) were chosen for calorimetric study. In each case a small excess (*ca.* 2%)

$$[Co_2(CO)_8](c) + 2Br_2(CCl_4\ soln.) \longrightarrow 2CoBr_2(c) + 8CO(g) \quad (1)$$

$$[Co_3(CBr)(CO)_9](c) + 4.5\ Br_2(CCl_4\ soln.) \longrightarrow 3CoBr_2(c) + 9CO(g) + CBr_4(CCl_4\ soln.) \quad (2)$$

$$[Co_3(CCl)(CO)_9](c) + 4.5\ Cl_2(CCl_4\ soln.) \longrightarrow 3CoCl_2(c) + 9CO(g) + CCl_4(l) \quad (3)$$

of halogen was used and the carbon tetrachloride was initially saturated at 25 °C with carbon monoxide so that carbon monoxide of reaction was evolved in its standard state. Reaction was rapid (*ca.* 60 s) only when the CCl_4 was scrupulously dried as described earlier and consequently a small quantity of anhydrous cobalt(II) halide was added to the carbon tetrachloride immediately prior to closing the calorimeter. It was established that both $CoBr_2$ and $CoCl_2$ are insoluble in dry CCl_4. The stoicheiometry was checked

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* Throughout this paper 1 cal = 4.184 J, 1 Torr = (101.325/760) kPa, 1 in = 0.0254 m, and 1 Å = 10^{-10} m.

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by collecting the precipitated cobalt halide on a sinter, dissolving in water, and estimating the halide gravimetrically as silver(I) halide. The possibility of the presence of a significant quantity of $COBr_2$ in the reaction medium was discounted in view of the known[19] low rate of reaction at room temperature between CO(g) and Br_2(g) to establish an unfavourable equilibrium with respect to $COBr_2$(g). [Photolysis for *ca.* 80 d is required to achieve equilibrium at 293 K and it is unlikely that the rate will be markedly enhanced in a non-polar solvent.] Also, unchanged excess of bromine could be extracted quantitatively from the post-reaction calorimetric liquid. The presence of significant quantities of $COCl_2$ was discounted on similar kinetic grounds[20] and by i.r. and u.v. analyses of the post-reaction liquid and the gas above it.

TABLE 1

Sample masses and enthalpy changes for reactions (1)—(4) at 298.15 K

m_1 [a]/g	$-\Delta H_1$ [b]/ kcal mol^{-1}	m_2 [a]/g	$-\Delta H_2$ [b]/ kcal mol^{-1}
0.050 32$_5$	19.92	0.064 30	107.0
0.044 07	18.77	0.045 07	110.6
0.043 82	20.39	0.044 42	110.3
0.047 10	19.80	0.068 03	103.7
0.144 47	20.21	0.046 47	110.5$_5$
0.117 06	18.41	0.049 77	107.7$_5$
0.119 26	19.91	0.050 47	107.5
0.126 26	19.03	0.059 98	106.5
0.122 76	20.17	0.051 97	104.0
0.116 46	18.43	0.051 02	106.7
Mean (±2σ)	19.5 ± 0.5	Mean (±2σ)	107.5 ± 1.6
m_3 [a]/g	$-\Delta H_3$ [b]/ kcal mol^{-1}	m_4/g	ΔH_4/ kcal mol^{-1}
0.024 84	190.6$_5$	1.3249	3.07
0.021 26	192.5	1.2952	3.08
0.021 77	190.6	0.9996	3.09
0.022 20	191.9		
Mean (±2σ)	191.4 ± 1.0	Mean (±2σ)	3.08 ± 0.1

[a] Sample mass *in vacuo*. [b] Enthalpies are corrected for thermal loss on gas evolution. The evolved CO (assumed ideal; use of a real equation of state did not yield a significantly different result) was assumed to become saturated with CCl_4 vapour at its vapour pressure at 298.15 K (D. L. Hildenbrand and R. A. McDonald, *J. Phys. Chem.*, 1959, **63**, 1521).

TABLE 2

Vapour pressures and constants from the equation $\log_e(p/\text{Torr}) = -(A/T) + B$ for $[Co_2(CO)_8]$, $[Co_3(CBr)(CO)_9]$, and $[Co_3(CCl)(CO)_9]$

A/K	7 865 ± 412	12 481 [a]	11 958 ± 195	14 132 ± 295
B	23.83 ± 1.40	40.526	33.13 ± 0.64	40.66 ± 0.98
Range/K	288—298	288—315	292—318	294—308
p(298.15 K)/Torr	0.078	0.263	0.000 93	0.001 18
ΔH_T(sublimation) [b]/kcal mol^{-1}	15.6 ± 0.8	24.8 ± 0.3	23.8 ± 0.4	28.1 ± 0.6
T/K	293	302	305	301

[a] From ref. 24. [b] The sensitivity of ΔH_T to choice of collision diameter was −0.3, −0.07, and −0.06 kcal mol^{-1} Å^{-1} for $[Co_2(CO)_8]$, $[Co_3(CBr)(CO)_9]$, and $[Co_3(CCl)(CO)_9]$ respectively. In subsequent calculations the uncertainty in ΔH_T was assumed to include the correction of ΔH_T to ΔH_{298}.

RESULTS

The enthalpy changes for reactions (1)—(3) are collected in Table 1 together with the results for the heat of solution of CBr_4 in CCl_4 [reaction (4)], required as an ancillary

$$CBr_4(c) + nCCl_4(l) \longrightarrow CBr_4{\cdot}nCCl_4(\text{soln.}) \qquad (4)$$

datum. The standard enthalpies of formation were obtained from equations (5)—(7). The heats of dilution of

$$\Delta H_f^{\ominus}\{[Co_2(CO)_8],c\} = 2\Delta H_f^{\ominus}(CoBr_2,c) + 8\Delta H_f^{\ominus}(CO,g) - 2\Delta H_f^{\ominus}(Br_2,CCl_4\ \text{soln.}) - \Delta H_1 \qquad (5)$$

$$\Delta H_f^{\ominus}\{[Co_3(CBr)(CO)_9],c\} = 3\Delta H_f^{\ominus}(CoBr_2,c) + 9\Delta H_f^{\ominus}(CO,g) + \Delta H_f^{\ominus}(CBr_4,c) - 4.5\Delta H_f^{\ominus}(Br_2,CCl_4\ \text{soln.}) - \Delta H_2 + \Delta H_4 \qquad (6)$$

$$\Delta H_f^{\ominus}\{[Co_3(CCl)(CO)_9],c\} = 3\Delta H_f^{\ominus}(CoCl_2,c) + 9\Delta H_f^{\ominus}(CO,g) + \Delta H_f^{\ominus}(CCl_4,l) - 4.5\Delta H_f^{\ominus}(Cl_2,CCl_4\ \text{soln.}) - \Delta H_3 \qquad (7)$$

the halogens and CBr_4 in CCl_4 were ignored. The following ancillary data were used: $\Delta H_f^{\ominus}(CoBr_2,c) = -52.8 \pm 0.5$;[21] $\Delta H_f^{\ominus}(CO,g) = -26.417 \pm 0.041$;[22] $\Delta H_f^{\ominus}(Br_2,CCl_4\ \text{soln.}) = 0.71 \pm 0.02$;[21] $\Delta H_f^{\ominus}(CBr_4,c) = 4.5 \pm 0.4$;[21] $\Delta H_f^{\ominus}(CoCl_2,c) = -74.7 \pm 0.5$;[21] $\Delta H_f^{\ominus}(CCl_4,l) = -33.0 \pm 1.5$;[23] and $\Delta H_f^{\ominus}(Cl_2, CCl_4\ \text{soln.}) = -4.44 \pm 0.10$ kcal mol^{-1}.[21] Ref. 21 does not quote error limits to its data and those given above are realistic estimates.

From the vapour pressures obtained by effusion manometry and their temperature dependence, enthalpies of sublimation (Table 2) were derived. Baev[24] reported vapour pressures and an enthalpy of sublimation for $[Co_2(CO)_8]$ over the range 15—42 °C that are significantly higher than the present results. Both the absolute pressure and the rate of increase of pressure with temperature will be erroneously high if inadequate correction for thermal decomposition is made and hence we prefer our results. That the enthalpy of sublimation of $[Co_3(CCl)(CO)_9]$ is higher than the corresponding figure for $[Co_3(CBr)(CO)_9]$ is somewhat surprising. However, sublimation enthalpy is not only a function of the molecular mass but of lattice-packing effects and of the intermolecular forces within the crystal. For example, the compounds P_2I_4, PI_3, and I_2 have approximately the same enthalpy of sublimation (*ca.* 15.5 ± 1.0 kcal mol^{-1}) notwithstanding very different molecular masses.

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Using the results in Tables 1 and 2 with the ancillary thermodynamic data listed above in equations (5)—(7), the standard enthalpies of formation in Table 3 were obtained. Connor *et al.*,[6] using a thermal-decomposition technique, reported $\Delta H_f^\ominus\{[Co_2(CO)_8],c\} = 298.0 \pm 2.0$ kcal mol^{-1}, in good agreement with the result in Table 3.

TABLE 3

Standard enthalpies of formation (kcal mol^{-1}) at 298.15 K

Compound	$\Delta H_f^\ominus$(c)	$\Delta H_f^\ominus$(g)
$[Co_2(CO)_8]$	-298.9 ± 1.2	-283.3 ± 1.4
$[Co_3(CBr)(CO)_9]$	-284.3 ± 2.2	-260.5 ± 2.2
$[Co_3(CCl)(CO)_9]$	-283.5 ± 2.4	-255.4 ± 2.5

DISCUSSION

The main uses of heats of formation are (*i*) in the prediction of enthalpy changes (and hence the temperature coefficients of equilibria) for reactions involving the compounds of interest, and (*ii*) in the derivation of resonance, strain, and bond energies from which deductions about stability and chemical reactivity are made. The latter application is exploited in this work. In obtaining a bond energy from the heat of formation of a polyatomic molecule (containing *n* different bond types) it is always necessary to make assumptions about the strength of the $(n - 1)$ other bonds from corresponding data on structurally similar molecules. In this unavoidable assumption of bond-energy transferability lies the principal weakness of bond-energy schemes and hence it is important to establish that a given bond energy is only as reliable as the ancillary assumptions that were made to derive it. Consequently it is not possible to apply meaningful error limits to bond energies. (This situation will not apply to a bond-dissociation energy of the same bond in the same molecule as such energies are a consequence of processes in which only one bond is broken.) Bond energies become successively more reliable as more species containing the bond of interest are studied thermodynamically and yield bond energies of the same order. It is only in restricted classes of compounds, *e.g.* hydrocarbons[25] and aliphatic alcohols, where thermodynamic data are plentiful, that this situation obtains and bond energies have a high precision. For the organocobalt carbonyls no results, other than those discussed below, exist and hence the derived bond energies must be applied with caution.

By measuring an enthalpy of thermal decomposition Connor *et al.*[6] derived $\Delta H_f^\ominus\{[Co_4(CO)_{12}],c\} = -441 \pm 4$ kcal mol^{-1} which, with an estimate (25 kcal mol^{-1}) of the enthalpy of sublimation, gives $\Delta H_f^\ominus\{[Co_4(CO)_{12}],g\} = -416$ kcal mol^{-1} {the vapour pressure of $[Co_4(CO)_{12}]$ is too low below 333 K (onset of decomposition) for it to be measured by effusion manometry}. The compounds $[Co_2(CO)_8]$ and $[Co_4(CO)_{12}]$ contain three bond types: cobalt–cobalt; cobalt–carbon monoxide (terminal); and cobalt–carbon monoxide (bridging). Thus we may write the bond-energy equations (8) and (9) containing these three unknown bond energies. The

$$2\Delta H_f^\ominus(Co,g) + 8\Delta H_f^\ominus(CO,g) - \Delta H_f^\ominus\{[Co_2(CO)_8],g\} = E(Co\text{–}Co) + 6E(Co\text{–}CO)_t + 4E(Co\text{–}CO)_b \quad (8)$$

$$4\Delta H_f^\ominus(Co,g) + 12\Delta H_f^\ominus(CO,g) - \Delta H_f^\ominus\{[Co_4(CO)_{12}],g\} = 6E(Co\text{–}Co) + 9E(Co\text{–}CO)_t + 6E(Co\text{–}CO)_b \quad (9)$$

assumptions implicit in these equations are (*i*) that the carbonyls retain their crystalline phase structure in the gas and (*ii*) bonds of the same type in each molecule have identical energies in the gas-phase species.

For the specific example of the cobalt carbonyls there are no gas-phase structural data to justify the first assumption, although partial support for the retention of a bridged structure for $[Co_2(CO)_8]$ in the gas comes from the predominance[26,27] of binuclear fragments produced under electron impact. This mass-spectral evidence is clearly equivocal, however, for Bidinosti and McIntyre[28] assume $[Co_2(CO)_8]$ to be entirely non-bridged in the gas between 35 and 85 °C. In support of this view, the equilibrium between the bridged and non-bridged (D_{3d}) forms of $[Co_2(CO)_8]$ has been studied[29] in dilute pentane solution by i.r. spectroscopy and the D_{3d} structure is favoured at higher temperatures. This study also revealed that the enthalpy difference between the two structures in solution is small (≈1.3 kcal mol^{-1}), so if this result can be extrapolated to the gas phase the presence of two co-existing structures is irrelevant in the context of bond-energy calculations as it implies equation (10). In extrapolating this enthalpy difference

$$2E(Co\text{–}CO)_b \approx E(Co\text{–}CO)_t \quad (10)$$

to the gas phase and writing equation (10) we are assuming that (to within 1—2 kcal mol^{-1}) (*a*) the heats of solution in pentane of the two forms are the same (very probable), (*b*) their heats of sublimation are the same (likely), and (*c*) there is no redistribution of energy in the molecules beyond that which accompanies $4(Co\text{–}CO)_b$ becoming $2(Co\text{–}CO)_t$; in particular, it is assumed that $E(Co\text{–}Co)$ is the same in each form. This final assumption, (*c*), in common with the second primary assumption [(*ii*) above] is usually justified on other than thermodynamic grounds. For example, the Co–Co bond length is nearly constant in $[Co_4(CO)_{12}]$ (2.49 Å)[30] and $[Co_2(CO)_8]$ (2.52 Å)[11] and is substantially unchanged by the absence of bridging carbonyls {2.47 Å in $[Co_3(CMe)(CO)_9]$[31]}.

With these assumptions simultaneous solution of equations (8) and (9) gives $E(Co\text{–}Co) = 20.6$ kcal mol^{-1} and $[3E(Co\text{–}CO)_t + 2E(Co\text{–}Co)_b] = 127$ kcal mol^{-1}. The composite bridging and terminal bond-energy sum may be resolved with equation (10) whence $E(Co\text{–}CO)_t = 32$

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kcal mol^{-1}; $E(\text{Co–CO})_b = 16$ kcal mol^{-1}. Assuming E(Co–Co) and $E(\text{Co–CO})_t$ have identical values in the halogenomethylidynetricobalt enneacarbonyls we may write bond-energy equations for these species and derive $3E(\text{Co–C}) + E(\text{C–Br}) = 178$ kcal mol^{-1} for $[\text{Co}_3(\text{CBr})(\text{CO})_9]$ and $3E(\text{Co–C}) + E(\text{C–Cl}) = 175$ kcal mol^{-1} for $[\text{Co}_3(\text{CCl})(\text{CO})_9]$. There is considerable evidence [8,32] for electron delocalization over the three cobalt–carbon and carbon–halogen bonds in the cobalt clusters. Thus it is somewhat incautious to divide the composite terms by substitution of E(C–X) in CX_4 (65 and 78 kcal mol^{-1} for X = Br and Cl respectively). However this procedure gives $E(\text{Co–C}) \approx 32$ kcal mol^{-1} in $[\text{Co}_3(\text{CCl})(\text{CO})_9]$ and $E(\text{Co–C}) \approx 37$ kcal mol^{-1} in $[\text{Co}_3(\text{CBr})(\text{CO})_9]$ (the uncertainty in these results must be of the order of ± 5 kcal mol^{-1}). Thus for the bromo-cluster the metal–carbon bond energy is probably greater than the metal–carbon monoxide bond energy, in common with calculations [33] made for methyl-substituted manganese and rhenium carbonyls.

The additional ancillary data [21] for the bond-energy calculations were $\Delta H_f^\ominus(\text{Co,g}) = 101.5$, $\Delta H_f^\ominus(\text{Br,g}) = 26.741$, $\Delta H_f^\ominus(\text{C,g}) = 171.291$, and $\Delta H_f^\ominus(\text{Cl,g}) = 29.082$ kcal mol^{-1}.

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