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# Standard enthalpies of combustion of the six dichlorophenols by rotating-bomb calorimetry

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The standard ($p^\circ = 0.1$ MPa) molar enthalpies of combustion in oxygen of each of the six dichlorophenols, at the temperature 298.15 K, were measured by rotating-bomb calorimetry from which the standard molar enthalpies of formation, in the crystalline phase were derived. The standard molar enthalpies of sublimation, at the temperature 298.15 K, were measured by microcalorimetry.

| | $-\Delta_f H^\circ_m(\mathrm{cr})/(\mathrm{kJ \cdot mol^{-1}})$ | $\Delta^g_{cr} H^\circ_m/(\mathrm{kJ \cdot mol^{-1}})$ |
|---|---|---|
| 2,3-dichlorophenol (2,3-$Cl_2C_6H_3OH$) | $223.3 \pm 1.1$ | $71.7 \pm 2.2$ |
| 2,4-dichlorophenol (2,4-$Cl_2C_6H_3OH$) | $226.4 \pm 1.5$ | $70.1 \pm 1.1$ |
| 2,5-dichlorophenol (2,5-$Cl_2C_6H_3OH$) | $232.0 \pm 1.2$ | $73.6 \pm 2.1$ |
| 2,6-dichlorophenol (2,6-$Cl_2C_6H_3OH$) | $222.1 \pm 1.1$ | $75.8 \pm 1.0$ |
| 3,4-dichlorophenol (3,4-$Cl_2C_6H_3OH$) | $231.6 \pm 1.1$ | $81.3 \pm 2.3$ |
| 3,5-dichlorophenol (3,5-$Cl_2C_6H_3OH$) | $231.0 \pm 1.0$ | $82.8 \pm 1.1$ |

The derived standard molar enthalpies of formation of the gaseous compounds were compared with values estimated assuming the enthalpy increment for substitution of chlorine in phenol to be the same as for substitution into benzene.

## 1. Introduction

The availability of thermodynamic quantities is of fundamental importance to the understanding and investigation of many problems of considerable importance associated with practical combustion, such as, for example, destruction of waste materials in incinerators. However, very few experimental thermodynamic quantities are available for a large number of compounds and although simple estimation schemes for these are possible, they need to be based on reliable experimental results for key compounds.

Among the atmospheric pollutants there are compounds which either are known to be precursors, leading, under appropriate conditions, to the formation of toxic substances, or are themselves extremely toxic(1) like the dioxins. Several chlorinated phenols are commonly used(2) as pesticide components, insecticides, and antimicrobial agents, and are known to be precursors to the formation of chlorinated dioxins,(1) but energies of combustion are known only for 3-chlorophenol,(3)

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4-chlorophenol,(3) and pentachlorophenol.(4) No thermochemical values are available for the other chlorophenols, in particular for any of the dichlorophenols, which also have important chemical and industrial applications. For instance 2,4-dichlorophenol is a key intermediate in the synthesis(5) of the herbicide 2,4-D, {(2,4-dichlorophenoxy)acetic acid}, and 2,6-dichlorophenol is important in isolation and identification as the sex pheromone of the lone-star tick.(6)

In view of the little knowledge and the large importance of thermochemical quantities for these compounds, we have measured the standard energy of combustion of each of the six crystalline isomers of dichlorophenol as well as their standard enthalpies of sublimation at the temperature 298.15 K.

## 2. Experimental

The six dichlorophenols (Aldrich Chemical) studied in this work were purified by repeated sublimation at reduced pressure and the purities of the samples were checked by C,H,O microanalyses. 4-Chlorobenzoic acid (Aldrich Chemical) was purified by repeated crystallization from butanone and the purity was checked by C,H,O microanalyses.

The enthalpies of combustion were measured using a rotating-bomb calorimeter formerly developed by Professor Stig Sunner at the University of Lund, Sweden. Since a complete description will be published later, only a brief description of the apparatus will be given here. The twin-valve combustion bomb is of stainless steel, with an internal volume of 0.258 $\mathrm{dm}^3$ and wall thickness 1 cm. The bomb is lined with platinum and the internal fittings are machined from platinum. In each experiment the bomb is suspended from the lid of the calorimeter can. Water was added to the calorimeter from a weighed glass vessel; as the mass of water differed slightly for each experiment, corrections were made to the energy equivalent of the calorimeter for the deviation from the average mass: 5222.5 g.

Calorimeter temperatures were measured to $\pm 10^{-4}$ K at time intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz thermometer interfaced to an Olivetti M 250E microcomputer programmed to compute the adiabatic temperature change.

The isothermal jacket consisted of a thermostatic bath containing a cavity of exactly the same shape as the calorimeter can, but 1 cm larger in each dimension, enclosed by a hollow lid. The jacket and lid were filled with water maintained at a temperature $T \approx 303.5$ K to $\pm 10^{-4}$ K using a temperature controller (Tronac PTC 41), so that the calorimeter was completely surrounded by a constant-temperature enclosure.

The electrical energy for ignition was determined from the change in potential difference across a 1400 μF capacitor on discharge through the platinum wire. For each experiment, the ignition temperature was chosen so that the final temperature would be close to 298.15 K. Fore-period readings were taken for about 20 min, the main-period was about 25 min, and the after-period about 20 min.

The rotating mechanism allowed simultaneous axial and end-over-end rotation of the bomb. Rotation of the bomb was started when the temperature rise in the main-period reached about 0.6 of its final value and was continued throughout the rest of the experiment. It has been shown(7) that by adopting this procedure the frictional work done by the rotation of the bomb is automatically included in the corrections for the work of stirring and for the heat exchanged with the surrounding thermostat.

The energy equivalent of the calorimeter was determined using the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard CRM-190n) having a specific energy of combustion, under standard bomb conditions of $-(26433.0 \pm 3.9)\ \mathrm{J \cdot g^{-1}}$, hence $\Delta_c u^\circ = -(26412.6 \pm 3.9)\ \mathrm{J \cdot g^{-1}}$. Combustion was carried out in oxygen at the pressure 3.04 MPa in the presence of a volume $1.00\ \mathrm{cm^3}$ of water added to the bomb. Two sets of at least six calibrations experiments were performed, due to minor changes in the calorimeter. From these calibration experiments, the values of the energy equivalent of the calorimeter were: $\varepsilon(\text{calor}) = (25181.3 \pm 2.0)\ \mathrm{J \cdot K^{-1}}$ and $\varepsilon(\text{calor}) = (25177.5 \pm 1.7)\ \mathrm{J \cdot K^{-1}}$, where the uncertainties quoted are the standard deviations of the mean; $\varepsilon(\text{calor}) = (25181.3 \pm 2.0)\ \mathrm{J \cdot K^{-1}}$ was used for the combustion experiments of 4-chlorobenzoic acid and 2,4-dichlorophenol and $\varepsilon(\text{calor}) = (25177.5 \pm 1.7)\ \mathrm{J \cdot K^{-1}}$ for all the other dichlorophenols experiments. Table 1 lists results for a typical calibration experiment where the terms are as previously defined.(8) 4-Chlorobenzoic acid was recommended as a test substance for bomb-combustion calorimetry of organic chlorine compounds.(9) Hence, the accuracy of the calorimeter was checked by measuring the energy of combustion of 4-chlorobenzoic acid. The samples were burned, in pellet form, in oxygen at the pressure 3.04 MPa and with a volume $20.00\ \mathrm{cm^3}$ of $0.07869\ \mathrm{mol \cdot dm^{-3}}$ $As_2O_3(aq)$ in the bomb. The standard molar enthalpy of combustion obtained was $\Delta_c H_m^\circ = -(3064.5 \pm 1.2)\ \mathrm{kJ \cdot mol^{-1}}$, in good agreement with the values of Hu *et al.*,(9) for three series of measurements, under widely varied conditions, using three different rotating-bomb calorimeters: $\{-(3062.98 \pm 0.75), -(3062.8 \pm 1.0)$ and $-(3062.94 \pm 0.84)\}\ \mathrm{kJ \cdot mol^{-1}}$. Values of $\Delta_c H_m^\circ$ refer to the reaction with

TABLE 1. Typical combustion results ($p^\circ = 0.1$ MPa) for B = $Cl_2C_6H_3OH$

| | Calibration | 2,3-B | 2,4-B | 2,5-B | 2,6-B | 3,4-B | 3,5-B |
|---|---|---|---|---|---|---|---|
| $m(\text{BA})/\text{g}$ | 1.09741 | — | — | — | — | — | — |
| $m'(\text{cpd.})/\text{g}$ | — | 0.94192 | 1.30803 | 0.95301 | 0.94740 | 0.95882 | 0.97681 |
| $m''(\text{Melinex})/\text{g}$ | — | 0.05743 | 0.05578 | 0.05676 | 0.05594 | 0.05528 | 0.05124 |
| $m'''(\text{fuse})/\text{g}$ | 0.00410 | 0.00449 | 0.00421 | 0.00447 | 0.00327 | 0.00446 | 0.00435 |
| $\Delta T_{ad}/\text{K}$ | 1.15429 | 0.70386 | 0.95362 | 0.70788 | 0.70535 | 0.71109 | 0.71861 |
| $\varepsilon_i(\text{cont.})/\text{K}$ | 13.84 | 177.82 | 177.84 | 178.07 | 177.90 | 177.83 | 177.93 |
| $\varepsilon_f(\text{cont.})/\text{K}$ | 15.01 | 172.83 | 172.22 | 172.78 | 172.79 | 172.81 | 172.82 |
| $\Delta m(H_2O)/\text{g}$ | +0.2 | −4.8 | −0.1 | −0.1 | +0.9 | +0.4 | +0.9 |
| $-\Delta U(\text{IBP})/\text{J}$ | 29008.81 | 17832.10 | 24182.33 | 17948.23 | 17886.41 | 18030.38 | 18222.79 |
| $\Delta U(HNO_3)/\text{J}$ | 4.42 | 2.88 | 1.65 | 3.01 | 2.74 | 2.75 | 2.74 |
| $\Delta U(As_2O_3)/\text{J}$ | — | 438.21 | 656.10 | 434.56 | 443.14 | 442.05 | 423.94 |
| $\Delta U(H_2PtCl_6)/\text{J}$ | — | 1.04 | 1.18 | 1.17 | 1.25 | 1.34 | 1.14 |
| $\Delta U(\text{ign.})/\text{J}$ | 0.63 | 0.59 | 0.59 | 0.46 | 0.77 | 0.81 | 0.77 |
| $\Delta U_\Sigma/\text{J}$ | — | 73.93 | 98.46 | 74.11 | 73.86 | 74.78 | 75.29 |
| $\varepsilon(\text{calor})/(\mathrm{J \cdot K^{-1}})$ | 25177.97 | 25177.4 | 25180.9 | 25177.1 | 25181.3 | 25179.2 | 25181.3 |
| $-m''\Delta_c u^\circ(\text{Melinex})/\text{J}$ | — | 1315.17 | 1277.47 | 1299.87 | 1281.14 | 1266.05 | 1173.54 |
| $-m'''\Delta_c u^\circ(\text{fuse})/\text{J}$ | 66.58 | 72.93 | 68.37 | 72.59 | 53.10 | 72.43 | 70.64 |
| $-\Delta_c u^\circ(\text{cpd.})/(\mathrm{J \cdot g^{-1}})$ | — | 16910.08 | 16879.66 | 16854.93 | 16921.24 | 16865.50 | 16866.64 |

$HCl \cdot 600H_2O(l)$ as the chlorine-containing product in the final state. Within the precision of the analytical method, no evidence was found for oxidation of the diarsenic trioxide solution after the bomb had been charged with oxygen at the pressure 3.04 MPa and left for a time up to 5 h at room temperature. The dichlorophenols were burned, in pellet form, in oxygen at the pressure 3.04 MPa. Since the dichlorophenols are very volatile, it was necessary to seal the pellets of the compounds in polyester bags made from Melinex (0.025 mm thickness) using the technique described by Skinner and Snelson(10) who determined the specific energy of combustion of dry Melinex as $\Delta_c u^\circ = -(22902 \pm 5)\ J \cdot g^{-1}$. This value has been confirmed by combustion of Melinex samples in our laboratory. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032) and the mass of carbon dioxide produced from it was calculated using the factor previously reported.(10) As 2,4-dichlorophenol is very hygroscopic,(11) for this compound the pelleting procedure was performed as rapidly as possible and each pellet was stored over phosphorus pentoxide in a desiccator for several days. A volume of 40.00 $cm^3$ of aqueous solution $As_2O_3$ was placed in the bomb to reduce to hydrochloric acid the free chlorine produced by the combustion. Several solutions of $As_2O_3$ were used during the combustion studies of these compounds; the concentrations of the different solutions were close to 0.09 $mol \cdot dm^{-3}$.

For the cotton thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $\Delta_c u^\circ = -16250\ J \cdot g^{-1}$.(8) The nitric acid formed was determined using the Devarda's-alloy method(12) and corrections were based on $-59.7\ kJ \cdot mol^{-1}$ for the molar energy of formation of 0.1 $mol \cdot dm^{-3}$ $HNO_3(aq)$ from $O_2(g)$, $N_2(g)$, and $H_2O(l)$.(13) The extent of oxidation of the diarsenic trioxide was determined by titration with standardized iodine solution. The amount of $H_2PtCl_6(aq)$ was determined from the loss of mass of platinum parts of the system. An estimated value of $(\partial u/\partial p)_T = -0.1\ J \cdot g^{-1} \cdot MPa^{-1}$ at the temperature 298.15 K was assumed for all the dichlorophenols and the literature value:(9) $(\partial u/\partial p)_T = -0.16\ J \cdot g^{-1} \cdot MPa^{-1}$ for 4-chlorobenzoic acid was used. $\Delta U_\Sigma$, the standard state correction, and the heat capacities of the bomb contents, $\varepsilon_i$ and $\varepsilon_f$, were calculated by the procedure given by Hubbard *et al.*(8) using the solubility constants and energies of solution of $O_2$ and $CO_2$ as given by Hu *et al.*(9)

The standard molar enthalpies of sublimation of the compounds were measured by the "vacuum sublimation" drop-microcalorimetric method.(14) Samples of mass about 7 mg, contained in a small thin glass capillary tube sealed at one end, were dropped at room temperature into the hot reaction vessel in the Calvet High-Temperature Microcalorimeter (Setaram, Lyon, France) held at the temperature 364 K, and were then removed from the hot zone by vacuum sublimation. The microcalorimeter was calibrated *in situ* by making use of the reported standard molar enthalpy of sublimation of naphthalene.(15) From the experimental results the standard molar enthalpy of sublimation at the temperature 298.15 K, $\Delta_{cr}^{g} H_m^\circ(298.15\ K)$, was calculated using $\Delta_{298.15\ K}^{364\ K} H_m^\circ(g) = 10.15\ kJ \cdot mol^{-1}$ estimated by group-additivity methods, *i.e.* from {phenol + 2(chlorobenzene) − 2(benzene)}, using values of Stull *et al.*(15)

The relative atomic masses were those recommended by the IUPAC in 1991.(16)

TABLE 2. Values of $\Delta_c u^\circ$ at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for B = $Cl_2C_6H_3OH$

| 2.3-B | 2.4-B | 2.5-B | 2,6-B | 3.4-B | 3,5-B |
|---|---|---|---|---|---|
| $-\Delta_c u^\circ/(J \cdot g^{-1})$ | | | | | |
| 16915.56 | 16904.88 | 16850.56 | 16915.46 | 16860.31 | 16866.38 |
| 16910.08 | 16891.83 | 16864.32 | 16915.04 | 16861.89 | 16868.09 |
| 16911.44 | 16879.66 | 16861.95 | 16921.24 | 16854.14 | 16865.50 |
| 16904.99 | 16893.64 | 16865.11 | 16922.84 | 16864.68 | 16866.64 |
| 16917.12 | 16892.23 | 16854.93 | 16923.41 | 16866.16 | 16861.88 |
| 16916.73 | 16897.44 | 16862.19 | 16921.30 | 16865.50 | 16864.80 |
| $\langle -\Delta_c u^\circ/(J \cdot g^{-1}) \rangle$ | | | | | |
| 16912.6 ± 1.9 | 16893.3 ± 3.4 | 16859.8 ± 2.4 | 16919.9 ± 1.5 | 16862.1 ± 1.8 | 16865.5 ± 0.9 |

Carbon, hydrogen, and oxygen analyses were carried out at the Department of Chemistry, Faculty of Science, University of Porto, Portugal.

## 3. Results and discussion

Table 1 lists typical combustion results; the terms are as defined previously;(8) $\Delta m(H_2O)$ is the deviation in the mass of water added to the calorimeter from 5222.5 g. Table 2 lists the individual values of $\Delta_c u^\circ$ together with the mean and its standard deviation. $\Delta_c u^\circ$ refers to the combustion reaction:

$$C_6H_4OCl_2(cr) + 6O_2(g) + 1199H_2O(l) = 6CO_2(g) + 2HCl \cdot 600H_2O(l), \qquad (1)$$

Table 3 lists the derived standard molar enthalpies of combustion and the standard molar enthalpies of formation of the six dichlorophenols in the crystalline state at the temperature 298.15 K. In accordance with normal thermochemical practice, the uncertainties assigned are twice the overall standard deviation of the mean and include the uncertainties in calibration and in the values of the auxiliary quantities used. To derive $\Delta_f H_m^\circ$ from $\Delta_c H_m^\circ$, the standard molar enthalpies of formation of $H_2O(l)$: $-(285.83 \pm 0.04)\ kJ \cdot mol^{-1}$,(17) $CO_2(g)$: $-(393.51 \pm 0.13)\ kJ \cdot mol^{-1}$,(17) and HCl in $600H_2O(l)$: $-(166.619 \pm 0.005)\ kJ \cdot mol^{-1}$,(13) were used.

The individual values of the standard molar enthalpies of sublimation, at $T = 298.15$ K, together with the mean and twice the standard deviation of the mean are given in table 4. The derived standard molar enthalpies of formation in the crystalline state, standard molar enthalpies of sublimation, and standard molar enthalpies in the gaseous state for the six dichlorophenols, are summarized in table 5.

A decade ago, Shaub(18) described a procedure for estimating the standard enthalpies of formation of aromatic compounds, and applied it to chlorinated

TABLE 3. Derived standard molar values at $T = 298.15$ K ($p^\circ = 0.1$ MPa) for B = $Cl_2C_6H_3OH$

| | 2,3-B | 2,4-B | 2,5-B | 2,6-B | 3,4-B | 3,5-B |
|---|---|---|---|---|---|---|
| $-\Delta_c H_m^\circ(cr)/(kJ \cdot mol^{-1})$ | 2756.8 ± 0.8 | 2753.7 ± 1.3 | 2748.1 ± 0.9 | 2758.0 ± 0.7 | 2748.6 ± 0.8 | 2749.1 ± 0.6 |
| $-\Delta_f H_m^\circ(cr)/(kJ \cdot mol^{-1})$ | 223.3 ± 1.1 | 226.4 ± 1.5 | 232.0 ± 1.2 | 222.1 ± 1.1 | 231.5 ± 1.1 | 231.0 ± 1.0 |

TABLE 4. Results of calorimetric standard molar enthalpies of sublimation of $B = Cl_2C_6H_3OH$ at $T = 298.15$ K

| 2,3-B | 2,4-B | 2,5-B | 2,6-B | 3,4-B | 3,5-B |
|---|---|---|---|---|---|
| | | $\Delta_{cr}^{g}H_m^{\circ}/(kJ \cdot mol^{-1})$ | | | |
| 74.35 | 69.90 | 72.95 | 76.22 | 79.26 | 84.26 |
| 69.49 | 69.10 | 73.26 | 77.55 | 79.55 | 82.69 |
| 68.40 | 69.07 | 70.80 | 74.74 | 84.59 | 83.77 |
| 74.68 | 70.03 | 73.54 | 74.96 | 79.50 | 81.93 |
| 70.41 | 72.17 | 77.25 | 75.45 | 83.67 | 81.32 |
| 73.12 | | | | | |
| | | $\langle\Delta_{cr}^{g}H_m^{\circ}/(kJ \cdot mol^{-1})\rangle$ | | | |
| 71.7 ± 2.2 | 70.1 ± 1.1 | 73.6 ± 2.1 | 75.8 ± 1.0 | 81.3 ± 2.3 | 82.8 ± 1.1 |

benzenes, phenols, and dioxins, for which he estimated(18) the following values for $\Delta_f H_m^{\circ}(g)/(kJ \cdot mol^{-1})$: for 2,3-$Cl_2C_6H_3OH$, $-(178.6)$; for 2,4-$Cl_2C_6H_3OH$, $-(175.6)$; for 2,5-$Cl_2C_6H_3OH$, $-(185.1)$; for 2,6-$Cl_2C_6H_3OH$, $-(106.0)$; and for 3,4-$Cl_2C_6H_3OH$, $-(194.4)$. These estimated values differ considerably from the experimental ones reported in this paper, being all more negative by (20 to 44) $kJ \cdot mol^{-1}$, with the exception of that estimated for 2,6-dichlorophenol which is 40 $kJ \cdot mol^{-1}$ more positive than the experimental value. This shows that Shaub's procedure yields poor estimates which should be used only with great reserve.

The derived standard molar enthalpies of formation of the gaseous compounds can also be compared with values estimated using the Cox scheme,(19) by assuming that each group when substituted into the benzene ring produces a characteristic increment in $\Delta_f H_m^{\circ}(g)$, *i.e.* for the dichlorophenols, from $\Delta_f H_m^{\circ}(g)\{C_6H_5OH + 2(C_6H_5Cl) - 2(C_6H_6)\}$. Corrections terms of $+4\ kJ \cdot mol^{-1}$ for each *ortho*-pair of substituents and additionally $+4\ kJ \cdot mol^{-1}$ for each set of three substituents in positions 1, 2, 3 were applied. To obtain the estimated values the following $\Delta_f H_m^{\circ}(g)/(kJ \cdot mol^{-1})$ values were used: $C_6H_5OH$, $-(96.4 \pm 0.9)$; $C_6H_5Cl$, $(52.0 \pm 1.3)$; $C_6H_6$, $(82.6 \pm 0.7)$.(20) The comparison is made in table 6.

For the monochlorophenols, there is known the standard molar enthalpy of formation of two isomers: 3-chlorophenol, $\Delta_f H_m^{\circ}(cr) = -(206.4 \pm 8.4)\ kJ \cdot mol^{-1}$;(3) and 4-chlorophenol, $\Delta_f H_m^{\circ}(cr) = -(197.7 \pm 8.4)\ kJ \cdot mol^{-1}$.(3) We measured the enthalpies of sublimation of these compounds by the "vacuum sublimation" drop-microcalorimetric method and obtained, respectively, the values

TABLE 5. Derived standard molar values at $T = 298.15$ K

| | $-\Delta_f H_m^{\circ}(cr)/(kJ \cdot mol^{-1})$ | $\Delta_{cr}^{g}H_m^{\circ}/(kJ \cdot mol^{-1})$ | $-\Delta_f H_m^{\circ}(g)/(kJ \cdot mol^{-1})$ |
|---|---|---|---|
| 2,3-$Cl_2C_6H_3OH$ | 223.3 ± 1.1 | 71.7 ± 2.2 | 151.6 ± 2.5 |
| 2,4-$Cl_2C_6H_3OH$ | 226.4 ± 1.5 | 70.1 ± 1.1 | 156.3 ± 1.9 |
| 2,5-$Cl_2C_6H_3OH$ | 232.0 ± 1.2 | 73.6 ± 2.1 | 158.4 ± 2.4 |
| 2,6-$Cl_2C_6H_3OH$ | 222.1 ± 1.1 | 75.8 ± 1.0 | 146.3 ± 1.5 |
| 3,4-$Cl_2C_6H_3OH$ | 231.6 ± 1.1 | 81.3 ± 2.3 | 150.3 ± 2.5 |
| 3,5-$Cl_2C_6H_3OH$ | 231.0 ± 1.0 | 82.8 ± 1.1 | 148.2 ± 1.5 |

TABLE 6. Experimental and estimated values of $\Delta_f H^\circ_m(g)$ at $T = 298.15$ K

| | $\Delta_f H^\circ_m(g)/(kJ \cdot mol^{-1})$ | | $\frac{\Delta}{kJ \cdot mol^{-1}}$ |
|---|---|---|---|
| | Experimental | Estimated | |
| 2,3-$Cl_2C_6H_3OH$ | $-151.6 \pm 2.5$ | $-145.6 \pm 3.1$ | $-6.0 \pm 4.0$ |
| 2,4-$Cl_2C_6H_3OH$ | $-156.3 \pm 1.9$ | $-153.6 \pm 3.1$ | $-2.7 \pm 3.6$ |
| 2,5-$Cl_2C_6H_3OH$ | $-158.4 \pm 2.4$ | $-153.6 \pm 3.1$ | $-4.8 \pm 3.9$ |
| 2,6-$Cl_2C_6H_3OH$ | $-146.3 \pm 1.5$ | $-145.6 \pm 3.1$ | $-0.7 \pm 3.4$ |
| 3,4-$Cl_2C_6H_3OH$ | $-150.3 \pm 2.5$ | $-153.6 \pm 3.1$ | $+3.3 \pm 4.0$ |
| 3,5-$Cl_2C_6H_3OH$ | $-148.2 \pm 1.5$ | $-157.6 \pm 3.1$ | $+9.4 \pm 3.4$ |

$(69.4 \pm 1.8)$ kJ · mol$^{-1}$ and $(69.5 \pm 1.6)$ kJ · mol$^{-1}$, at $T = 298.15$ K. From the above results, the standard molar enthalpies of formation, in the gaseous phase were derived: $\Delta_f H^\circ_m(g)/(kJ \cdot mol^{-1})$: $-(137.0 \pm 8.6)$ for 3-chlorophenol and $-(128.2 \pm 8.6)$ for 4-chlorophenol. The application of the Cox scheme to these two monochlorophenols, using the same parameters as stated above for the dichlorophenols, leads to the estimated value of the standard molar enthalpy of formation of $-(127.0 \pm 1.8)$ kJ · mol$^{-1}$ for each of them.

Although high uncertainties ($\pm 8.4$ kJ · mol$^{-1}$) are associated with the experimental values of the standard molar enthalpies of formation of both crystalline monochlorophenols, it seems that the deviations $\Delta$ found between the experimental values and those estimated by the Cox scheme,(19) both for mono- and dichlorophenols, are less than $\pm 10$ kJ · mol$^{-1}$ giving support to the Cox scheme, which yields much more accurate predictions than the procedure suggested by Shaub.(18) However, the above results suggest that redetermination of the standard molar enthalpies of formation of the monochlorophenols, in the condensed phase, is desirable.

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## REFERENCES

1. Esposito, M. P.; Tiernan, T. O.; Dryden, F. E. *Dioxines*. EPA-600/2-80-197, EPA Industrial Environmental Research Laboratory: Cincinnati, OH. **1980**.
2. Godish, T. *Air Quality*. Lewis Publishers Incorporation: Chelsea. **1985**.
3. Smith, L.; Bjellerup, L.; Kroops, S.; Westermark, H. *Acta Chem. Scand.* **1953**, 7, 65.
4. Sinke, G. S.; Stull, D. R. *J. Phys. Chem.* **1958**, 62, 797.
5. Pokorny, F. *J. Am. Chem. Soc.* **1941**, 63, 1768.
6. Berger, R. S. *Science*, **1972**, 177, 704.
7. Good, W. D.; Scott, D. W.; Waddington, G. *J. Phys. Chem.* **1960**, 60, 1080.
8. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry*. Vol. 1, chap. 5. Rossini, F. D.: editor. Interscience: New York. **1956**.
9. Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodynamics* **1972**, 4, 283.

10. Skinner, H. A.; Snelson, A. *Trans Faraday Soc.* **1960,** 56, 1776.
11. Perrin, D. D.; Armarego, W. L.; Perrin, D. R. *Purification of Laboratory Chemicals.* Pergamon: Oxford. **1980.**
12. Vogel, A. I. *Quantitative Inorganic Analysis.* Longmans: London. **1978.**
13. *The NBS Tables of Chemical Thermodynamic Properties. J. Chem. Phys. Ref. Data* **1982,** 11, Supplement no. 2.
14. Adedeji, F. A.; Brown, D. L. S.; Connor, J. A.; Leung, M.; Paz-Andrade, M. I.; Skinner, H. A. *J. Organometallic Chem.* **1975,** 97, 221.
15. Stull, D. R.; Westrum, E. F., Jr.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds.* Wiley: New York. **1969.**
16. *Pure Appl. Chem.* **1979,** 51, 409.
17. *J. Chem. Thermodynamics* **1991,** 63, 975.
18. Shaub, W. M. *Thermochimica Acta* **1982,** 55, 59.
19. Cox, J. D. *A method for estimating the enthalpies of formation of benzene derivatives in the gas state.* NPL Report CHEM 83, June **1978.**
20. Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds.* 2nd edition. Chapman and Hall: London. **1986.**