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ENTHALPIES OF VAPORIZATION AND VAPOUR PRESSURES OF *n*-PROPYLCHLOROFORMATE AND BENZYLCHLOROFORMATE

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ABSTRACT

The enthalpies of vaporization of *n*-propylchloroformate and benzylchloroformate, 40.676 ±0.410 kJ mol^{-1} and 38.53±0.11 kJ mol^{-1} respectively, were derived from a series of measurements of vapour pressures in the range 293.17–303.66 K. An independent value for the enthalpy of vaporization of *n*-propylchloroformate, 40.742±0.403 kJ mol^{-1}, was determined using direct vaporization calorimetry. Bond energy parameters are discussed for these compounds.

INTRODUCTION

Esters of carbonochloridic acid, ClCOOH, are commonly called chloroformates. While preparative and chemical aspects have been extensively studied and reviewed [1,2], thermodynamic data are extremely sparse [3,4]. In this paper we report precise measurements, using vapour pressure and also calorimetric procedures, on *n*-propylchloroformate, C_3H_7OCOCl, and on benzylchloroformate, $C_6H_5CH_2OCOCl$.

EXPERIMENTAL

Materials

n-Propylchloroformate (Koch-Light) was fractionally distilled under dry nitrogen using a 60 cm column; the first and last 5 cm^3 of distillate were discarded. The middle fraction boiled at 114.2 ° C (lit. [5] 114.4–115 ° C). A sample was hydrolysed and analysed for chlorine using Volhard's method: a purity of 99.8% was indicated.

Benzylchloroformate (Eastman Kodak Company) was fractionally distilled under reduced pressure, and the fraction boiling at 75 ° C at 1–2 mmHg was collected (lit. [6] 76–78 ° C at 1–2 mmHg). Analysis for chlorine

(5 samples) via Volhard's method after prolonged hydrolysis using refluxing aqueous potassium hydroxide indicated a purity of 99.4%. Further details are reported elsewhere [7].

VAPOUR PRESSURE MEASUREMENTS

A Texas Instruments Bourdon-tube gauge (model 144-01) fitted with a type 11A capsule was employed. Rigorously purified benzene [8] was used as calibrant over the range 293.77–302.34 K; within this range the gauge factor, G, was found to vary with pressure, P (in Pascal), according to

$$p = G(114.531 \pm 0.099) + 0.255 \pm 0.041 \qquad (1)$$

Vapour pressures, p, were calculated using the Ambrose equation [9], and selected temperatures were maintained using the water bath thermostatted to $\pm 0.005\,^{\circ}\mathrm{C}$.

For both compounds results were well expressed by the formula $\ln p = A + B/T$, where p is in Pa and T is in K. From the Clapeyron equation the value of A is $\Delta H_v/\Delta ZR$, where ΔH_v is the enthalpy of vaporization and $\Delta Z = p(V_g - V_{liq})/RT$, where V_g and V_{liq} are molar volumes of vapour and

TABLE 1

Values of vapour pressures p of benzyl chloroformate as functions of temperature T

Experiment	Number of measurements	Range of p (Pa)	ΔH_v (kJ mol^{-1})	Mean T (K)
1	13	1291–2170	38.611	298.278
2	12	1329–2120	38.535	298.512
3	13	1277–2130	38.509	298.840
4	12	1334–2013	38.387	298.900
5	20	1262–2537	38.593	298.338

[a] $\ln p = (22.977 \pm 0.037) - (4633.991 \pm 1.325)/T$.
$\Delta H_v[C_6H_5CH_2COCl(298.15\ K)] = 38.53 \pm 0.11$ kJ mol^{-1}.

TABLE 2

Values of vapour pressures p of n-propylchloroformate as functions of temperature T

Experiment	Number of measurements	Range of p (Pa)	ΔH_v (kJ mol^{-1})	Mean T (K)
1	14	2409–3998	40.4003	298.287
2	14	2360–3996	40.9552	298.055
3	14	2392–3878	40.3916	298.844
4	14	2322–3968	40.7487	298.835

$\ln p = (24.424 \pm 0.159) - (4886.208 \pm 52.869)/T$.
$\Delta H_v[C_3H_7OCOCl(198.15\ K)] = 40.676 \pm 0.410$ kJ mol^{-1}.

liquid respectively and R is the gas constant. The deviation of ΔZ from unity was estimated and found to be negligible. Correction to 298.15 K was made using Watson's equation [10].

$$\Delta H_{v,2} = \Delta H_{v,1}[(1 - T_{r,2})/(1 - T_{r,1})]^{n} \quad (2)$$

where $\Delta H_{v,1}$ and $\Delta H_{v,2}$ are enthalpies of vaporization and $T_{r,1}$ and $T_{r,2}$ are the reduced temperatures, calculated from Lydersen's increments [11]. The value of n lies between 0.3 and 0.4.

Collated results of vapour pressures, p, and enthalpies of vaporization, ΔH_v, for benzylchloroformate (five runs, 70 measurements) and *n*-propylchloroformate (four runs, 56 measurements) are given in Tables 1 and 2.

CALORIMETRY

A vaporization calorimeter was constructed, based on a design by Arnett, in which the amount of electrical energy needed to vaporize a measured amount of liquid was determined; full details are given elsewhere [7].

The performance of the calorimeter was assessed using benzene as a test substance. The value of $\Delta H_v^{\ominus}$ (198.15) found, 33.64 ± 0.13 kJ mol^{-1} is in good agreement with the accepted value [8], 33.94 ± 0.42 kJ mol^{-1}.

Collated values (five runs, 33 measurements) for *n*-propylchloroformate are given in Table 3. The mean value, +40.74 ± 0.40 kJ mol^{-1} is in excellent agreement with the value derived from vapour pressure measurements, viz. 40.68 ± 0.41 kJ mol^{-1}.

DISCUSSION

Using recently published [3] values of standard enthalpies of formation of liquid *n*-propyl chloroformate and liquid benzylchloformate, −524.396 ± 0.767 kJ mol^{-1} and −375.144 ± 1.09 kJ mol^{-1} respectively, and adding values for the enthalpies of vaporization derived from this work, 40.709 kJ

TABLE 3

Values of enthalpy of vaporization ΔH_v of *n*-propylchloroformate at 298.15 K

Experiment	Number of measurements	ΔH_v (kJ mol^{-1})
1	7	41.0567
2	7	40.2202
3	6	40.6756
4	6	40.9406
5	7	40.8142

$\Delta H_v[C_3H_7OCOCl(198.15\ K)] = 40.7415 \pm 0.403$ kJ mol^{-1}.

mol^{-1} and 38.53 kJ mol^{-1} respectively, we calculated gas-phase enthalpies of formation as: $\Delta H_f^\ominus[C_3H_7OCOCl(g)] = -492.7 \pm 0.76$ kJ mol^{-1} and $\Delta H_f[C_6H_5CH_2OCOCl(g)] = -336.71 \pm 1.09$ kJ mol^{-1}.

Application of bond energy schemes, e.g. that of Allen [12],is restricted owing to the impossibility of separating, in the group R–(CO)Cl, interactions involving R from those intrinsic to the –(CO)Cl group. The contribution of –(CO)Cl to $\Delta H_f^\ominus$(g) can be calculated using tabulated values for bond and bond-interaction parameters, but the value will implicitly contain contributions from the substituent R.

Application of Allen's scheme leads to a value of −310.7 kJ mol^{-1} for the contribution of the –(CO)Cl group to the overall enthalpy. A similar calculation made by Davies et al. [3] for ethyl chloroformate gave a value of −298 kJ mol^{-1} for the contribution of the –(CO)Cl group, which was compared with a value of −214.4 kJ mol^{-1} derived from data for acetyl chloride, CH_3COCl. Hence there is close agreement, viz. −86 kJ mol^{-1} and −84 kJ mol^{-1} respectively, between the differences in contributions of the (CO)Cl group in acetyl chloride, compared with that in *n*-propylchloroformate and ethylchloroformate, respectively. Thus, the alkoxy oxygen confers significant stabilization of the −(CO)Cl group compared with the alkyl carbon. A similar trend has been noted [3] when comparing the –(CO)CH_3 group in ethyl acetate and acetone. Since the Allen scheme does not include data for aromatic compounds, extension to benzylchloroformate is not possible.

Application of the Laidler bond energy scheme [7] leads to a value of −268.5 kJ mol^{-1} for the (CO)Cl contribution, based on our value of −336.7 kJ mol^{-1} for the standard enthalpy of gaseous benzylchloroformate. This is considerably more negative than the values obtained for ethylchloroformate and propylchloroformate, and presumably reflects the effect of the aromatic groups.

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