

FUNDAMENTAL METAL CARBONYL EQUILIBRIA

III *. A QUANTITATIVE STUDY OF THE EQUILIBRIUM BETWEEN DIRHODIUM OCTACARBONYL AND TETRARHODIUM DODECACARBONYL UNDER CARBON MONOXIDE PRESSURE. A CORRECTION

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Summary

Previously reported (*J. Organomet. Chem.*, 246 (1983) 309) experimental data for the equilibrium constants and thermodynamic parameters of the reversible reaction $2 \text{Rh}_2(\text{CO})_8 \rightleftharpoons \text{Rh}_4(\text{CO})_{12} + 4 \text{CO}$ have been re-evaluated using more reliable values for the solubility of carbon monoxide in hexane at lower than room temperature and introducing also a fugacity vs. pressure correction for carbon monoxide. The new values are: $\Delta H^0 = 58.6 \pm 10 \text{ kJ mol}^{-1}$ and $\Delta S^0 = 305 \pm 25 \text{ J mol}^{-1} \text{ K}^{-1}$.

Recently [1] we described the first quantitative study of the reversible reaction 1, which was examined at +30 to –30°C in hexane solution. After the publication of



our results it became evident that neglecting the variation of the solubility of carbon monoxide with temperature and especially using the same numerical value in this low-temperature region as in our previous high-temperature (105 to 145°C) study of the analogous cobalt carbonyl system [2], was an unjustified oversimplification and leads to values for the thermodynamic parameters, which are well outside the error limits indicated in our paper [1]. We present below revised calculations and the corrected values of the parameters.

Unfortunately no directly measured solubility data for carbon monoxide in

* For part II see ref. 1.

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hexane are available. Therefore we calculated the low-temperature solubilities by the use of the solution enthalpy value of 2 kJ mol^{-1} , which is the average of the value between 1.8 and 2.2 kJ mol^{-1} reported for other solvents [3,4]. In this way we obtained α $0.0105 \text{ mol dm}^{-3} \text{ bar}^{-1}$ for -20°C and 0.0113 for 0°C , based on the value of α 0.012 accepted for $+20^\circ\text{C}$ [5].

Furthermore, in contrast to the situation in our previous studies [2,5], the deviation of the fugacity from the observed pressure values cannot be neglected in the present system; instead, for 200 bar carbon monoxide pressure we have to use a fugacity coefficient of 0.887 at -20°C and one of 0.945 at 0°C [6].

The numerical values recalculated by taking account of these corrections are as follows. Equation 6 of ref. 1 defining the temperature dependence of the equilibrium constant K_c has to be replaced by equation 6':

$$\ln K_c = 36.6 - 7050 \times 1/T \quad (6')$$

with uncertainty limits of ± 0.6 for the first term, and ± 150 for the second. The value of K_c is now given by:

$$K_c = \frac{[\text{Rh}_4(\text{CO})_{12}] \cdot p_{\text{CO}}^4 \cdot \alpha^4 \cdot \gamma_{\text{CO}}^4}{[\text{Rh}_2(\text{CO})_8]^2 \cdot (1 + 0.001 p_{\text{CO}})^4}$$

where α is the calculated solubility factor for carbon monoxide in hexane (in mol bar^{-1} units), γ_{CO} is the fugacity coefficient for carbon monoxide and p_{CO} is the CO partial pressure (bar). The second term in the denominator allows for the increase of volume of the liquid phase under pressure. The value of this coefficient (i.e. $0.001 \text{ vol parts/bar}$) has been determined experimentally [7], and was used in our previous studies [2,5].

The recalculated thermodynamic parameters are: $\Delta H^0 = 14.0 \pm 2.5 \text{ kcal mol}^{-1}$ ($58.6 \pm 10 \text{ kJ mol}^{-1}$), and $\Delta S^0 = 73 \pm 6 \text{ kcal mol}^{-1} \text{ K}^{-1}$ ($305 \pm 25 \text{ J mol}^{-1} \text{ K}^{-1}$). Although even these new values cannot be considered as definitive in the absence of reliable solubility data for carbon monoxide in hexane, we believe them to be more satisfactory than those previously published. They certainly give a fair estimate of the thermodynamic characteristics of this system, especially in comparison to similar data for related reactions.

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