Standard molar enthalpy of combustion and formation of quaternary ammonium tetrachlorozincate \([n-C_nH_{2n+1}N(CH_3)_3]_2ZnCl_4\)

Biyan Ren\(^1\), Shuying Zhang\(^2\), Bei Ruan\(^1\), Kezhong Wu\(^*\) and Jianjun Zhang\(^1\)

Abstract

The standard molar enthalpy of combustion (\(\Delta_{c}H_{o}m\)) and formation (\(\Delta_{f}H_{o}m\)) of quaternary ammonium tetrachlorozincate \([n-C_nH_{2n+1}N(CH_3)_3]_2ZnCl_4\) have been determined for the hydrocarbon chain length from even number 8 to 18 of carbon atoms (n) by an oxygen-bomb combustion calorimeter. The results indicated that the values of \(\Delta_{c}H_{o}m\) increased and \(\Delta_{f}H_{o}m\) decreased with increasing chain length and showed a linear dependence on the number of carbon atoms, which were caused by that the order and rigidity of the hydrocarbon chain decreased with increasing the carbon atoms. The linear regression equations are \(-\Delta_{c}H_{o}m = 1440.50n + 3730.67\) and \(-\Delta_{f}H_{o}m = -85.32n + 1688.22\).

Keywords: Combustion calorimeter, Energy of combustion, Enthalpy of combustion, Enthalpy of formation, Quaternary ammonium tetrachlorozincate

Introduction

The quaternary ammonium tetrachlorometallate with the general formula \([n-C_nH_{2n+1}NR_3]_2MX_4\) (M = Cu, Mn, Cd, Zn, Co, ..., X = Cl, Br, I, R is alkyl, or aryl) (short notation: C\(_n\)C\(_3\)M) have been attracted considerable attention because of their physical properties including ferro-, piezo- or pyroelectricity, ferr-, antiferro- or piezomagnetism and their technical application for electro- or magneto-optical devices (Blachnik et al. 1996; Kezhong et al. 2010). The advances in synthesis along with the ease of controlling various structural parameters (metal, halogen and number of carbon atoms in the alkylammonium ion) have made them ideal objects for studies by spectroscopy, calorimetry, diffraction, and a variety of other techniques (Abid et al. 2011; Donghua et al. 2011; Shymkiv et al. 2011). In addition, several theoretical studies have been undertaken to predict the behavior of the C\(_n\)C\(_3\)M (Francesco et al. 2002; Gosniowska et al. 2000). However, the thermodynamic properties of the C\(_n\)C\(_3\)M have been reported rarely in the literature. In the present work, the series of quaternary ammonium tetrachlorozincate \([n-C_nH_{2n+1}N(CH_3)_3]_2ZnCl_4\) (n = 8, 10, 12, 14, 16, 18) are synthesized from ethanol solutions. The standard molar enthalpy of formation (\(\Delta_{f}H_{o}m\)) and the standard molar enthalpy of combustion (\(\Delta_{c}H_{o}m\)) of the C\(_n\)C\(_3\)Zn have been determined by an oxygen-bomb combustion calorimeter with increasing chain length at \(T = 298.15\) K.

Experimental procedure

ZnCl\(_2\), concentrated HCl and absolute ethanol were analytical grade. \(n\)-Octyltrimethylammonium chloride (A.P.), were purchased from TOKYO CHEMICAL INDUSTERY CO LTD (Japan). \(n\)-Decyltrimethylammonium chloride(A.P.), \(n\)-Dodecyltrimethylammonium chloride(A.P.), \(n\)-Tetradeceyltrimethylammonium chloride(A. P.), \(n\)-Hexadecyltrimethylammonium chloride(A.P.), \(n\)-Trimethylstearlammonium chloride(A.P.) were purchased from J & K CHEMICAL LTD. For the synthesis of C\(_n\)C\(_3\)Zn, the hot absolute ethanol solutions of ZnCl\(_2\) concentrated HCl and the corresponding quaternary ammonium were mixed in a 1:2:2 molar ratios. The solutions were concentrated by boiling for 1 h, and then cooled to room temperature. After filtration, the products were recrystallized twice from absolute ethanol and then were placed in a vacuum desiccator for 10 h at about 353 K.
The CnC3Zn were analyzed with an MT-3 CHN elemental analyzers (Japan) are listed in the following: Elemental analyses calc. (%) for C8C3Zn: C 47.88, H 9.43, N 5.08, Cl 25.75; Found: C 47.45, H 9.50, N 5.13, Cl 24.99. Anal. Calcd for C10C3Zn: C 51.37, H 9.88, N 4.61, Cl 23.38; Found: C 50.98, H 9.45, Cl 22.81. Anal. Calcd for C12C3Zn: C 54.26, H 10.25, N 4.22, Cl 21.41; Found: C 53.93, H 10.34, Cl 21.25. Anal. Calcd for C14C3Zn: C 56.72, H 10.56, N 3.89, Cl 19.74; Found: C 56.06, H 10.20, N 3.84, Cl 19.03. Anal. Calcd for C16C3Zn: C 58.84, H 10.84, N 3.61, Cl 18.31; Found: C 58.91, H 10.77, N 3.36, Cl 17.55.

The combustion experiments were performed with a static bomb calorimeter (XRY-1A Shanghai). Benzoic acid (Thermochemical Standard, BCS-CRM-190r) was used as calibrant of the bomb calorimeter. Its massic

Table 1 The values of the combustion energies of the quaternary ammonium tetrachlorometallate CnC3Zn

|       | No. | mCnC3Zn/g | ΔT/K   | Δmign/g | Uign/J | VNaOH/ml | UNaOH/J | U/nm/kJ·g⁻¹ |
|-------|-----|-----------|--------|---------|--------|-----------|----------|-------------|
| C8C3Zn | 1   | 0.4816    | 0.950  | 0.0033  | 10.71  | 3.88      | 23.20    | 27.478      |
|       | 2   | 0.5028    | 0.990  | 0.0031  | 10.06  | 3.78      | 22.60    | 27.432      |
|       | 3   | 0.4725    | 0.940  | 0.0041  | 13.30  | 4.08      | 24.40    | 27.703      |
|       | 4   | 0.3775    | 0.750  | 0.0028  | 9.09   | 4.00      | 23.92    | 27.658      |
|       | 5   | 0.5193    | 1.034  | 0.0025  | 8.11   | 4.40      | 26.31    | 27.741      |
| Ave.  |     | 0.5081    | 1.085  | 0.0041  | 13.30  | 2.85      | 17.04    | 27.602 ± 0.139 |
| C10C3Zn| 1   | 0.5081    | 1.120  | 0.0039  | 12.66  | 2.89      | 17.28    | 29.422      |
|       | 2   | 0.5306    | 1.070  | 0.0038  | 12.33  | 3.39      | 20.33    | 29.631      |
|       | 3   | 0.4403    | 0.895  | 0.0030  | 9.74   | 2.30      | 13.75    | 29.804      |
|       | 4   | 0.4630    | 0.950  | 0.0030  | 9.74   | 2.90      | 17.34    | 29.640      |
| Ave.  |     | 0.5081    | 1.120  | 0.0041  | 13.30  | 2.85      | 17.04    | 29.652 ± 0.149 |
| C12C3Zn| 1   | 0.4907    | 1.115  | 0.0047  | 15.25  | 3.03      | 18.12    | 31.666      |
|       | 2   | 0.4591    | 1.040  | 0.0049  | 15.90  | 2.93      | 17.54    | 31.563      |
|       | 3   | 0.4706    | 1.060  | 0.0044  | 14.28  | 3.25      | 19.44    | 31.385      |
|       | 4   | 0.4566    | 1.040  | 0.0032  | 10.38  | 3.20      | 19.14    | 31.744      |
|       | 5   | 0.4673    | 1.055  | 0.0040  | 12.98  | 3.55      | 21.23    | 31.455      |
| Ave.  |     | 0.4907    | 1.115  | 0.0047  | 15.25  | 3.03      | 18.12    | 31.563 ± 0.147 |
| C14C3Zn| 1   | 0.4699    | 1.120  | 0.0025  | 8.11   | 2.45      | 14.65    | 33.238      |
|       | 2   | 0.5225    | 1.251  | 0.0037  | 12.01  | 3.65      | 21.83    | 33.372      |
|       | 3   | 0.4130    | 0.985  | 0.0039  | 12.66  | 2.46      | 14.71    | 33.241      |
|       | 4   | 0.5325    | 1.270  | 0.0047  | 15.25  | 2.45      | 14.65    | 33.251      |
|       | 5   | 0.4362    | 1.040  | 0.0042  | 13.63  | 3.75      | 22.43    | 33.214      |
| Ave.  |     | 0.4699    | 1.120  | 0.0025  | 8.11   | 2.45      | 14.65    | 33.263 ± 0.062 |
| C16C3Zn| 1   | 0.5125    | 1.270  | 0.0046  | 14.93  | 2.50      | 14.97    | 34.549      |
|       | 2   | 0.4720    | 1.160  | 0.0042  | 13.63  | 2.44      | 14.57    | 34.262      |
|       | 3   | 0.4902    | 1.210  | 0.0027  | 8.76   | 3.04      | 18.18    | 34.417      |
|       | 4   | 0.4758    | 1.170  | 0.0043  | 13.95  | 3.01      | 17.99    | 34.274      |
|       | 5   | 0.4577    | 1.130  | 0.0044  | 14.28  | 3.94      | 23.56    | 34.396      |
| Ave.  |     | 0.5125    | 1.270  | 0.0046  | 14.93  | 2.50      | 14.97    | 34.379 ± 0.118 |
| C18C3Zn| 1   | 0.5605    | 1.430  | 0.0030  | 9.74   | 3.04      | 18.18    | 35.580      |
|       | 2   | 0.5755    | 1.475  | 0.0058  | 18.82  | 3.03      | 18.12    | 35.729      |
|       | 3   | 0.5283    | 1.348  | 0.0062  | 20.12  | 3.42      | 20.45    | 35.557      |
|       | 4   | 0.4465    | 1.140  | 0.0034  | 11.03  | 3.65      | 21.83    | 35.583      |
|       | 5   | 0.4459    | 1.130  | 0.0038  | 12.33  | 3.65      | 21.83    | 35.315      |
| Ave.  |     | 0.5605    | 1.430  | 0.0030  | 9.74   | 3.04      | 18.18    | 35.552 ± 0.149 |
energy of combustion is \( \Delta cU = -(26460 \pm 3.8) \text{ J} \cdot \text{g}^{-1} \) under certificate conditions. The massic energy of combustion \( \Delta cU \) for each C\(_n\)C\(_3\)Zn was fitted with equation

\[
\Delta cU = \left[ -e_{\text{calib}} \cdot \Delta T + \Delta m_{\text{ign}} \cdot u_{\text{ign}} + V_{\text{NaOH}}(\text{aq}) \right]/m_{\text{CnC3Zn}}
\]

where \( e_{\text{calib}} \) is the energy equivalent of the calorimeter, \( \Delta T \) is the calorimeter temperature change corrected, \( \Delta m_{\text{ign}} \) is the mass of the Nickel-chromium alloy for ignition and the massic energy is \( \Delta cU \). The massic energy of combustion are, in each case, equal to twice the overall standard deviation of the mean and include the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, equal to twice the overall standard deviation of the mean and include the uncertainties in calibration (Henoc et al. 2009). The results are referred to the following reactions (1 ~ 6) and the following equation (7 ~ 9):

\[
[C_8H_{17}N(CH_3)_3]_2ZnCl_4(s) + \frac{69}{2} O_2(g) = ZnO(s) + 22CO_2(g) + 4HCl(l) + 24H_2O(l) + N_2(g)
\]

(1)

\[
[C_{10}H_{21}N(CH_3)_3]_2ZnCl_4(s) + \frac{81}{2} O_2(g) = ZnO(s) + 26CO_2(g) + 4HCl(l) + 28H_2O(l) + N_2(g)
\]

(2)

\[
[C_{12}H_{25}N(CH_3)_3]_2ZnCl_4(s) + \frac{93}{2} O_2(g) = ZnO(s) + 30CO_2(g) + 4HCl(l) + 32H_2O(l) + N_2(g)
\]

(3)

\[
[C_{14}H_{29}N(CH_3)_3]_2ZnCl_4(s) + \frac{105}{2} O_2(g) = ZnO(s) + 34CO_2(g) + 4HCl(l) + 36H_2O(l) + N_2(g)
\]

(4)

**Table 2 The value of thermochemical functions of the quaternary ammonium tetrachlorometallate C\(_n\)C\(_3\)Zn**

| \( \Delta f^\circ H_m \) /kJ · mol\(^{-1} \) | C\(_6\)C\(_3\)Zn | C\(_{10}\)C\(_3\)Zn | C\(_{12}\)C\(_3\)Zn | C\(_{14}\)C\(_3\)Zn | C\(_{16}\)C\(_3\)Zn | C\(_{18}\)C\(_3\)Zn |
|-------------------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|
| C\(_6\)C\(_3\)Zn                            | 15268          | 18010          | 20938          | 23929          | 26657          | 29557          |
| C\(_{10}\)C\(_3\)Zn                          | 15297          | 18044          | 21009          | 24006          | 26740          | 29647          |
| C\(_{12}\)C\(_3\)Zn                          | 991.66         | 908.02         | 819.66         | 734.02         | 649.66         | 565.02         |
| C\(_{14}\)C\(_3\)Zn                          |                |                |                |                |                |                |
| C\(_{16}\)C\(_3\)Zn                          |                |                |                |                |                |                |

**Results and discussion**

The individual results of all combustion experiments, together with the mean values and their standard deviations, are given for each compound in Table 1. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpies of combustion are, in each case, equal to twice the overall standard deviation of the mean and include the uncertainties in calibration (Henoc et al. 2009). The results are referred to the following reactions (1 ~ 6) and the following equation (7 ~ 9):

\[
[C_8H_{17}N(CH_3)_3]_2ZnCl_4(s) + \frac{69}{2} O_2(g) = ZnO(s) + 22CO_2(g) + 4HCl(l) + 24H_2O(l) + N_2(g)
\]

(1)

\[
[C_{10}H_{21}N(CH_3)_3]_2ZnCl_4(s) + \frac{81}{2} O_2(g) = ZnO(s) + 26CO_2(g) + 4HCl(l) + 28H_2O(l) + N_2(g)
\]

(2)

\[
[C_{12}H_{25}N(CH_3)_3]_2ZnCl_4(s) + \frac{93}{2} O_2(g) = ZnO(s) + 30CO_2(g) + 4HCl(l) + 32H_2O(l) + N_2(g)
\]

(3)

\[
[C_{14}H_{29}N(CH_3)_3]_2ZnCl_4(s) + \frac{105}{2} O_2(g) = ZnO(s) + 34CO_2(g) + 4HCl(l) + 36H_2O(l) + N_2(g)
\]

(4)
\[
[C_{16}H_{33}N(CH_3)_3]_2ZnCl_4(s) + \frac{117}{2} O_2(g) \\
= ZnO(s) + 38CO_2(g) + 4HCl(l) + 40H_2O(l) \\
+ N_2(g) 
\] (5)

\[
[C_{18}H_{37}N(CH_3)_3]_2ZnCl_4(s) + \frac{129}{2} O_2(g) \\
= ZnO(s) + 42CO_2(g) + 4HCl(l) + 44H_2O(l) \\
+ N_2(g) 
\] (6)

\[\Delta_cH^o_m = M\Delta_cU^o_m + \Delta nRT \] (7)

\[\Delta n = n_g(\text{product}) - n_g(\text{reactant}) \] (8)

\[\Delta_fH^o_m(C_nC_3Zn) = \sum V_{\text{R}}\Delta cH^o_m(B) - \Delta_cH^o_m \] (9)

Where \( R \) is the molar gas constant and \( M \) is the molar mass of the \( C_nC_3Zn \). The \( V_B \) is the stoichiometric coefficient and the \( \Delta_fH^o_m \) (B) is the standard molar enthalpy of formation of the combustion products. The standard molar enthalpies of formation of \( \text{ZnO(s), H}_2\text{O(l) and CO}_2(g) \) at \( T = 298.15 \text{ K} \) are: \(-348.28 \text{ kJ \cdot mol}^{-1} \), \(-285.830 \pm 0.042 \text{ kJ \cdot mol}^{-1} \) and \(-393.51 \pm 0.13 \text{ kJ \cdot mol}^{-1} \) (Manuel et al. 2010). The \( \Delta_fH^o_m \) of the \( C_nC_3Zn \) resulted from the \( \Delta_cH^o_m \) by an oxygen-bomb combustion calorimeter at \( T = 298.15 \text{ K} \). Table 2 lists the values of the standard molar energies \( \Delta_cU^o_m \) and the enthalpies of combustion \( \Delta_cH^o_m \) and the standard molar enthalpies of formation \( \Delta_fH^o_m \) result form \( \Delta_cU^o_m \) for the \( C_nC_3Zn \).

The influence of the hydrocarbon chain length on \( \Delta_cH^o_m \) and \( \Delta_fH^o_m \) of the \( C_nC_3Zn \) has been obtained for chain lengths from 8 to 18 carbon atoms. The values of \( \Delta_cH^o_m \) and \( \Delta_fH^o_m \) show a linear dependence on the number of carbon atoms from experimental data analysis. Figure 1, Figure 2 show a plot of the calculated \( -\Delta_cH^o_m \) and \( -\Delta_fH^o_m \) vs. C-atoms (n) that gave a straight line relationship from the values of Table 2. The linear regression equation are \( -\Delta_cH^o_m = 1440.50n + 3730.67 \) with a correlation coefficient \( r = 0.9998 \) and \( -\Delta_fH^o_m = -85.32n + 1688.22 \) with \( r = 0.9512 \). A striking feature is that \( \Delta_cH^o_m \) increased and \( \Delta_fH^o_m \) decreased with increasing the chain length. This reason is that the structures of \( C_nC_3Zn \) are characteristic of the piling of sandwiches in which a two-dimensional cavities of \( \text{ZnCl}_4^2^- \) tetrahedra is sandwiched between two alkylammonium layers. The layers are bound by van der Waals forces between \( \text{CH}_2\text{CH}_3 \) groups and by long-range Coulomb forces. The \(-\mathrm{N(CH}_3)_3^+ \) groups of the chains occupy the cavities of the \( \text{ZnCl}_4^2^- \) layers and are bonded by ion bonds to the chlorine atoms (Weizhen et al. 2011). As the hydrocarbon chain length increases, the formation of the chain conformer plays a more important role in the structural phase transitions. It is known that the order and rigidity of the hydrocarbon chain were decreased with increasing the carbon atoms, that is with increasing mean number of conformationally flexible chain in \( C_nC_3Zn \) (Nobuaki et al. 2011), furthermore, the intensities of the ion bonds and van der Walls force decrease with increasing the carbon atoms resulting in that the values of \( \Delta_cH^o_m \) and \( \Delta_fH^o_m \) show a linear dependence on the carbon atoms.

**Conclusions**

The standard molar enthalpy of combustion and formation of quaternary ammonium tetrachlorozincate \([n-\mathrm{C}_{n+1}H_{2n+1}N(\text{CH}_3)_3]_2\text{ZnCl}_4 \) \((n = 8, 10, 12, 14, 16, 18)\) have been measured by an oxygen-bomb combustion calorimeter. The results indicated that the values of the standard molar combustion enthalpies \( \Delta_fH^o_m \) of these compounds increased with increasing chain length and the standard molar formation enthalpies \( \Delta_fH^o_m \) of these compounds decreased with increasing chain length and showed a linear dependence on the number of carbon atoms.

**Competing interests**

The authors declare they have no competing interests in relation to this article.

**Authors’ contributions**

KZW participated in the design of the experiment; all authors equally participated in the preparation of the manuscript, read and approved the final manuscript.

**Acknowledgements**

This project was financially supported by National Natural Science Foundation of China (No.21073052, 21246006), Natural Science Foundation of Hebei Province (No. B2012050534), and Science Foundation of Hebei Normal University (L2011K04).

**Author details**

1Department of Chemistry and Material Science, Hebei Normal University, Shijiazhuang 050024, China. 2Department of Basic Course, the Chinese People’s Armed Police Force Academy, Langfang 065000, China.

**Received:** 28 December 2012 **Accepted:** 28 February 2013

**Published:** 9 March 2013

**References**

Abid H, Samet A, Dammak T (2011) Electronic structure calculations and optical properties of a new organic--inorganic luminescent perovskite: \( \text{CsH}_7\text{NH}_5\text{PbI}_3 \). J Lumin 131:1753–1757

Błachnik R, Siethoff C (1996) Thermoanalytical and X-ray study of some alkylammonium tetrachlorozincates. Thermochim Acta 278:39–47

Donghua H, Youying D, Zhucheng T (2011) Crystal structures and thermochemistry on phase change materials \((n-\text{C}_n\text{H}_{2n+1}\text{NH}_3)\text{CuCl}_3(s)\) \((n = 14 \text{ and } 15)\). Sol Energy Mater Sol Cells 95:2897–2906

Neve F, Francescangeli O, Crispiani A (2002) Crystal architecture and mesophase structure of long-chain N-alkylpyridinium tetrachlorometallates. Inorg Chim Acta 338:51–58

Gosniowska M, Ciunik Z, Bator G, Jakubas R, Baran J (2000) Structure and phase of a complexing \(\text{[N(CH}_3)_3]_2\text{ZnCl}_4\) with 2-tetrahedra is sandwiched in between two alkylammonium layers. J Mol Struct 555:243–253

Flores H, Adriana Camarillo E, Mentado J (2009) Enthalpies of combustion and formation of 2-acetylpyrrole, 2-acetylfuran and 2-acetylthiophene. J Mol Struct 911:92–98

Mats M, Monte MJS, Hillesheim DM (2002) Standard molar enthalpies of combustion of the three trans-methoxycinnamic acids. J Chem Thermodyn 34:499–509
Manuel AV, da Silva R, Ana IMC, Lobo F (2010) Enthalpies of combustion, vapour pressures, and enthalpies of sublimation of the 1,5- and 1,8-diaminonaphthalenes. J Chem Thermodyn 42:371–379
Shymkiv RM, Sveleba SA, Karpa IV, Katerinchuk IN, Kunyo IM, Phitsych EI (2011) Electronic spectra and phase transitions in thin [Ni(CH3)4]2CuCl4 microcrystals. J Appl Spectroscopy 78:823–828
Kitazawa N, Aono M, Watanabe Y (2011) Synthesis and luminescence properties of lead-halide based organic–inorganic layered perovskite compounds (CnH2n+1NH3)2 PbI4 (n = 4, 5, 7, 8 and 9). J Phys Chem Solids 72:1467–1471
Weizhen C, Kezhong W, Xiaodi L, Liuqin W, Biyan R (2011) Subsolidus binary phase diagram of the perovskite type layer materials (n-CnH2n+1NH3)2ZnCl4 (n = 10, 12, 14). Thermochim Acta 521:80–83

doi:10.1186/2193-1801-2-98
Cite this article as: Ren et al.: Standard molar enthalpy of combustion and formation of quaternary ammonium tetrachlorozincate [n-CnH2n+1 N(CH3)3]2 ZnCl4. SpringerPlus 2013, 2:98.