Heat of Formation of Dicobalt Octacarbonyl and the Metal–Carbon Monoxide Bond Strength in Carbonyls

By ANTHONY CARTNER and BRIAN ROBINSON
(*Department of Chemistry, Otago University, Dunedin, New Zealand*)
and PETER J. GARDNER*
(*Department of Chemistry, Royal Holloway College, Englefield Green, Surrey*)

Summary A calorimetric study of the reaction between bromine and $Co_2(CO)_8$ in carbon tetrachloride gave $\Delta H_f^0[Co_2(CO)_8(c)]298 = -298{\cdot}8_5 \pm 1{\cdot}1$ kcal mol^{-1} from which an estimate of 33 kcal for the mean cobalt–carbon monoxide bond dissociation energy is derived.

THERMODYNAMIC data for metal carbonyls are scarce, and further, those results obtained *via* static oxygen bomb calorimetry are subject to uncertainty because of the variability in composition of the final state. There is considerable current interest in bond energies in the metal carbonyls and this communication reports the heat of formation of $Co_2(CO)_8$ using a solution calorimetric technique and notes a trend in metal–carbon monoxide bond strengths.

Dicobalt octacarbonyl was shown to react quantitatively and rapidly ($t_{\frac{1}{2}}$ *ca.* 10 s) at room temperature with an excess (*ca.* 2%) of bromine, dissolved in carbon tetrachloride (5 p.p.m. H_2O) presaturated with carbon monoxide,

$$Co_2(CO)_8(c) + 2Br_2nCCl_4(soln.) = 2\,CoBr_2(c) + 8CO(g) + nCCl_4(liq) \tag{1}$$

according to equation (1). The possibility of the presence of a significant quantity of $COBr_2$ in the reaction medium was discounted in view of the known[1] 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) [*ca.* 80 d photolysis 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, unreacted excess bromine could be extracted quantitatively from the post-reaction calorimetric liquid.

TABLE *Metal-carbon monoxide bond strengths in carbonyls*

Carbonyl	$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Co_2(CO)_8$	$Ni(CO)_4$	$Mo(CO)_6$	$W(CO)_6$
$\bar{D}$(M–CO)/kcal mol^{-1}	26	24	29	33	35	36	42

Reaction (1) was examined thermochemically in a conventional solution calorimeter operating in the isoperibol mode and the mean enthalpy change at 298·15 K for 10 experiments was $-19{\cdot}5$ ($3\bar{s} = 0{\cdot}7$) kcal mol^{-1} (1 cal = 4·184J). Combining this result with ancillary thermodynamic data[2] we obtain $\Delta H_f^0[Co_2(CO)_8(c)]298 = -298{\cdot}8_5 \pm 1{\cdot}1$ kcal mol^{-1}. Preliminary experiments measuring the vapour pressure of $Co_2(CO)_8$ over the temperature range 287 to 207 K using an effusion manometer[3] show $\Delta H[Co_2(CO)_8,\ (c) \rightarrow (g)] = 18{\cdot}0 \pm 1{\cdot}5$ kcal mol^{-1} and hence $\Delta H_f^0[Co_2(CO)_8(g)]298 = -280{\cdot}9 \pm 1{\cdot}9$ kcal mol^{-1}. $Co_2(CO)_8$ decomposes on heating to $Co_4(CO)_{12}$ and Co with the evolution of CO. The effect of this decomposition on the sublimed masses was shown to be small by changing the sample and analysing it for Co after every three points. Assuming a decomposition mode either to Co or to $Co_4(CO)_{12}$ the proportional mass loss per point due to CO evolution was between 0·2 and 0·7 mass per cent over the experimental temperature range.

There are two literature reports of the cobalt–cobalt bond dissociation energy in $Co_2(CO)_8$ from appearance potential measurements, *ca.* 76[4] kcal mol^{-1} and $11{\cdot}5 \pm 4{\cdot}6$[5] kcal mol^{-1}. Our result for the heat of formation of $Co_2(CO)_8$ lends support to the lower value. A reanalysis of Winters and Kiser's results,[4] using our value for $\Delta H_f^0[Co_2(CO)_8(g)]$, yields an unrealistically large value of 141 kcal for the cobalt–cobalt bond dissociation energy. It seems likely that the fragmentation ascribed by Winters and Kiser to the appearance potential, *A.P.* $(Co^+) = 16{\cdot}9 \pm 0{\cdot}4$ eV, is erroneous.

Mean metal–carbon monoxide bond dissociation energies for mononuclear and binuclear carbonyls are defined by equations (2) and (3) respectively.

$$\frac{1}{n}M(CO)_n(g) = \frac{1}{n}M(g) + CO(g) \quad \Delta H(2) = \bar{D}(M{-}CO) \tag{2}$$

$$\frac{1}{m}M_2(CO)_m(g) = \frac{2}{m}M(g) + CO(g) \quad \Delta H(3) = \bar{D}(M{-}CO) + \frac{1}{m}E(M{-}M) \tag{3}$$

Making the reasonable approximation in equation (3) that $E(M{-}M) = D[(CO)_{m/2}\,M{-}M(CO)_{m/2}]$, values of $\bar{D}$(M–CO) are collected in the Table for those carbonyls for which thermodynamic data are available[6] {using[2] $\Delta H_f^0[CO(g)]298 = -26{\cdot}416$ kcal mol^{-1} and $\Delta H_f^0[Co(g)]298 = 101{\cdot}5$ kcal g $atom^{-1}$ in the calculation}. The energy difference between the bridged $[(CO)_3Co(CO)_2Co(CO)_3]$ and non-bridged $[(CO)_4CoCo(CO)_4]$ isomers of $Co_2(CO)_8$ is small[7] so this molecule is considered in its non-bridged form in the calculation. In the absence of this assumption of the energy equivalence of the isomers, the value of 33 kcal may be rigorously identified only with $\bar{D}$(Co–CO) in the radical $Co(CO)_4$(g) rather than with $\bar{D}$(Co–CO) defined by equation (3). From the limited results available it appears that $\bar{D}$(M–CO) increases steadily across the latter half of the first transition series and down group VIB.

Preliminary results using this calorimetric technique have been obtained for $Co_3(CO)_9CBr$, $Co_4(CO)_{12}$, and $TlCo(CO)_4$, and it is clear that the method has considerable potential for obtaining thermodynamic data for organometallic compounds.

(*Received, 5th March* 1973; *Com.* 292.)

---

[1] B. K. Dunning and H. O. Pritchard, *J. Chem. Thermodynamics*, 1972, **4**, 213.

[2] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, 'Selected Values of Chemical Thermodynamic Properties,' National Bureau of Standards Technical Notes 270–3 (1968) and 270–4 (1969).

[3] A. Finch, P. J. Gardner, and A. Hameed, *J. Inorg. Nuclear Chem.*, 1970, **32**, 2869.

[4] R. E. Winters and R. W. Kiser, *J. Phys. Chem.*, 1965, **69**, 1618.

[5] D. R. Bidinosti and N. S. McIntyre, *Chem. Comm.*, 1967, 1.

[6] J. A. Connor, H. A. Skinner, and Y. Virmani, *J.C.S. Faraday I*, 1972, 1754.

[7] K. Noack, *Helv. Chim. Acta.*, 1964, **47**, 1064.