Thermochimica Acta, 148 (1989) 341–346
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

PHENOL DETERMINATION BY THERMOMETRIC TITRIMETRY

J.O. HILL and S. KORCE
Department of Chemistry, La Trobe University, Bundoora, Victoria 3083, Australia.

ABSTRACT

Some thermometric titrimetry data are reported for the phenol, p-nitrophenol, p-methoxyphenol and phenol/pentachlorophenol - thallium ethoxide interactions in benzene as solvent. These thermochemical data are interpreted in terms of the structure of the relevant phenol and 'end-point curvature' is rationalised in terms of a phenoxide ion interference effect. Some evidence is also reported for acid-anion complex formation at the mid-point of the thermometric titration. The method is significant in terms of analytical applications.

INTRODUCTION

Phenols are generally classified as very weak acids and hence are difficult to determine in aqueous solution by direct thermometric titration with bases although phenols have been determined by this method in aqueous micellar media [1] and various aqueous sodium phenates have been determined by thermometric titration with diazonium salts [2].

In non-aqueous solvents, the direct thermometric titration of phenols with bases invariably gives poorly defined end points, although phenols in tar acids have been routinely determined by thermometric titration with alcoholic potassium hydroxide in pyridine as solvent [3]. End-point definition in these types of titration is generally improved by bromination of the phenol prior to determination with ethanolic base [4], however, it appears that brominated phenol mixtures give only total acidity via thermometric titration with ethanolic base. The dimerisation of acetone in the presence of OH^- to give diacetone alcohol has been used as a thermochemical indicator in thermometric titrations of phenols with ethanolic base in acetone as solvent [5]. Further, a wide variety of free and bound phenols in commercial products such as

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Thermal Analysis Highlights, 9th ICTA, Jerusalem, Israel, 21–25 August 1988.

0040-6031/89/$03.50

resins, oils and vegetable tannins have been determined in various non-aqueous solvents by thermometric titrimetry, using the OH^- catalysed polymerisation of acrylonitrile as a thermochemical indicator [6-12]. Belisle [13] has employed a novel titrant, thallium ethoxide, to determine phenol, p-methoxyphenol and m-nitrophenol in anhydrous benzene as solvent and reported that stoichiometric 1:1 reactions are involved and in each case, sharp, well-defined end-points are obtained. This latter procedure is further investigated in the present work.

EXPERIMENTAL

Calorimeter and Accessories. The thermometric titrimetric system employed and associated data analysis procedures have been described in detail by bin Ahmad *et al.* [14,15]. All derived thermochemical data refer to 298K and the relevant uncertainty is quoted as the standard deviation from the mean.

Analytical Procedures. Reaction heat Q_R and molar reaction enthalpy $\Delta_R H_m^\circ$ (kJ mol^{-1}) are calculated on the basis of the determined temperature variation, ΔT(mV) for the relevant quantitative calorimetric reaction and the associated average heat capacity, $\bar{C}_p$ (kJ mV^{-1}), determined from the measured heat capacities of the calorimeter and contents before (C_{p_B}) and after (C_{p_A}) the thermometric titration:

$$Q_R = -\bar{C}_p \Delta T = n_p \Delta_R H_m^\circ$$

where n_p = number of moles of product formed. $\Delta_R H_m^\circ$ is determined on the assumption of a 1:1 titrant:titrate reaction. Titrant dilution heats, as determined by titration of thallium ethoxide/benzene solvent into anhydrous benzene, were found to be less than the overall experimental error of $\pm 5 \times 10^{-5}$ in ΔT determination.

Calibration. Two 'test' reactions were employed: NaOH/HCl and THAM/HCl. The derived $\Delta_R H_m^\circ$ for these reactions was -55.17 ± 0.94 (lit. [16] -55.75) and -47.01 ± 0.75 (lit. [17] -47.36 kJ mol^{-1} respectively).

Titrants and Titrates. A 1.0 mol dm^{-3} thallium(I) ethoxide (Aldrich) titrant stock solution was prepared under nitrogen by mixing 1.77 cm^3 with anhydrous benzene (Mallinckrodt - 'Nanograde') in a 25 cm^3 dry standard flask and stored in the dark. A fresh titrant solution was prepared daily.

A stock solution of 0.0222 mol dm^{-3} phenol titrate was prepared by dissolving 1.04572 g of phenol (BDH AnalaR) in benzene in a 500 cm^3 standard flask.

A stock solution of 0.00501 mol dm^{-3} p-nitrophenol titrate was prepared by dissolving 0.06973 g of p-nitrophenol (Aldrich Gold Label) in benzene in a 100cm^3 standard flask.

A stock solution of 0.00900 mol dm^{-3} p-methoxyphenol titrate was prepared by dissolving 0.27916 g of p-methoxyphenol (Aldrich 98%) in benzene in a 250 cm^3 standard flask.

A stock solution of 0.0222 mol dm^{-3} of pentachlorophenol titrate was prepared by dissolving 1.47772 g of pentachlorophenol (TCl 95%) in benzene in a 250 cm^3 standard flask.

These various titrate solutions were diluted as appropriate with anhydrous benzene, using a 200-1000 µL 'Finn pipette' for sampling operations.

RESULTS AND DISCUSSION

Thermometric titration data for the phenol (0.00444-0.02220 mol dm^{-3}), p-nitrophenol (0.00296-0.00501 mol dm^{-3}) and p-methoxyphenol (0.00450-0.00900 mol dm^{-3})/thallium ethoxide (1.00000 mol dm^{-3}) systems are given in Table 1. In all cases, stoichiometric, 1:1, exothermic reactions were involved and sharp, well-defined 'end-points' were obtained. Such data provisionally suggest that thallium(I) ethoxide is a suitable titrant for the direct thermometric titrimetric determination of phenols in aprotic solvents.

In each case, a minor slope change was noted at approximately the mid-point of the linear reaction period. This phenomenon was also noted by Belisle [13] in phenol/thallium ethoxide thermometric titrations and by Harlow and Bruss [18] in non-aqueous potentiometric titrations of phenols with tetra-n-butyl ammonium hydroxide. The latter explained such irregular behaviour in terms of the formation of a 1:1 phenol/phenoxide 'anion complex', formed via intermolecular hydrogen bonding between the phenol acidic proton and the phenoxide moiety. The 'anion complex' is stabilised by non-polar solvents such a benzene.

Thermometric titration for the binary pentachlorophenol/phenol mixture (1:1 mole ratio) (0.0074-0.0148 mol dm^{-3})/thallium(I) ethoxide (1.0000 mol

Table 1.

Thermometric Titration: Phenols/Thallium(I) Ethoxide (Benzene Solvent)

[TITRATE] (mol dm^{-3})	ΔT_R (mV)	C_{PB}	C_{PA} (J mV^{-1})	$\bar{C}_P$	$-Q_R$ (J)	$-\Delta_R H^{\circ}_m$ (kJ mol^{-1})	$\frac{n_{TITRATE}}{n_{TlOEt}}$
Phenol							
0.00444	0.1907	46.27	46.72	46.52	8.87	22.20	0.93
0.00888	0.3095	57.04	57.91	57.48	17.79	22.26	0.97
0.01332	0.4740	57.33	57.95	57.64	27.32	22.79	0.98
0.01776	0.6274	57.23	58.68	57.96	36.36	22.76	1.00
0.02220	0.7879	58.10	59.51	58.81	46.33	23.17	1.00
p-Nitrophenol							
0.00296	0.2289	53.89	52.79	53.34	12.21	45.84	0.86
0.00444	0.3569	46.60	47.12	46.86	16.72	41.85	1.01
0.00501	0.3429	52.25	47.80	50.02	17.15	38.04	0.93
p-Methoxyphenol							
0.00450	0.1465	52.76	52.81	52.79	7.74	19.10	0.90
0.00600	0.2089	52.78	52.23	52.51	11.21	20.31	0.95
0.00900	0.3144	52.11	52.69	52.40	16.48	20.34	0.98

Means	$-\Delta_R H^{\circ}_m$ (kJ mol^{-1})	$\frac{n_{PHENOL}}{n_{TlOEt}}$
Phenol	22.64 ± 0.40	0.98 ± 0.03
p-Nitrophenol	41.91 ± 3.90	0.93 ± 0.08
p-Methoxyphenol	19.92 ± 0.71	0.94 ± 0.04

dm^{-3}) system are given in Table 2. The titration sequence is in the order of increasing pK value (pentachlorophenol: pK = 4.5 [19], phenol: pK = 10.0 [20]). Sequential stoichiometric, 1:1, exothermic reactions are involved, and in each titration, two 'end-points' are obtained. The second end-point is less well-defined than the first which is reflected in different values for $\Delta_R H^{\circ}_m$ for phenol as derived from the binary mixture and single component data respectively. The curvature associated with the final end-point is explained in terms of the relatively high concentration of phenolate ions present forming a hydrogen-bonded 'cage' around the 'last' phenol molecules - thereby

Table 2.

Thermometric Titrations: Phenol-Pentachlorophenol/Thallium(I) Ethoxide (Benzene Solvent).

	PENTACHLOROPHENOL				PHENOL			
[PHENOL]	ΔT_R (mV)	$-Q_R$ (J)	$-\Delta_R H^{\circ}_m$ (kJ mol^{-1})	$\frac{n_{PHENOL}}{n_{TlOEt}}$	ΔT_R (mV)	$-Q_R$ (J)	$-\Delta_R H^{\circ}_m$ (kJ mol^{-1})	$\frac{n_{PHENOL}}{n_{TlOEt}}$
0.0074	0.6044	31.36	47.09	0.86	0.3494	18.13	27.22	0.86
0.0111	0.6782	35.30	35.33	1.13	0.5386	28.03	28.06	1.11
0.0148	0.8176	42.56	31.96	1.22	0.7409	38.57	28.96	1.19

Means	$-\Delta_R H^{\circ}_m$ (kJ mol^{-1})	$\frac{n_{PHENOL}}{n_{TlOEt}}$
Pentachlorophenol	38.13 ± 7.94	1.07 ± 0.19
Phenol	28.08 ± 0.87	1.05 ± 0.17

preventing interaction of phenol with ethoxide ion. However the overall data indicate the potential of thallium(I) ethoxide for the thermometric titrimetric determination of phenol mixtures.

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