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STANDARD ENTHALPIES OF FORMATION OF n-PROPYLCHLOROFORMATE AND BENZYL CHLOROFORMATE VIA SOLUTION CALORIMETRY

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ABSTRACT

Enthalpies of hydrolysis in aqueous sodium hydroxide of 1:4 dioxan solutions of n-propylchloroformate and of benzylchloroformate at 298.15 K have been measured using an isoperibol calorimeter. Values of standard enthalpies of formation at 298.15 K of -533.40 ± 0.76 and -375.24 ± 1.09 kJ mol^{-1} have been calculated for $C_3H_7OCOCl(1)$ and $C_6H_5CH_2OCOCl(1)$, respectively.

INTRODUCTION

Alkyl and aryl chloroformates, ROCOCl, are readily synthesized [1,2] and numerous kinetic studies, in both aqueous and non-aqueous media, have been reported [3,4]. Thermochemical data, however, are sparse [5] and none exist for the title compounds.

EXPERIMENTAL

Reagents

A commercial sample (Koch-Light) of n-propylchloroformate was distilled under dry nitrogen using a 60 cm^3 fractionating column. The middle fraction boiled at 114.2 °C (literature value [6] is 114.4–114.5 °C). Titrimetric estimation of chlorine after aqueous hydrolysis indicated a purity of ca. 99.8%.

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Benzylchloroformate (Eastman-Kodak) was fractionated under reduced pressure: a middle fraction boiled at 75 °C at 1–2 mmHg (literature value [7] is 76 °C to 78 °C at 1–2 mmHg). Titrimetric estimation of chlorine after aqueous hydrolysis indicated a purity of ca. 99.4%.

Samples of both compounds were stored under nitrogen in desiccators.

Apparatus and method

A commercial calorimeter (LKB-8700 Precision Calorimeter System) with a 100 cm^3 calorimeter vessel at 298.15 K was used throughout. The system was periodically and successfully checked using the neutralization of tris-hydroxymethylaminomethane (THAM) in aqueous hydrochloric acid, and the solution of THAM in aqueous sodium hydroxide, as test reactions [8] for, respectively, exothermic and endothermic processes.

Calorimetric reaction

Although chloroformates are quantitatively hydrolysed in aqueous base to chloride, carbonate, and the appropriate alcohol, their limited aqueous miscibility renders the reaction too slow for isoperibol calorimetry. Hence, known masses of chloroformates were pre-dissolved in known masses of rigorously-dried 1 : 4 dioxan (D) in ampoules. Subsequent reaction, using excess NaOH (1 mol l^{-1}) as calorimetric liquid, was satisfactorily rapid; typically $t_{1/2} \leqslant 2$ min. The calorimetric reaction is hence

$$[\mathrm{ROCOCl} \cdot x\mathrm{D}](\mathrm{l}) + [(y+3)\mathrm{NaOH}](\mathrm{aq}) \rightarrow [\mathrm{ROH} + \mathrm{NACl} + \mathrm{Na_2CO_3} + x\mathrm{D} + y\mathrm{NaOH}](\mathrm{aq}) \qquad (1)$$

RESULTS

If the enthalpy change associated with the calorimetric reaction is Q, then $Q = n'\Delta H_1^{\ominus} + n''\Delta H_2^{\ominus}$, where n' and n'' are the number of moles of chloroformate and D, respectively, and $\Delta H_1^{\ominus}$ and $\Delta H_2^{\ominus}$ are the molar enthalpy changes corresponding to the hydrolysis of chloroformate and the dissolution of dioxan, respectively, each in aqueous sodium hydroxide. Separate calorimetric measurements were made for the latter and are collated in Table 1. No significant dilution effect is apparent, and we hence report $\Delta H_2^{\ominus} = -9.475 \pm 0.003$ kJ mol^{-1}. Collated results for the calorimetric reaction are given in Table 2, whence we derive, for n-propylchloroformate and benzylchloroformate, respectively, $\Delta H_1^{\ominus} = -228.89 \pm 0.31$ and $\Delta H_1^{\ominus} = -178.79 \pm 0.71$, kJ mol^{-1}. Additional ancillary solubility measurements in 1.0 M NaOH are collated in Table 3 and include: sodium

TABLE 1

Enthalpy of solution of 1 : 4 dioxan in aqueous NaOH (100 cm^3, 1.0 M) at 298.15 K

1 : 4 dioxan (g)	n [a]	$-\Delta H_2^\ominus$ (kJ mol^{-1})
0.72134	679	9.4781
0.53641	913	9.475
0.47499	1031	9.473
0.48350	1013	9.475

Mean $\Delta H_2^\ominus = -9.475 \pm 0.003$

[a] Mole ratio, solvent to solute.

TABLE 2

Enthalpies of hydrolysis of benzyl chloroformate (a) and of n-propyl chloroformate (b) in 1 : 4 dioxan, and solution by excess sodium hydroxide (100 cm^3, 1 mol l^{-1}) at 298.15 K (D)

a (g)	D (g)	$-Q_h$ (J)	$-\Delta H_1^\ominus$ (kJ mol^{-1}) [a]	b (g)	D (g)	$-Q_h$ (J)	$-\Delta H_1^\ominus$ (kJ mol^{-1}) [b]
0.02562	0.58219	89.328	177.902	0.09685	0.61016	108.7	228.62
0.01806	0.53555	76.521	179.126	0.07385	0.40028	137.9	228.88
0.02347	0.63918	93.342	178.910	0.11761	0.34370	64.95	229.10
0.01927	0.52110	76.242	178.909	0.03476	0.57829	156.7	228.96
0.02576	0.66299	98.360	179.125				

[a] Mean = -178.79 ± 0.71 kJ mol^{-1}.
[b] Mean = -228.89 ± 0.31 kJ mol^{-1}.

carbonate, sodium chloride, $\Delta H_3^\ominus$ and $\Delta H_4^\ominus$, respectively, and n-propanol and benzyl alcohol, $\Delta H_5^\ominus$ and $\Delta H_5^\ominus$, respectively. Solution measurements in 1 : 4 dioxan for n-propylchloroformate and benzylchloroformate are $\Delta H_6^\ominus$ and $\Delta H_6^\ominus$, respectively.

Ancillary values of standard enthalpies of formation (kJ mol^{-1}, 298.15 K) taken from standard sources [9–11] are: NaCl(c), -411.270 ± 0.109; Na_2CO_3(c), -1129.18 ± 0.23; NaOH(c), -425.576 ± 0.079; H_2O(l), -285.830 ± 0.042; C_3H_7OH(l), -302.70 ± 0.60; $C_6H_5CH_2OH$(l), -114.80 ± 0.70; $\Delta H_{sol}^\ominus$ (NaOH, 1 mol l^{-1}) = -42.480 ± 0.010.

Values of the standard enthalpies of formation were then calculated as follows: *

$$\begin{aligned}\Delta H_f^\ominus(C_3H_7OCOCl)(l) &= \Delta H_f^\ominus(C_3H_7OH)(l) + \Delta H_5^\ominus + \Delta H_f^\ominus NaCl(c) \\ &+ \Delta H_4^\ominus + \Delta H_f^\ominus Na_2CO_3(c) + \Delta H_3^\ominus + \Delta H_f^\ominus H_2O(l) \\ &- 3[\Delta H_f^\ominus NaOH(c) + \Delta H_{sol}^\ominus(NaOH,c,\ 1\ mol\ l^{-1})](aq) \\ &- \Delta H_6^\ominus - \Delta H_1^\ominus = -533.40 \pm 0.76\ kJ\ mol^{-1} \qquad (2)\end{aligned}$$

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* Confidence values are calculated using Student's t values at the 95% level.

TABLE 3

Mean enthalpies of solution at 298.15 K

$-\Delta H_3$ (J)	ΔH_4 (J)	$-\Delta H_5$ (J)	ΔH_6 (J)	$\Delta H_5'$ (J)	$-\Delta H_6'$ (J)
27.86 ± 0.31	2.73 ± 0.02	8.45 ± 0.13	0.90 ± 0.056	0.49 ± 0.01	1.52 ± 0.01
$2034 \leqslant n \leqslant 4001$ [a]	$619 \leqslant n \leqslant 1186$	$1044 \leqslant n \leqslant 7669$	$211 \leqslant n \leqslant 723$	$1685 \leqslant n \leqslant 2183$	$204 \leqslant n \leqslant 218$
4 [b]	3	6	4	4	4

[a] Mole ratio, solvent to solute.

[b] Number of measurements.

$$\begin{aligned}\Delta H_f^{\ominus}(C_6H_5CH_2OCOCl)(l) &= \Delta H_f^{\ominus}(C_6H_5OH)(l) + \Delta H_5^{\ominus} + \Delta H_f^{\ominus}NaCl(c)\\ &+ \Delta H_4^{\ominus} + H_f^0 Na_2CO_3(c) + \Delta H_3^{\ominus} + \Delta H_f^{\ominus}H_2O(l) - 3[\Delta H_f^{\ominus}NaOH(c)\\ &+ \Delta H_{sol}^{\ominus}\ (NaOH, 1\ mol\ l^{-1})]\,\Delta H_6^{\ominus} - \Delta H_1^{\ominus}\\ &= -376.24 \pm 1.09\ kJ\ mol^{-1} \qquad (3)\end{aligned}$$

Values of gas-phase enthalpies and bond energy calculations rely on accurate values of enthalpies of vaporization, and will be presented elsewhere.

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