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THE VAPOR PRESSURE AND BOILING POINT OF HYDRIDOCOBALT TETRACARBONYL, $HCo(CO)_4$

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Summary

From vapor partial pressure measurements of $HCo(CO)_4$ swept out of decane solution with CO, the normal boiling point of $HCo(CO)_4$ is estimated to be 47 ± 3°C.

Introduction

In connection with our studies [1] on the stoichiometric hydroformylation of formaldehyde with hydridocobalt tetracarbonyl we noted that the vapor pressure of $HCo(CO)_4$ appeared to be less than anticipated. Solid $HCo(CO)_4$ has been reported to melt at between —26.2 [2] and —33°C [3] but immediately upon melting the liquid decomposes and hence the boiling point of the liquid has never been reported. However, careful measurements of the vapor pressure of solid $HCo(CO)_4$ have been performed [2] in the temperature range of —29 to —37°C. Extrapolation of these data leads to an estimated boiling point of about 10°C for $HCo(CO)_4$ [4] compared to 43 and 103°C for $Ni(CO)_4$ and $Fe(CO)_5$, respectively. We wish to report data obtained by the transpiration method which we believe lead to a better estimate of the vapor pressure of $HCo(CO)_4$ above its melting point as well as its boiling point at atmospheric pressure.

Results and discussion

$HCo(CO)_4$ was prepared as a solution in decane, and the concentration immediately determined as previously described [5]. About 20 ml of this solution was placed in a thermostatted trap. A second trap, containing pure hexane,

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was placed in series with the first and was maintained at −78° C (dry-ice/acetone temperature). Dry CO was bubbled through the system at a constant flow rate, trapping the $HCo(CO)_4$ in hexane. The concentration of the hexane solution was determined periodically by titration [5] and plotting these data showed a first order rate of loss of $HCo(CO)_4$ from decane. The vapor pressure of the original solution was then calculated, assuming ideal gas behavior for $HCo(CO)_4$. The results at two temperatures are shown in Table 1. Using the two vapor pressure values, and assuming ideal solution behavior [6] a boiling point of approximately 47° C is predicted for pure $HCo(CO)_4$ at 760 Torr. Employing Trouton's Rule [6] such a boiling point would lead to a heat of vaporization of 6.7 kcal/mol.

In order to verify the boiling point prediction, cyclopentane (b.p. 50° C) was employed as a solvent for $HCo(CO)_4$ and CO gas passed through the solution at 25° C. Assuming ideal solution behavior, both the gas phase and solution phase should have very similar concentrations. After about one-third of the original solution had been collected in an empty trap cooled to −78° C, the concentration of the remaining solution and the trapped gas phase were determined to be 0.0528 and 0.0540 *M*, respectively. Since the original solution is slightly depleted in $HCo(CO)_4$ compared to the condensed vapor, it thus appears that $HCo(CO)_4$ is slightly more volatile than cyclopentane, consistent with its predicted behavior.

In order to reduce possible deviations from ideal behavior, a solution of $HCo(CO)_4$ in $Ni(CO)_4$ was prepared. A stream of CO was passed over 10 ml of this solution and after about a third of the original volume had been evaporated it was found that the original concentration of 0.105 *M* $HCo(CO)_4$ in $Ni(CO)_4$ had been increased to 0.128 *M* indicating that $Ni(CO)_4$ is somewhat more volatile than $HCo(CO)_4$. From these rather crude measurements we estimate that the boiling point of $HCo(CO)_4$ is probably 47 ± 3° C.

Because the vapor pressure appears to be lower and the boiling point of $HCo(CO)_4$ higher than previously estimated, the possibility of solution dimers of $HCo(CO)_4$ was suspected. However, molecular weight determinations in benzene and in cyclohexane by freezing point depression [7], gave correct values, ±7%, for the monomeric form.

TABLE 1

VAPOR PRESSURE OF $HCo(CO)_4$ IN DECANE UNDER FLOWING CARBON MONOXIDE

T (°C)	CO (ml/min)	$[(HCo(CO)_4)] \times 10^{-2}$		Rate of vapor [a] ($\times 10^{-3}$ mmol/min)	Total [b] pressure	P_V [c]
		Initial	Mol fract.			
0.0	57.6	5.28	1.02	3.02	796	0.852
22.0	68.2	5.13	0.978	9.75	806	2.48

[a] This rate of vaporization is the initial rate of loss of $HCo(CO)_4$ obtained by extrapolation from rate data, ±2%. [b] System pressure in torr. [c] Vapor pressure of $HCo(CO)_4$ in torr calculated from (ml of $HCo(CO)_4$)/(ml of CO) × 760.

References

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