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The Metal–Metal Bond Dissociation Energy in Cobalt Octacarbonyl

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THE mass-spectrometric technique[1] which has been used to produce and identify[2] the radical $\cdot\mathrm{Mn(CO)_5}$ has now been successfully applied to the radical $\cdot\mathrm{Co(CO)_4}$. Cobalt octacarbonyl vapour was decomposed thermally in a graphite effusion reactor located adjacent to the ion source in a mass spectrometer. The vapour was introduced into this pyrolysis cell through a needle valve from an external reservoir. The pyrolysis products effusing from a pin-hole in the cell passed through the ionization chamber where a fraction of the molecular beam is ionized and mass analysed. For effusion-cell pressures in the range 10^{-2}—10^{-3} torr and temperatures between 35 and 85°c, an ion current corresponding to $\mathrm{Co(CO)_4^+}$ was observed at electron-impact energies below that required to produce this ion by fragmentation of cobalt octacarbonyl. This, together with the observation that with increasing cell temperatures the ratios $\mathrm{Co_2(CO)_7^+/Co_2(CO)_8^+}$ and $\mathrm{Co_2(CO)_6^+/Co_2(CO)_8^+}$ remained constant whereas the ratios $\mathrm{Co_2(CO)_4^+/Co_2(CO)_8^+}$ and $\mathrm{Co(CO)_3^+/Co_2(CO)_8^+}$ increased, is taken as evidence for the production of the $\cdot\mathrm{Co(CO)_4}$ radical in the pyrolysis cell.

The ionization potential (I.P.) of $\cdot\mathrm{Co(CO)_4}$(1) and the appearance potential (A.P.) of $\mathrm{Co(CO)_4^+}$ from cobalt octacarbonyl(2) were measured relative to mercury vapour using Warren's method.[3]

$$\cdot\mathrm{Co(CO)_4} + e \rightarrow \mathrm{Co(CO)_4^+} + 2e \qquad (1)$$

$$\mathrm{Co_2(CO)_8} + e \rightarrow \mathrm{Co(CO)_4^+} + \cdot\mathrm{Co(CO)_4} + 2e \qquad (2)$$

The values obtained are I.P. = 8·30 ± 0·1 ev and A.P. = 8·80 ± 0·1 ev. If the ions produced in (1) and (2) are assumed to be energetically the same then the algebraic difference between (2) and (1) is the symmetric dissociation process (3)

$$\mathrm{Co_2(CO)_8} \rightarrow 2\ \cdot\mathrm{Co(CO)_4} \qquad (3)$$

for which $D[\mathrm{(CO)_4Co{-}Co(CO)_4}]$ = A.P. − I.P. = 11·5 ± 4·6 kcal. Winters and Kiser[4] have reported a value of 76 kcal. for this dissociation process (3). However their value, based upon the appearance potential of $\mathrm{Co^+}$ from cobalt octacarbonyl, required an estimate for the heat of formation of cobalt octacarbonyl vapour. A comparison of the temperature ranges over which cobalt octacarbonyl and manganese decacarbonyl[2] decompose suggests that $D[\mathrm{(CO)_4Co{-}Co(CO)_4}]$ should be less than 18·9 kcal.

Although *X*-ray measurements[5] on crystalline cobalt octacarbonyl indicate that two of the carbonyl groups are bridging, Noack[6] has demonstrated that in solution this compound exists in two isomeric forms, one of which does not contain bridging carbonyls. In addition, Noack has shown that the proportions of the two vary considerably over the temperature range −105° to +30°c, with the non-bridged, high-temperature form comprising 40% of the molecules at room temperature. For the pyrolysis temperatures used in this study a majority of the molecules will be in the non-bridged form. If we now consider process (2) and its appearance potential which is the *minimum* energy necessary for this process we see that the value 8·80 ev must correspond to the process of ionizing and fragmenting the highest-energy form of cobalt octacarbonyl, the non-bridged form. Thus the value 11·5 ± 4·6 kcal. can be identified with the cobalt–cobalt bond dissociation energy.

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