

Note

THERMODYNAMICS OF COMPLEX FORMATION REACTIONS IN NON-AQUEOUS SOLVENTS. PART 3. THE REACTION OF VO(acac)₂ WITH PYRIDINE

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The entropy titration method allows the calculation of thermodynamic data; ΔG , ΔH and ΔS , from a single titration curve [1,2]. The method should be of general usefulness in studying weak complexes. VO(acac)₂ (acac = acetylacetonate) is known to form a 1:1 complex with pyridine in non-aqueous solvents such as CHCl₃ or diethyl ether. The complex can be isolated from diethyl ether as a pale green solid. The calculation of the thermodynamic values from the experimental data was, however, found not to be as straightforward as one would expect it to be for a 1:1 complex formation reaction. We, therefore, wish to report the thermodynamic data obtained for the reaction and to discuss some of the problems encountered.

EXPERIMENTAL

The general experimental method which was followed and the apparatus used have been described previously [3]. VO(acac)₂ and VO(acac)₂ · pyr were prepared as described in the literature [4]. VO(acac)₂ was recrystallised from CHCl₃ before it was used to prepare the solutions for the titrations. Calorimetric measurements on the solid VO(acac)₂ · pyr, (10 mg in platinum sample holders) were carried out using a Du Pont 910 DSC and 1090 thermal analyser in a dynamic (40 cm³ min⁻¹) nitrogen atmosphere.

RESULTS AND DISCUSSION

The thermometric titration curve obtained for the reaction suggested that the equilibrium constant is small. No change in the slope of the curve was observed at the stoichiometric VO(acac)₂ · pyr endpoint. The method sug-

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gested by Christensen et al. [1] and reviewed by Wanders and Zwietering [5] was thought to be adequate for the calculation of starting values for the iterative calculation method. The method was, however, found to be inadequate since the starting values, $\Delta H = -4.3 \text{ kJ mol}^{-1}$ and $K = 767$, obtained differed appreciably from the actual values and therefore yielded meaningless results (negative K value) when used in the iterative calculation method.

A method, by which ΔH was determined more accurately, was then used to estimate a value which could be used with confidence as a starting value for the iterative calculation method. The method consisted of titrating an excess amount of pyridine (0.025 dm^{-3} ; 1 mol dm^{-3}) with a $\text{VO}(\text{acac})_2$ solution (0.002 dm^3 ; $1.0 \times 10^{-2} \text{ mol dm}^{-3}$). It was then assumed that at the end of the titration, only the 1:1 adduct had formed and that the heat liberated was only due to the formation of the complex. Successive determinations, using this approximation, gave a value for $\Delta H = -38.09 \pm 83 \text{ kJ mol}^{-1}$. Using this value as a starting value and $K = 10$, the iterative calculation method converged within four iteration steps to give $K = 14.5$ and $\Delta H = -38.30 \text{ kJ mol}^{-1}$. From these values, $\Delta G = -6.63 \text{ kJ mol}^{-1}$ and $\Delta S = -106.0 \text{ J mol}^{-1} \text{ K}^{-1}$ were calculated for the reaction at 25°C in chloroform.

Determination of the enthalpy of dissociation in the solid state, using the technique of DSC, gave a broad endothermic peak, $T_{\text{onset}} = 68.2^\circ\text{C}$ and $T_{\text{max}} = 90.6^\circ\text{C}$, from which $\Delta H_r = 43.7 \text{ kJ mol}^{-1}$ was calculated. Although solution and solid state thermodynamic data cannot be compared directly, it is interesting to note that the enthalpy of the formation reaction in chloroform and that of the dissociation reaction in the solid state are similar.

The results discussed above illustrate again, the strong correlation which exists between ΔH and K and that for even a seemingly simple system, such as that discussed above, the two-point procedure may fail in producing accurate enough starting values for the iterative calculation procedure. The method described above, to obtain a starting value for ΔH , seems to be adequate.

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