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Standard molar enthalpies of formation of some crystalline amine *N*-oxides

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Abstract

Based on the fact that *N*-oxide groups are kinetically reduced by titanium solution, a general thermochemical reaction, $3LO(c) + KX(c) = KXO_3(c) + 3L(l)$; $\Delta_r H_m^\circ$ (LO = *N*-oxide compound, L = amine, X = Cl, Br), was employed to determine through solution-reaction calorimetry the standard molar enthalpies of formation of crystalline *ortho*-, *meta*- and *para*-methylpyridine *N*-oxides, as well as those of triethyl- and tri-*n*-butylamine *N*-oxides, giving 10.3 ± 0.8, 8.8 ± 0.7, 12.9 ± 0.9, 9.0 ± 0.8 and 16.0 ± 1.1 kJ mol^{-1}, respectively. The advantage of this method is that it avoids combustion calorimetry in which it is difficult for this kind of substance to achieve complete combustion.

INTRODUCTION

When determining the standard molar enthalpies of formation of coordination compounds, thermochemists are faced with problems in experimental determinations when the standard molar enthalpies of the ligands involved in the complexes are unknown. These data are largely obtained through combustion calorimetric methods [1,2]. However, even if auxiliary material is used to ensure complete combustion, in some cases this objective might not be reached. A suitable illustration of this behaviour, recently observed by us [3], is provided by pyridine *N*-oxide [4], whose excessive hygroscopicity makes reliable determination of the standard molar enthalpy of formation difficult when combustion calorimetry is used.

Solution-reaction calorimetry can provide an alternative method for the determination of the standard molar enthalpy of formation as a convenient reaction process in solution is available. In the present case, the ability of titanium(III) solution to reduce *N*-oxides compounds rapidly [5,6] is explored. This paper deals with the determination of the standard molar enthalpies of formation of crystalline *ortho*- (opo), *meta*- (mpo) and *para*(ppo)-methylpyridine *N*-oxides, as well as those of triethyl- (teo) and tri-*n*-butyl(tbo)amine *N*-oxides.

EXPERIMENTAL

Chemicals

The *ortho*- (opy) (Merck), meta- (mpy) (Carlo Erba), *para*(ppy)-methylpyridines (Aldrich), triethyl- (te) (Riedel) and tri-*n*-butyl(tb)amines (BDH) were dried over potassium hydroxide, and distilled and stored over molecular sieves. KCl, KBr, $KClO_3$ and $KBrO_3$ (BDH) were dried in vacuo before use.

Preparation

Oxidation of the amines with hydrogen peroxide for several hours, following an established method [7], produced the respective *N*-oxide compounds, which were then purified by distillation under reduced pressure [8]. The resulting compounds were carefully protected from humidity and all operations took place in a dry box. The purity of the products was checked, by observing a sharp melting point in a fused capillary using a Mettler FP-52 instrument, as well as by recording their infrared spectra in Nujol mulls, using a Perkin–Elmer model 180 spectrophotometer.

Calorimetry

All reaction and solution enthalpies were measured in the LKB 8700 solution-reaction isoperibolic calorimeter system [3]. Ampoules were prepared under anhydrous conditions in a dry box under an atmosphere of dry nitrogen. The ampoules, containing 10–80 mg of the compounds, were sealed and broken into 0.10 dm^3 of thermostatted calorimetric solvent (0.08 mol dm^{-3} $TiCl_3 + 2.4$ mol dm^{-3} HCl) at 298.15 ± 0.02 K. At least four individual experiments were performed for each enthalpy determination. Details of measurements, procedure, apparatus and data processing have been described previously [9].

RESULTS AND DISCUSSION

Based on the property that *N*-oxide groups are kinetically favourable for reduction by titanium(III) solution [5,6], some crystalline heterocyclic amine *N*-oxides, (*ortho*-, *meta*- and *para*-methylpyridine *N*-oxides) and tertiary amine *N*-oxides (triethyl- and tri-*n*-butylamine *N*-oxides) have had their standar molar enthalpies of formation determined by solution-reaction calorimetry. A general thermochemical reaction was employed for these determinations:

$$3LO(c) + KX(c) = KXO_3(c) + 3L(l); \quad \Delta_r H_m^\circ \qquad (1)$$

TABLE 1

Molar enthalpies of reaction and solution in $TiCl_3 + HCl$ (solvent) with $KCl/KClO_3$ and KBr/KBr_3 systems at 298.15 K

i	Compound	Calorimetric solvent	Solution	$\Delta_i H_m^\circ$ kJ mol^{-1}	
				$KCl/KClO_3$	$KBr/KBrO_3$
1	opo(c)	Solvent	A_1	-242.57 ± 0.70	-242.16 ± 0.72
2	KX(c)	A_1	A_2	18.51 ± 0.03	18.40 ± 0.30
3	KXO_3(c)	Solvent	B_1	-747.39 ± 0.46	-747.43 ± 1.12
4	mpy(l)	B_1	B_2	-45.89 ± 0.21	-45.31 ± 0.41
1	mpo(c)	Solvent	C_1	-235.76 ± 0.70	-237.28 ± 0.68
2	KX(c)	C_1	C_2	19.21 ± 0.06	19.20 ± 0.27
3	KXO_3(c)	Solvent	D_1	-747.48 ± 0.50	-747.29 ± 1.09
4	mpy(l)	D_1	D_2	-46.17 ± 0.18	-46.33 ± 0.39
1	ppo(c)	Solvent	E_1	-243.00 ± 0.77	-242.17 ± 0.71
2	KX(c)	E_1	E_2	18.55 ± 0.06	18.42 ± 0.29
3	KXO_3(c)	Solvent	F_1	-747.41 ± 0.39	-747.22 ± 1.11
4	ppy(l)	F_1	F_2	-46.00 ± 0.30	-45.47 ± 0.39
1	teo(c)	Solvent	G_1	-501.13 ± 0.77	-500.12 ± 0.89
2	KX(c)	G_1	G_2	-23.31 ± 0.31	-22.80 ± 0.29
3	KXO_3(c)	Solvent	H_1	-746.39 ± 0.91	-744.91 ± 1.01
4	te(l)	H_1	H_2	-136.21 ± 0.29	-134.11 ± 0.39
1	tbo(c)	Solvent	I_1	-629.32 ± 0.91	-628.29 ± 0.70
2	KX(c)	I_1	I_2	-24.31 ± 0.32	-23.50 ± 0.30
3	KXO_3(c)	Solvent	J_1	-747.31 ± 0.45	-745.40 ± 1.12
4	tb(l)	J_1	J_2	-103.11 ± 0.42	-101.90 ± 0.40

The crystalline *N*-oxide compound (LO) is reduced to the respective amine (L); two experimental data series derive from the use of $KCl/KClO_3$ and $KBr/KBrO_3$ systems. $\Delta_r H_m^\circ$ values for both systems were obtained by measuring the enthalpy of solution of each reactant and product in the calorimetric solvent. The final solution resulting from dissolution of the reactants produces the same composition as that from the dissolution of the products. For each amine *N*-oxide, the individual enthalpy obtained for both systems are listed in Table 1. From these values, the enthalpies for each thermochemical reaction were calculated as

$$\Delta_r H_m^\circ = 3\Delta_1 H_m^\circ + \Delta_2 H_m^\circ - \Delta_3 H_m^\circ - 3\Delta_4 H_m^\circ \qquad (2)$$

These values are shown in Table 2.

The standard enthalpies of formation of all *N*-oxide compounds were calculated using the expression

$$3\Delta_f H_m^\circ(\mathrm{LO(c)}) = \Delta_f H_m^\circ(\mathrm{KXO_3(c)}) + 3\Delta_f H_m^\circ(\mathrm{L(l)}) - \Delta_f H_m^\circ(\mathrm{KX(c)}) - \Delta_r H_m^\circ \qquad (3)$$

TABLE 2

Standard molar enthalpies (kJ mol^{-1}) of reaction ($\Delta_r H_m^\circ$), formation ($\Delta_f H_m^\circ$) and the mean of formation ($\overline{\Delta_f H_m^\circ}$) for KCl/KClO$_3$ and KBr/KBrO$_3$ systems

Compound	KCl/KClO$_3$ system		KBr/KBrO$_3$ system		$\overline{\Delta_f H_m^\circ}$
	$\Delta_r H_m^\circ$	$\Delta_f H_m^\circ$	$\Delta_r H_m^\circ$	$\Delta_f H_m^\circ$	
opo	175.86 ± 2.24	11.1 ± 1.2	175.28 ± 2.74	9.5 ± 1.2	10.3 ± 0.8
mpo	197.92 ± 2.23	8.9 ± 1.0	193.64 ± 2.60	8.6 ± 1.1	8.8 ± 0.7
ppo	174.96 ± 2.51	13.9 ± 1.2	175.54 ± 2.69	11.9 ± 1.3	12.9 ± 0.9
teo	−371.68 ± 2.65	9.2 ± 1.1	−375.92 ± 3.10	8.8 ± 1.2	9.0 ± 0.8
tbo	−855.63 ± 3.06	16.6 ± 1.6	−857.27 ± 2.68	15.4 ± 1.5	16.0 ± 1.1

TABLE 3

Auxiliary data (kJ mol^{-1})

Compound	$\Delta_f H_m^\circ$	Reference
KCl(c)	−436.75 ± 0.01	10
KBr(c)	−393.80 ± 0.01	10
KClO$_3$(c)	−397.7 ± 0.1	10
KBrO$_3$(c)	−360.2 ± 0.1	10
opy	56.7 ± 0.8	2
mpy	61.9 ± 0.6	2
ppy	59.2 ± 0.9	2
te	−127.7 ± 0.6	2
tb	−281.6 ± 1.2	2

and the auxiliary data of Table 3. Two distinct series of values of $\Delta_f H_m^\circ$ are shown in Table 2. For the KCl/KClO$_3$ system, the $\Delta_r H_m^\circ$ values are somewhat higher. This tendency was first observed by us [3] in pyridine *N*-oxide and 2,2′-pyridine *N*,*N*′-oxide determinations, and is also evident in other pyridine *N*-oxide determinations [4]. The weighted mean values $\overline{\Delta_f H_m^\circ}$ are also listed in Table 2. This should be regarded as the best value for these amine *N*-oxides compounds.

In conclusion, the reduction properties of *N*-oxides might be successfully explored by solution-reaction calorimetry to determine the standard enthalpy of formation of these kinds of compounds, which cause some difficulties in combustion calorimetry.

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