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Thermodynamic Functions and Vapor Pressures of Triphenylphosphine Oxide and 1,4-Bis(diphenylphosphino)butane Near the Melting Point

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The enthalpies of vaporization/sublimation were derived from the temperature dependence of vapor pressures measured by the technique of simultaneous torsion and mass loss effusion in the pressure region of 0.1–1 Pa. In addition, specific heats and heats of fusion were determined by DTA. The results for triphenylphosphine oxide (solid) are $\Delta H^\circ_v(398.86 \text{ K}) = 131.0 \pm 2$ kJ mol^{-1}, $\Delta G^\circ_v(398.86 \text{ K}) = 3039 \pm 100$ J mol^{-1}, $p(398.86 \text{ K}) = 0.4 \pm 0.01$ Pa, $\Delta H^\circ_f(429.6 \text{ K}) = 23.4 \pm 0.25$ J mol^{-1}, $C_p^\circ(404.0 \text{ K}) = 431 \pm 3$ J mol^{-1} K^{-1}, and $C_p^\circ(444.0 \text{ K}) = 527 \pm 5$ J mol^{-1} K^{-1}. The results for 1,4-bis(diphenylphosphino)butane (liquid) are $\Delta H^\circ_v(443.22 \text{ K}) = 126.3 \pm 2$ kJ mol^{-1}, $\Delta G^\circ_v(443.22 \text{ K}) = 3377 \pm 100$ J mol^{-1}, $p(443.22 \text{ K}) = 0.4 \pm 0.01$ Pa, $\Delta H^\circ_f(405.9 \text{ K}) = 45.3 \pm 0.5$ kJ mol^{-1}, $C_p^\circ(384.0 \text{ K}) = 384 \pm 4$ J mol^{-1} K^{-1}, and $C_p^\circ(429.0 \text{ K}) = 520 \pm 5$ J mol^{-1} K^{-1}.

Introduction

Hydridocarbonyltris(triphenylphosphine)rhodium (I) dissolved in suitable solvents is being used as a heterogeneous catalyst in the hydroformylation of propylene. Because the catalyst is applied in large-scale chemical reactors and decomposes when the solvent has evaporated, it is necessary to use solvents having low vapor pressures under reaction conditions.

Knowledge of the vapor pressures of the pure substances as a function of the temperature is required to calculate the vaporization losses of the solvents in the reaction mixture in the reactor. Three suitable solvents, triphenyl-, tri-p-tolyl-, and tris(2-cyanoethyl)phosphine have been studied by de Kruif, Herman, and van den Berg (1).

The vapor pressures of two further solvents are presented in this paper. For the purpose of extrapolation of the vapor pressures of triphenylphosphine oxide to the temperature region of the supercooled liquid, needed for the calculation of losses

in the reactor, the melting heat and specific heats of this compound are also measured; for completeness the values for the butane compound are also given.

Experimental Section

Samples. Triphenylphosphine oxide (TPPO), obtained from Merck (West Germany), purity >98%, and 1,4-bis(diphenylphosphino)butane (BDPPB), obtained from Ventron (West Germany), purity >98%, were used without further purification because the measured vapor pressure of the compounds did not change significantly with loss of mass during the measurements.

The vapor pressure measurements were carried out with a simultaneous torsion and mass loss effusion apparatus as described in an earlier paper (de Kruif et al. (2)). The effusion cell is provided with two orifices 1 mm in diameter made in 6-μm platinum foil and are positioned 20 mm apart on opposite sides of the cell. The torsion effusion method measures the pressure as a recoil force (the rate of loss of momentum from the holes) and does not depend on the mass of the effusing molecules. In the mass loss effusion method the pressure is calculated from the rate of mass loss and depends on the mass of the effusing molecules by a factor $m^{-1/2}$. Decomposition of the sample or dimerization in the gas phase is easily recognized by comparison of the pressures measured by both methods. The calibration was done with naphthalene (Ambrose et al. (3)). The measuring procedure was started at a temperature corresponding with a vapor pressure of about 0.15 Pa. Five measurements at 30-s intervals were made followed by an increase of the oven temperature of about 0.9 K. The temperature of the sample was measured with a thermistor, calibrated on IPTS-68, positioned in the middle of the effusion cell. In order to allow the cell to come into temperature equilibrium with the surrounding oven, a period of 20 min was observed between the successive series of measurements. The procedure was continued until the pressure was about 1 Pa, giving a set of

Table I. Pressure–Temperature Table and Mean Values of the Parameters of Eq 1

	T/K	
p/Pa	TPPO	BDPPB
0.1	385.34	425.99
0.2	391.99	434.44
0.3	395.95	439.53
0.4	398.86	443.22
0.5	401.13	446.13
0.6	403.00	448.53
0.7	404.60	450.58
0.8	405.99	452.37
0.9	407.22	453.96
1.0	408.34	455.40
$\Delta H^\circ_v(\theta)$/kJ mol^{-1}	131.0 ± 2	126.3 ± 2
$\Delta G^\circ_v(\theta)$/J mol^{-1}	3039 ± 100	3377 ± 100
θ/K	398.86	443.22

about 18 × 5 data points over a temperature range of 20 K for both torsion and mass loss effusion measurements. This procedure was repeated four times or more.

The molar heat capacities and melting heats were measured by DTA on Setaram DSC111 apparatus.

Results

Each set of experimental vapor pressure data was fitted independently to the first two terms of the equation given by Clarke and Glew (4):

$$R \ln (p/p^\circ) = -\Delta G^\circ(\theta)/\theta + \Delta H^\circ(\theta)(1/\theta - 1/T) + \Delta C_p{}^\circ(\theta)\{\theta/T - 1 + \ln (T/\theta)\} \quad (1)$$

where θ is a reference temperature chosen in the middle of the measuring range. ΔG°, ΔH°, and $\Delta C_p{}^\circ$ are the differences in Gibbs energy, enthalpy, and specific heat, respectively, of the vapour and the condensed phases; $p^\circ = 1$ Pa. The mean values of the parameters $\Delta G^\circ(\theta)$ and $\Delta H^\circ(\theta)$ of eq 1 are given in Table I together with a pressure–temperature table calculated with these values. In Table II the molar heat capacities at chosen temperatures are given as well as the heat of melting at the melting point. We estimate the inaccuracy to be 1%.

Discussion

The scattering in the values of $\Delta H^\circ_v(\theta)$ for TPPO and BDPPB as obtained by fitting the vapor pressure sets to eq 1 is 1% and 0.5%, respectively. The values of $\Delta G^\circ_v(\theta)$ increase by 20 and 30 J, respectively, equivalent to a decrease in pressure of 1%, after 25% of the sample is evaporated, a usual amount also reported for the effusion of the calibration compound naphthalene. For this phenomenon a correction is applied. We obtained essentially the same values for the mass loss and torsion effusion measurements, indicating that no decomposition occurred.

Notwithstanding the good reproducibility, we present the ΔH° values with uncertainties of ±2 kJ and the ΔG° values with uncertainties of 100 J in order to account for possible systematic errors, of which the uncertainty in the temperature of the sample is the most important one. Even with the reported

Table II. Specific Heats and Heats of Melting of Triphenylphosphine Oxide (TPPO) and 1,4-Bis(diphenylphosphino)butane (BDPPB)

TPPO

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
	Solid		
314	339	364	390
324	350	374	402
334	361	384	412
344	371	394	422
354	380	404	431
	Liquid		
434	502	454	512
444	507	459	514
ΔH°_f/kJ mol^{-1}		23.4 ± 0.25	
T_f/K		429.6 ± 0.2	

BDPPB

T/K	C_p/J mol^{-1} K^{-1}	T/K	C_p/J mol^{-1} K^{-1}
	Solid		
264	354	379	371
369	359	384	384
374	363	389	402
	Liquid		
414	516	434	531
419	520	439	534
424	524	444	537
429	528		
ΔH°_f/kJ mol^{-1}		45.3 ± 0.5	
T_f/K		405.9 ± 0.2	

waiting period of 20 min for temperature equilibration, there may be a difference in the temperature given by the NTC and the temperature of the sample owing to lack of heat contact between sample and cell, self-cooling of the sample, and heat losses or gains by the leads of the NTC. It is not likely that within the temperature range of 20 K a possible temperature difference between NTC and sample will change very much. Therefore, ΔH° values, which are derived from the slope of the ln p–$1/T$ plot, will hardly be effected by an error in the absolute temperature of the sample. The pressure is an exponential function of the temperature and therefore more strongly influenced by such an error, and with it the values of $\Delta G^\circ(\theta)$ that are given by $R\theta$ in $(p(\theta)/p^\circ)$. Correction for this effect cannot be made by comparison with the calibration compound naphthalene because this compound is measured at a 150 K lower temperature.

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