High Temperature Infrared Spectrum of Dicobalt Octacarbonyl: Predominance of the Third Isomer

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Summary The changes observed in the i.r. spectrum of $Co_2(CO)_8$ between -165 and $+210$ °C can be interpreted in terms of variation of the relative concentrations of the three isomers of this compound, if the band at 2031 cm^{-1} is reassigned to the third isomer; a weak new feature in the spectrum at 2012 cm^{-1} is tentatively assigned to $Co(CO)_4$.

DURING a study of the kinetics and equilibria in the reactions of cobalt carbonyls at high temperatures and pressures[1] we obtained i.r. spectra of $Co_2(CO)_8$ in the carbonyl stretching region at temperatures up to 210 °C under 120 atm CO pressure.† Earlier work[2,3] did not lead to a satisfactory explanation of the reversible changes observed in the i.r. spectrum of $Co_2(CO)_8$ when heated in solution under CO

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† The solubility of carbon monoxide is higher in hexane than in liquid paraffin by a factor of 4–4·5 (R. Battino and H. L. Clever, *Chem. Rev.*, 1966, **66**, 395; J. C. Gjaldbaeck, *Acta Chem. Scand.*, 1952, **5**, 114; H. Luther and W. Hiemenz, *Chem. Ing. Techn.*, 1957, **29**, 530). Hence this pressure is sufficient to prevent decomposition.

pressure. We now report that after the reassignment of the band at 2031 cm^{-1} to the form (III)[4] the spectral changes observed between -165 and $+210$ °C can be satisfactorily explained by the shifts in the isomeric composition of the solution represented by the equilibrium in equation (1).

$$\text{form(I)} \rightleftharpoons \text{form(II)} \rightleftharpoons \text{form(III)} \qquad (1)$$

Increasing temperature →

The spectra‡ were found to be temperature dependent in a reversible manner. Variation of the pressure by a factor of two at constant temperature (195 °C) did not affect them. This observation gives strong evidence against the nonacarbonyl hypothesis.[2]

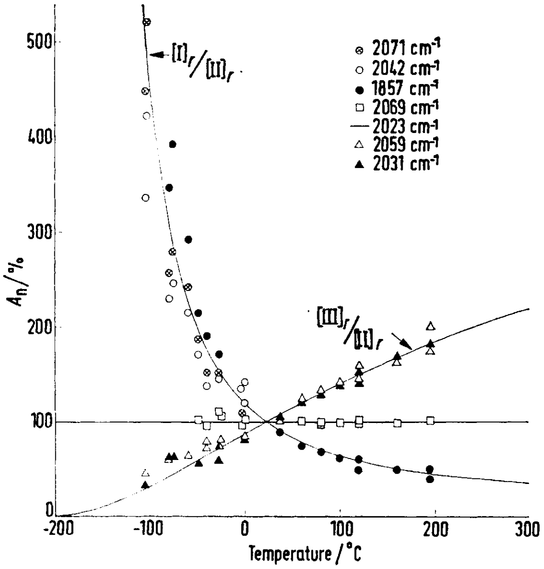

FIGURE 1. Symbols represent A_n values obtained with equation (2) from experimental band intensities. The superimposed lines are the equally normalized concentration ratios [*cf.* equation (3)] which were fitted to the experimental points by computer simulation assuming the three-compound equilibrium shown in equation (1). Points belonging to bands at 2042 and 2071 cm^{-1} [isomer(I)] were omitted above 22 °C because they are seriously affected by overlaps with bands due to the forms (II) and (III). The same holds true for the 2069 cm^{-1} band [isomer (II)] below -50 °C.

Because of the complexity of the spectral changes upon temperature variation an approximate intensity analysis was performed; the ratio of the experimental maximum absorbance values a_n of each band n at each temperature t to that of the band at 2023 cm^{-1} were determined, and the ratio of these values, expressed as a percentage, to the corresponding ratio at 22 °C, was then calculated [equation (2)]. These are represented as points in Figure 1

$$A_n = \frac{a_n(t)/a_{2023}(t)}{a_n(22\ ^\circ\mathrm{C})/a_{2023}(22\ ^\circ\mathrm{C})} \times 100 \qquad (2)$$

which shows that there are three groups of bands having different temperature dependences. The intensity increase of the band at 2031 cm^{-1} upon heating is closely parallel to that of the weak band at 2059 cm^{-1} which was assigned to the form(III).[4,5] A re-evaluation of the low temperature spectra[6] also proves that the intensity of the band at 2031 cm^{-1} decreases faster upon cooling than that of the strong band at 2023 cm^{-1} which belongs to the form(II). Therefore the band at 2031 cm^{-1} must be reassigned to the form(III) rather than to (II),[4,6,7] in agreement with the observation[5] that in the spectra of $Co_2(CO)_8$ in low temperature matrices, form(III) has its strongest band at frequencies between 2042 and 2029 cm^{-1}, specifically at 2032·8 cm^{-1} in N_2 and at 2031·1 cm^{-1} in CO.

The intensity changes attributed to the equilibrium in equation (1) were analysed by computer simulation. The relative concentration ratios [percent, equation (3)]

$$[(\mathrm{I})]_r/[(\mathrm{II})]_r = \frac{[(\mathrm{I})\ (t)]/[(\mathrm{I})\ (22\ ^\circ\mathrm{C})]}{[(\mathrm{II})\ (t)]/[(\mathrm{II})\ (22\ ^\circ\mathrm{C})]} \times 100 \qquad (3)$$

and $[(\mathrm{III})]_r/[(\mathrm{II})]_r$, respectively, were calculated assuming different numerical values and temperature dependences for the equilibrium constants. The most satisfactory fit with the points of the intensity ratios according to equation (2) is shown in Figure 1, and the corresponding isomeric concentration *vs.* temperature curves are given in Figure 2. They show that the isomer (III) becomes the dominating form at higher temperatures.

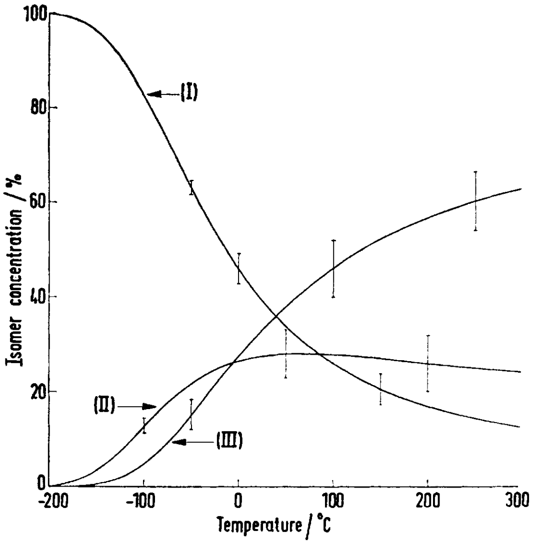

FIGURE 2. Computed concentration *vs.* temperature relationships of the three isomers of $Co_2(CO)_8$ corresponding numerically to the drawn lines in Figure 1. Error bars have been estimated from the range of equilibrium constants which gave a satisfactory fit with the data shown in Figure 1.

They are also in line with the intensity *vs.* temperature shifts of the Co–Co stretching bands observed in the Raman spectra,[8] if the band at 185 cm^{-1} is assigned to the form(II) and that at 157 cm^{-1} to (III).

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‡ Perkin–Elmer 325 spectrophotometer combined with a slightly modified (U.K. Dietler, Thesis no. 5428, E.T.H., Zurich) pressure cell (K. Noack, *Spectrochim. Acta*, 1968, **24A**, 1917); solvent, n-hexane. In some cases $Mo(CO)_6$ and/or ethyl propionate were added as internal intensity standards. Low temperature spectra were obtained as described in ref. 6. Copies of the high temperature spectra (to be published elsewhere) are available on request from G.B.

A new feature in the spectra, a shoulder at 2012 cm^{-1}, appears only above 120 °C and thereafter its intensity increases faster than the bands of the form(III). It is likely to arise from monomeric $Co(CO)_4$ units since the following frequencies were reported in frozen gas matrices for $Co(CO)_4$: 2011·5 cm^{-1} in Ar[9] and 2010·7 cm^{-1} in CO.[10]

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