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Standard molar enthalpy of combustion and formation of quaternary ammonium tetrachlorozincate [n-C_nH_{2n+1} $N(CH_3)_3]_2$ $ZnCl_4$

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Abstract

The standard molar enthalpy of combustion ($\Delta_cH^o_m$) and formation ($\Delta_fH^o_m$) 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 $\Delta_cH^o_m$ increased and $\Delta_fH^o_m$ 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 $-\Delta_cH^o_m$ =1440.50n +3730.67 and $-\Delta_fH^o_m$ = −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 $[n\text{-}C_nH_{2n+1}NR_3]_2MX_4$ (M = Cu, Mn, Cd, Zn, Co, . . ., X = Cl, Br, I, R is alkyl, or aryl) (short notation: C_nC_3M) have been attracted considerable attention because of their physical properties including ferro-, piezo- or pyroelectricity, ferri-, 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_nC_3M (Francesco et al. 2002; Gosniowska et al. 2000). However, the thermodynamic properties of the C_nC_3M 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 ($\Delta_fH^o_m$) and the standard molar enthalpy of combustion ($\Delta_cH^o_m$) of the C_nC_3Zn 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 INDUSTRY CO LTD (Japan). n-Decyltrimethylammonium chloride(A.P.), n-Dodecyltrimethylammonium chloride (A.P.), n-Tetradecyltrimethylammonium chloride(A.P.), n-Hexadecyltrimethylammonium chloride(A.P.), n-Trimethylstearylammonium chloride(A.P.) were purchased from J & K CHEMICAL LTD. For the synthesis of C_nC_3Zn, 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.

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The C_nC_3Zn were analyzed with an MT-3 CHN elemental analyzers (Japan) are listed in the following: Elemental analyses calc. (%) for C_8C_3Zn: 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 $C_{10}C_3Zn$: C 51.37, H 9.88, N 4.61, Cl 23.38; Found: C 50.98, H 9.95, N 4.58, Cl 22.81. Anal. calcd for $C_{12}C_3Zn$: C 54.26, H 10.25, N 4.22, Cl 21.41; Found: C 53.93, H 10.34, N 4.26, Cl 21.25. Anal. Calcd for $C_{14}C_3Zn$: 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 $C_{16}C_3Zn$: C 58.84, H 10.84, N 3.61, Cl 18.31; Found: C 58.91, H 10.77, N 3.62,Cl18.72. Anal. Calcd for $C_{18}C_3Zn$: C 60.65, H 11.07, N 3.37, Cl 17.08; Found: C 60.56, H 11.04, 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 C_nC_3Zn

	No.	m_{CnC3Zn}/	ΔT/K	Δm_{ign}/g	U_{ign}/J	V_{NaOH}/ml	U_{NaOH}/J	$-\Delta_C U_m$/kJ · g^{-1}
C_8C_3Zn	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.							27.602 ± 0.139
$C_{10}C_3Zn$	1	0.5081	1.085	0.0041	13.30	2.85	17.04	29.762
	2	0.5306	1.120	0.0039	12.66	2.89	17.28	29.422
	3	0.5035	1.070	0.0038	12.33	3.39	20.33	29.631
	4	0.4403	0.895	0.0030	9.74	2.30	13.75	29.804
	5	0.4630	0.950	0.0030	9.74	2.90	17.34	29.640
	Ave.							29.652 ± 0.149
$C_{12}C_3Zn$	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.							31.563 ± 0.147
$C_{14}C_3Zn$	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.							33.263 ± 0.062
$C_{16}C_3Zn$	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.							34.379 ± 0.118
$C_{18}C_3Zn$	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.							35.552 ± 0.149

Table 2 The value of thermochemical functions of the quaternary ammonium tetrachlorometallate C_nC_3Zn

	C_8C_3Zn	$C_{10}C_3Zn$	$C_{12}C_3Zn$	$C_{14}C_3Zn$	$C_{16}C_3Zn$	$C_{18}C_3Zn$
$-\Delta_c U_m^\circ$/kJ · mol^{-1}	15268	18010	20938	23929	26657	29557
$-\Delta_c H_m^\circ$/kJ · mol^{-1}	15297	18044	21009	24006	26740	29647
$-\Delta_f H_m^\circ$/kJ · mol^{-1}	991.66	908.02	660.38	380.47	364.10	174.46

energy of combustion is $\Delta_c U = -(26460 \pm 3.8)$ J · g^{-1} under certificate conditions. The massic energy of combustion $\Delta_c U_m$ for each C_nC_3Zn was fitted with equation $\Delta_c U_m = [-\varepsilon_{(calor)} \cdot \Delta T + \Delta m_{ign} \bullet u_{ign} + V_{NaOH} \bullet (-59.7)]/m_{CnC3Zn}$, where ε_{cal} is the energy equivalent of the calorimeter, ΔT is the calorimeter temperature change corrected, Δm_{ign} is the mass of the Nickel-chromium alloy for ignition and the massic energy is $u_{ign} = -3.245$ kJ · g^{-1}($U_{ign} = \Delta m_{ign} \bullet u_{ign}$). m_{CnC3Zn} is the mass of the C_nC_3Zn which were burned, V_{NaOH} is the volume of sodium hydroxid which consumed by nitric acid, the corrections for nitric acid formation were based on −59.7 kJ · mol^{-1} for the molar energy of formation of 0.1 mol · dm^{-3} HNO_3 (aq) from N_2, O_2, and H_2O(l) (Matos et al. 2002). The calibration results were corrected to the average mass of water added to the calorimeter: 2500.0 g and the volume of oxygen bomb was 300 ml. From five independent calibration experiments between T = 295.15 K and T = 299.15 K, the energy equivalent ε_{cal} = (13965.4 ± 4.7) J · K^{-1} was obtained, where the uncertainty quoted is the standard deviation of the mean. For all experiments, ignition was made at T = (298.150 ± 0.001) K. Combustion experiments were performed in oxygen at a pressure p = 3.00 MPa and in the presence of 10.00 cm^3 of water added to the bomb (Matos et al. 2002).

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):

$$\left[C_8H_{17}N(CH_3)_3\right]_2ZnCl_4(s) + \frac{69}{2}O_2(g) = ZnO(s) + 22CO_2(g) + 4HCl(l) + 24H_2O(l) + N_2(g) \quad (1)$$

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

$$\left[C_{12}H_{25}N(CH_3)_3\right]_2ZnCl_4(s) + \frac{93}{2}O_2(g) = ZnO(s) + 30CO_2(g) + 4HCl(l) + 32H_2O(l) + N_2(g) \quad (3)$$

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

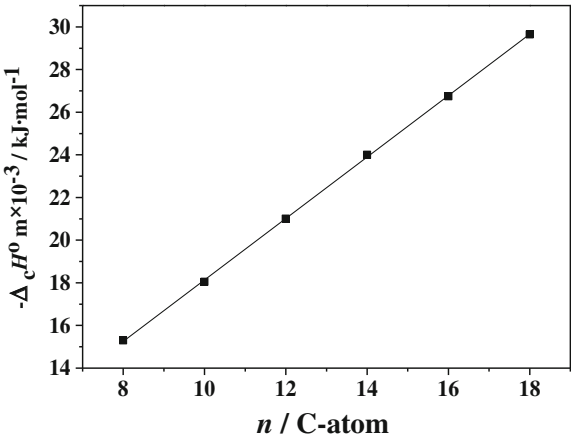

Figure 1 Plot of $\Delta_c H_m^\circ$ vs. number(n) of carbon-atoms in the quaternary ammonium tetrachlorometallate C_nC_3Zn.

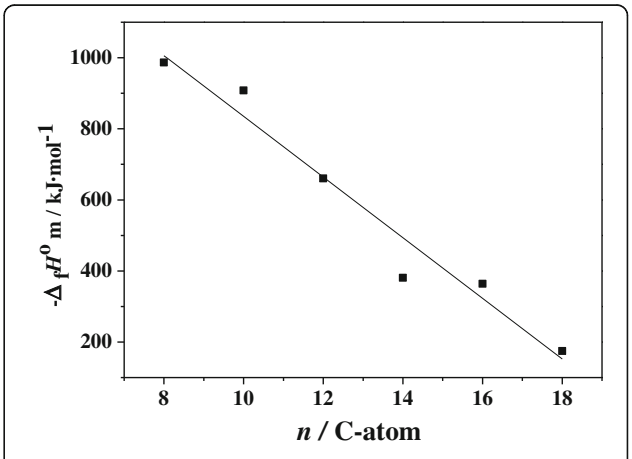

Figure 2 Plot of $\Delta_f H_m^\circ$ vs. number(n) of carbon-atoms in the quaternary ammonium tetrachlorometallate C_nC_3Zn.

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

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

$$\Delta_c H^o{}_m = \mathrm{M}\Delta_c U^o{}_m + \Delta n RT \quad (7)$$

$$\Delta n = n_g(\text{product}) - n_g(\text{reactant}) \quad (8)$$

$$\Delta_f H^o{}_m(C_nC_3Zn) = \Sigma V_B \Delta_f H_m{}^o(B) - \Delta_c H^o{}_m \quad (9)$$

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 ZnO(s), H_2O (l) and CO_2(g) at $T = 298.15$ K, –(348.28) kJ · mol^{-1}, –(285.830 ± 0.042) kJ · mol^{-1} and – (393.51 ± 0.13) kJ · 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 $T = 298.15$ K. Table 2 lists the values of the standard molar energies $\Delta_cU^o_m$, 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 $ZnCl_4^{2-}$ tetrahedra is sandwiched between two alkylammonium layers. The layers are bound by van der Waals forces between $(CH_2)_nCH_3$ groups and by long-range Coulomb forces. The $-N(CH)_3^{3+}$ groups of the chains occupy the cavities of the $ZnCl_4^{2-}$ 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-C_nH_{2n+1} $N(CH_3)_3]_2ZnCl_4$ (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 $\Delta_cH^o_m$ 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.

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