# Standard enthalpy of formation of 2-chloro-6-(trichloromethyl)pyridine [a]

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The standard enthalpy of formation of 2-chloro-6-(trichloromethyl)pyridine(cr) was determined to be $-(55.4 \pm 1.8)$ kJ·mol$^{-1}$ at 298.15 K by rotating-bomb oxygen combustion calorimetry using paraffin oil as a combustion aid and As$_2$O$_3$(aq) as a reducing agent for Cl$_2$ formed. Nitric acid and chlorometallic acids of noble metals present in the final bomb solution were analysed by ion-chromatographic and atomic-absorption spectrometric methods, respectively. The effect of catalytic pre-oxidation of As$_2$O$_3$(aq) was evaluated. The standard molar energy of combustion was calculated using a computation form derived by combining that for CHON compounds with that for CHOCl compounds. The modifications of the form are described.

## 1. Introduction

2-Chloro-6-(trichloromethyl)pyridine, abbreviated as CTP in this paper, is an effective inhibitor against the aerobic oxidation of NH$_4^+$ ion in nitrogen fertilizer to NO$_3$ or NO$_2^-$ ion by nitrifying bacteria in soil. Heat capacities and derived thermodynamic quantities were reported recently for this substance.[1, 2] In the present paper, the result of a combustion calorimetric study of this substance is reported.
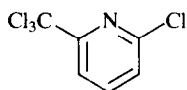


In the modern literature, no paper that reports rotating-bomb combustion calorimetry of organic compounds containing both chlorine and nitrogen can be found except references 3 and 4. The reduction scheme to standard states is described rather briefly in the former, while comparison experiments were carried out in place of ordinary calibration experiments in the latter. For organic nitrogen[5] and for organic chlorine[6] compounds, a computation form is available at present with

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which standard molar energies of combustion can be derived from combustion-calorimetric and auxiliary quantities. In this paper, a computation form is described which was obtained by combining the above-mentioned ones.[5,6] Furthermore, modern techniques of ion-chromatography and atomic-absorption spectrometry were introduced to combustion calorimetry for the determinations of nitric acid and chlorometallic acids of noble metals (Pt, Au, and Pd), respectively, present as by-products in the final bomb solution.

## 2. Experimental

CTP was prepared by chlorination of 2-methylpyridine at 460 to 480 K by chlorine. The crude product in lumpy brown crystalline form was preliminarily purified by repeated recrystallization (more than three times) using industrial alcohol as solvent, until a purity higher than 99 moles per cent was attained. The crystal was then purified by recrystallizations from ethanol solutions (five times) followed by drying at ambient temperatures under vacuum for 14 h until a constant mass was attained. The purity of the final product was better than 99.95 moles per cent by h.p.l.c. analysis.

Arsenious oxide (Merck, pro analysi) was dissolved in water and was used as a reducing reagent for chlorine. The concentration was determined by potentiometric titration at 331 K with potassium permanganate solution using potassium iodate as catalyst. The concentration of the potassium permanganate solution was in turn determined by potentiometric titration at 298 K of sodium oxalate (Wakō, standard reagent, the certified purity being 99.96 mass per cent). An isoperibol rotating-bomb combustion calorimeter[7,8] equipped with a platinum-lined bomb (Parr 1004C) was used. Temperature was detected by a thermistor,[9] calibrated against a quartz thermometer (Hewlett-Packard 2801A). Resistance was converted to the output potential difference of a Wheatstone bridge (Yokogawa, 2768) with a fixed dial setting and the potential readings were made at the rate of 22 to 24 readings per 10 s by a digital multimeter (Hewlett-Packard 3478A) and converted to temperature. Mean temperatures in every 10 s interval were recorded.

In the present study, the scheme of experiments was slightly changed from the previous one[10] owing to the change of the temperature sensor to the thermistor. An experiment is composed of four rating periods each including 120 temperature readings (20 min). When 90 s passed in the second rating period, rotation of the bomb was started and continued to the end of the third rating period. The energy equivalent of the empty calorimeter proper was determined by burning thermo-chemical standard benzoic acid (N.B.S. SRM 39i, $\Delta_c u_{cert} = -26434 \, J \cdot g^{-1}$) under certificate conditions. In calibration experiments, nitric acid formed by the oxidation of a small amount of nitrogen contained in the oxygen gas as an impurity was determined by the measurement of absorbance at a u.v. absorption maximum at 201 nm, attributable to $NO_3^-(aq)$, and $\Delta_{dec} U_m(HNO_3)$ was taken to be 59.0 kJ·mol$^{-1}$. The contribution from nitric-acid formation to the total energy change was less than 0.005 per cent. The mean and standard deviation of the mean of observed energy equivalents was $(15390.52 \pm 0.31) \, J \cdot K^{-1}$ from eight runs.

In the combustion calorimetric experiments on CTP, paraffin oil (Wakō) was used as a combustion aid and also as a source of hydrogen to be combined with chlorine liberated in the combustion. The standard specific energy of combustion of the paraffin oil was $\Delta_c u^{\circ} = -(45909.3 \pm 4.1)\,\mathrm{J\cdot g^{-1}}$, where the uncertainty is the standard deviation of the mean. CTP in pellet form (0.62 g) was put on a simple triangular support with three legs, made of thin platinum wires, and placed in a platinum crucible. The paraffin oil (0.45 g) placed in the crucible was ignited at the oxygen pressure of 3.04 MPa in the presence of 20 cm³ of aqueous $As_2O_3$ solution ($c = 0.06627\,\mathrm{mol\cdot dm^{-3}}$) in the bomb. No carbon monoxide was detected from the bomb gas after any experiment. A trace of carbon was detected by visual observation of the crucible in some of the experiments in the CTP series. However, no significant effect was found on the derived standard molar energy of combustion.

Pre-oxidation of arsenious oxide in the platinum-lined bomb under oxygen was examined by the method of Stridh.[11] Significant pre-oxidation was observed by the measurement of pH change with time. The time elapsed from the charge of oxygen into the bomb to the ignition of a sample was recorded and the effect of the pre-oxidation was taken into account in the calculation of standard molar energy combustion.

The final bomb solution was made up to 100 cm³ (CTP series) and analysed for $As_2O_3(aq)$, $HNO_3(aq)$, $H_2PtCl_6$, $HAuCl_4$, and $H_2PdCl_4$. Arsenious oxide was determined by potentiometric titration at 298 K with the standardized potassium permanganate solution, by using a measured small amount of potassium iodate as catalyst. In the CTP series, the u.v. absorption method was not applicable for the determination of nitric acid owing to the presence of a strong band due to $AsO_4^{3-}$ (aq) in the same region; therefore, nitric acid was determined by using an ion-chromatographic analyzer (Yokogawa IC500) equipped with an electric-conductivity detector using columns PAX1-035 and SAX1-205. The peak of the $NO_3^-$ ion was found to overlap partly with a strong peak of the $AsO_4^{3-}$ ion, as shown in figure 1. The two peaks were separated by subtracting the contribution of the $AsO_4^{3-}$ ion using a master curve taken for an aqueous solution containing only $AsO_4^{3-}$ ion as an anion. A calibration curve was obtained for solutions with various concentrations of nitric acid and with a fixed concentration of $AsO_4^{3-}$ similar to that of the final bomb solutions. The calibration curve showed that the peak height of the resultant $NO_3$ peak was sufficiently proportional to the concentration of $NO_3^-(aq)$. Consequently, the resultant peak height was adopted for the determination of amount of nitric acid. From the scatter of plots in the calibration curve, the possible error in the determination of nitric acid was evaluated to be less than 1 per cent. The amount of nitrous acid was determined by using the Griess–Ilosvay reagent.

Platinum(IV), palladium(II), and gold(III) were determined by atomic-absorption spectrometric method using an atomic-absorption spectrometer (Nippon Jarrell-Ash, type AA-845) at 266.0 nm, 244.8 nm, and 242.8 nm for Pt, Pd, and Au, respectively. Calibration curves were made for solutions with concentrations of As(III) and As(V) that were similar to those of the final bomb solutions. Most of the gold initially present as $HAuCl_4$ in the final bomb solution deposited as Au(cr) after storage for more than 120 d at ambient temperatures. Au(cr) was dissolved with *aqua regia* and
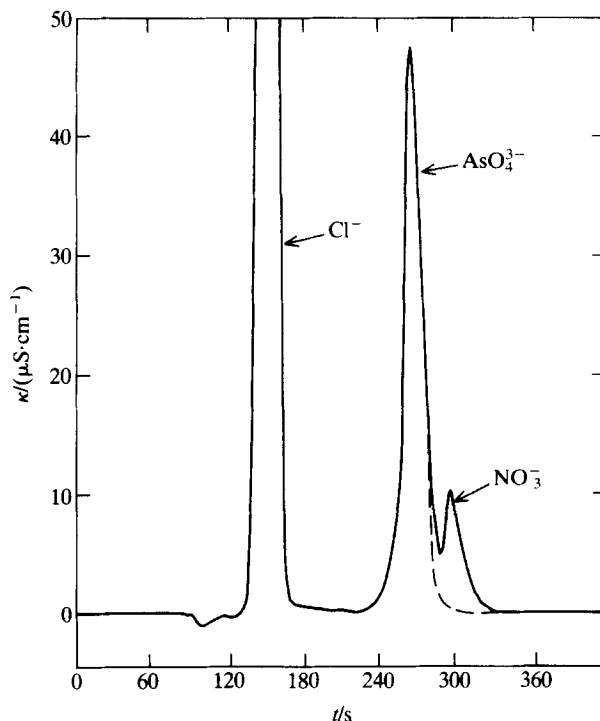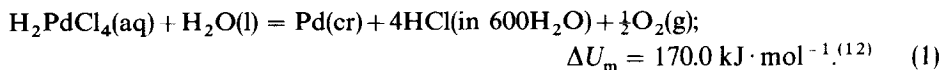
FIGURE 1. Ion-chromatogram of a final bomb solution. $\kappa$, Electric conductivity; $t$, retention time; $\cdots\cdots$, the contribution from $AsO_4^{3-}$(aq) estimated by using a peak for a solution containing only $AsO_4^{3-}$(aq) as anion as a master curve.

analysed by the atomic-absorption spectroscopic method. Corrections for the formation of $H_2PtCl_6$(aq) and $HAuCl_4$(aq) are described in the form given in reference 6 and that for the formation of $H_2PdCl_4$(aq) was made as follows:

$$H_2PdCl_4(aq) + H_2O(l) = Pd(cr) + 4HCl(in\ 600H_2O) + \tfrac{1}{2}O_2(g);$$
$$\Delta U_m = 170.0\ kJ \cdot mol^{-1}.^{(12)} \qquad (1)$$

The standard energy of combustion of CTP was calculated by using a scheme for CHOCl compounds[6] modified by additive combination of the scheme for CHON compounds.[5] The modification was made in the following items of the computation form given in reference 6.†

Item 1,　　change $C_{a'}H_{b'}O_{c'}Cl_{d'}$ to $C_{a'}H_{b'}O_{c'}Cl_{d'}N_{e'}$.
Item 3,　　add $e'M(N)$ to the right-hand side of the equation.
Item 22a (new item),　$e = n'e'$.
Item 24,　　add $eM(N)$ to the right-hand side of the equation.
Item 39a (new item),　$n^f(N_2^*) = 0.5\{e - n^f(HNO_3)\}$.
Item 40,　　add $-0.5n^f(HNO_3)$ to the right-hand side of the equation.

† Throughout these modifications to the form given in reference 6, in which some non-SI units were used: atm $= 101325$ Pa; $cal_{th} = 4.184$ J.

Item 41, add $M(HNO_3)n^f(HNO_3)$ to the right-hand side of the equation.

Item 42c (new item), $w(HNO_3) = M(HNO_3)n^f(HNO_3)/m^f(soln)$.

Item 44, add $+0.54w(HNO_3)$ to the right-hand side of the equation.

Item 51, add $+0.001n^f(HNO_3)/V^f(soln)$ to the right-hand side of the equation.

Item 56, add $-1.25n^f(HNO_3)$ to the right-hand side of the equation.

Item 57, change to $K^f(O_2) = [0.001260 - 0.000089\{n^f(HCl)/mol\}$
$- 0.00005\{n^f(HNO_3)/mol\}]/\{V^f(soln)/dm^3\}$ mol·dm$^{-3}$·atm$^{-1}$.†

Item 60, substitute $\{n^f(O_2, tot) + n^f(N_2^*)\}$ for $n^f(O_2, tot)$ on the right-hand side of the equation.

Item 62, add $+n^f(N_2^*)$ to the right-hand side of the equation.

Item 63a (new item), $x(O_2) = n^f(O_2, g)/n^f(gas)$.

Item 63b (new item), $x(N_2^*) = n^f(N_2^*)/n^f(gas)$.

Item 66, add $-0.667w(HNO_3)$ to the right-hand side of the equation.

Item 69, change to: $(\partial e/\partial p)_T^f(soln)$
$= \{-0.00185 - 0.0000685w(HNO_3)\}$ cal$_{th}$·g$^{-1}$·atm$^{-1}$.†

Item 71a, add $-530n^f(HNO_3)/V^f(soln)$ into the bracket on the right-hand side of the equation.

Item 71b, add $-200n^f(HNO_3)/V^f(soln)$ into the bracket on the right-hand side of the equation.

Item 71d, change to: $c(H^+) = \{n^f(HCl) + n^f(HNO_3)\}/V^f(soln)$.

Item 71f (new item), $\Delta_{dil}E_m(HNO_3)$. Values of $\Delta_{dil}E_m(HNO_3)$ are given in reference 5, p. 107.

Item 76, add $+C_V(N_2)n^f(N_2^*)$ and $+1.08w(HNO_3)$ to the right-hand sides of the equations for $\varepsilon^f(cont)$ and $A^f/(cal_{th} \cdot g^{-1} \cdot K^{-1})$,† respectively.

Item 86d (new item), $\Delta_{dec}E^f(H_2PdCl_4) = \Delta_{dec}E_m(H_2PdCl_4)n^f(H_2PdCl_4)$.

$\Delta_{dec}E_m(H_2PdCl_4) = 40.6$ kcal$_{th}$·mol$^{-1}$.[9]†

Item 91a (new item), $\Delta_{dil}E^f(HNO_3) = \Delta_{dil}E_m(HNO_3)n^f(HNO_3)$.

Item 93, change to:

$$[\Delta E^f(g)]_{p^f(gas)}^0 = -(\partial E/\partial p)_T(O_2, g)[x(O_2, g) + 0.908x(N_2^*, g) + 2.691x(CO_2) + 1.69\{x(CO_2)\}^2]p^f(gas)n^f(g).$$

In the present paper, the standard pressure was taken to be $10^5$ Pa. Accordingly, one of the limit pressures of items 82, 83, and 89 was changed from 1 atm to 0.98692 atm ($= 10^5$ Pa).† The experimental results are based on relative atomic masses recommended by the IUPAC Commission on Atomic Weights (1979).[13] The values of density $\rho$, specific heat capacity $c_p$, and compression energy $(\partial u/\partial p)_T$ at 298.15 K, used for correction of the weighings in air to masses and reduction of experimental results to the standard state, are shown in table 1. The density of CTP was determined by measuring the mass and volume of a disk pellet produced in an evacuable die under a high pressure. Other auxiliary quantities were as follows: $V(bomb) = 0.3469$ dm$^3$, $\Delta_{dec}U_m(HNO_3) = 58.9$ kJ·mol$^{-1}$ as in reference 6, and $\Delta_c u^\circ(fuse) = -16507$ J·g$^{-1}$.

† Throughout these modifications to the form given in reference 6, in which some non-SI units were used: atm $= 101325$ Pa; cal$_{th} = 4.184$ J.

TABLE 1. Auxiliary quantities. Estimated values are parenthesized

| Compound | Formula | $\dfrac{\rho}{g \cdot cm^{-3}}$ | $\dfrac{c_p}{J \cdot K^{-1} \cdot g^{-1}}$ | $\dfrac{-(\partial u/\partial p)_T}{J \cdot MPa^{-1} \cdot g^{-1}}$ |
|---|---|---|---|---|
| CTP | $C_6H_3Cl_4N$ | 1.69 | $0.83^{(1,2)}$ | (0.069) |
| Fuse | $CH_{1.86}O_{0.93}$ | 1.50 | 1.70 | 0.29 |
| Oil | $CH_{1.885}$ | 0.882 | 2.22 | 0.254 |

The standard molar energy of combustion relates to the following idealized combustion reaction at 298.15 K:

$$C_6H_3Cl_4N(cr)+(23/4)O_2(g)+(4801/2)H_2O(l)$$
$$= 6CO_2(g)+4(HCl \cdot 600H_2O)(l)+(1/2)N_2(g). \quad (2)$$
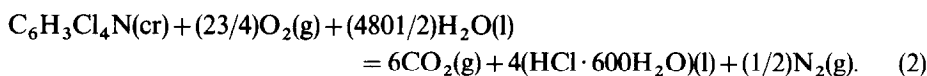
## 3. Results and discussion

It was found difficult to burn CTP completely without a combustion aid. In addition, the number of chlorine atoms in a CTP molecule is larger than that of hydrogen atoms. For both of these reasons, the use of a combustion aid was required. Initially, the thermochemical standard benzoic acid was used as a combustion aid, but its effect was not satisfactory: deposition of a small amount of carbon was found in the platinum crucible after every experiment. Consequently, paraffin oil was used. The mole ratio $n(H)/n(Cl)$ in the combustible substances was increased from 0.75 to about 6.5, while the contribution from CTP to the total standard energy change (item 95) was decreased to about 27 per cent.

Details of the combustion calorimetric experiments on CTP are presented in table 2. The symbols in this table are similar to those used in reference 6. Energy changes that contribute to the total standard energy change (item 95) are given as a typical example for the second experiment in table 2 as follows:

(81), $\Delta_{vap}U^i(H_2O) = 19.10$ J;     (82), $[\Delta U^i(soln)]_{p°}^{p^i(gas)} = -4.21$ J;

(83), $[\Delta U^i(sub)]_{p°}^{p^i(gas)} = -0.45$ J;     (84), $\Delta_{sol}U^i(O_2) = -6.46$ J;

(85), $[\Delta U^i(gas)]_0^{p^i(gas)} = -80.51$ J;     (86), $\Delta_{IBP}U = -28535.77$ J;

(86a), $\Delta_{dec}U^f(HNO_3) = 28.38$ J;     (86b), $\Delta_{dec}U^f(HAuCl_4) = 0.33$ J;

(86c), $\Delta_{dec}U^f(H_2PtCl_6) = 0.94$ J;     (86d), $\Delta_{dec}U^f(H_2PdCl_4) = 0.28$ J;

(87), $\Delta_{sol}U^f(CO_2) = 34.58$ J;     (88), $\Delta_{sol}U^f(O_2) = 4.89$ J;

(89), $[\Delta U^f(soln)]_{p^f(gas)}^{p°} = 4.90$ J;     (91), $\Delta_{dil}U^f(HCl) = -7.01$ J;

(91a), $\Delta_{dil}U^f(HNO_3) = -0.08$ J;     (92), $\Delta_{dec}U^f(As_2O_5) = -304.05$ J;

(93), $[\Delta U^f(gas)]_{p^f(gas)}^0 = 81.27$ J;     (94), $\Delta_{vap}U^f(H_2O) = -19.59$ J;

and

(95), $n\Delta_c U°(sub) = -28175.19$ J,

TABLE 2. Combustion-calorimetric results on CTP

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $m$(compd)/g | 0.61662 | 0.61069 | 0.61947 | 0.61933 | 0.61908 | 0.61770 | 0.61734 |
| $m$(oil)/g | 0.42559 | 0.45017 | 0.43013 | 0.45048 | 0.45070 | 0.45096 | 0.45208 |
| $m$(fuse)/g | 0.00156 | 0.00138 | 0.00138 | 0.00157 | 0.00186 | 0.00181 | 0.00204 |
| $(T_i/K)-273.15$ | 23.18260 | 23.18167 | 23.17904 | 23.17843 | 23.17925 | 23.18119 | 23.18334 |
| $(T_f/K)-273.15$ | 24.99016 | 25.05845 | 25.00438 | 25.06161 | 25.06485 | 25.06674 | 25.07495 |
| $\Delta T_{corr}/K$ | 0.02291 | 0.02295 | 0.02338 | 0.02016 | 0.02185 | 0.02327 | 0.02439 |
| $n^i$(As$_2$O$_3$, preox)/mmol[a] | 0.0090 | 0.0089 | 0.0123 | 0.0114 | 0.0077 | 0.0068 | 0.0077 |
| $n^f$(As$_2$O$_3$)/mmol | 0.3955 | 0.3662 | 0.3693 | 0.3784 | 0.3652 | 0.4277 | 0.3766 |
| $n^f$(HNO$_3$)/mmol | 0.446 | 0.482 | 0.493 | 0.478 | 0.483 | 0.483 | 0.491 |
| $n^f$(H$_2$PtCl$_6$)/$\mu$mol | 5.79 | 3.88 | 3.80 | 3.57 | 4.30 | 4.00 | 4.37 |
| $n^f$(HAuCl$_4$)/$\mu$mol | 3.2 | 4.0 | 3.7 | 10.2 | 10.7 | 6.7 | 3.4 |
| $n^f$(H$_2$PdCl$_4$)/$\mu$mol | 1.12 | 1.66 | 2.13 | 2.26 | 1.56 | 1.44 | 1.76 |
| $\Delta U_{ign}/J$ | 2.8 | 2.8 | 2.7 | 2.8 | 2.8 | 2.7 | 2.8 |
| $\varepsilon^i$(cont)/(J·K$^{-1}$) | 96.8 | 96.7 | 96.9 | 96.9 | 96.9 | 96.9 | 96.9 |
| $\varepsilon^f$(cont)/(J·K$^{-1}$) | 96.0 | 96.0 | 96.1 | 96.2 | 96.2 | 96.2 | 96.2 |
| $\Delta m$(H$_2$O)/g[b] | −22.14 | −22.18 | −24.62 | −24.30 | −24.51 | −24.59 | −25.61 |
| $\Delta U$(std. state)/J[c] | 27.3 | 28.1 | 27.2 | 28.7 | 28.8 | 28.5 | 28.4 |
| $\Delta_{dec} U^f$(HNO$_3$)/J | 26.3 | 28.4 | 29.0 | 28.1 | 28.4 | 28.4 | 28.9 |
| $\Delta_{dec} U^f$(As$_2$O$_5$)/J | 294.6 | 304.1 | 302.0 | 299.3 | 304.8 | 285.0 | 301.1 |
| $-\Delta_{IBP} U/J$ | 27471.7 | 28536.0 | 27719.6 | 28661.4 | 28670.8 | 28647.7 | 28715.8 |
| $-\Delta_c u^\circ$/(kJ·g$^{-1}$) | 12.2592 | 12.2578 | 12.2552 | 12.2680 | 12.2541 | 12.2595 | 12.2609 |
| $-\Delta_c U_m^\circ$/(kJ·mol$^{-1}$) | 2830.76 | 2830.45 | 2829.84 | 2832.80 | 2829.59 | 2830.84 | 2831.16 |

[a] Amount of As$_2$O$_3$(aq) consumed by catalytic oxidation with O$_2$(aq) prior to ignition of a sample.

[b] Deviation of the mass of calorimeter water from a predetermined value.

[c] Includes items 81 to 85, 86b to 89, 91a, 93, and 94 of the revised scheme described in the text.

where the parenthesized numbers are the item numbers of the form given in reference 6 and modified in this study and $p^\circ = 10^5$ Pa. The mean and standard deviation of the mean of observed standard molar energies of combustion are $-(2830.78 \pm 0.40)$ kJ·mol$^{-1}$.

The most significant contribution from the side reactions is the oxidation of arsenious oxide by chlorine: As$_2$O$_3$(aq) + 4Cl$_2$(g) + 2H$_2$O(l) = As$_2$O$_5$(aq) + 4HCl(aq), and correction was made for the reaction: As$_2$O$_5$(aq) = As$_2$O$_3$(aq)+O$_2$(g). In the present study, 70 per cent of the arsenious oxide initially present in the bomb was consumed by the reaction with Cl$_2$. This means that 35 per cent of chlorine initially appeared as Cl$_2$ in the combustion, the rest as HCl. The contribution to the total standard energy change (item 95) from the side reaction was 1.1 per cent; hence an error of 0.1 per cent in the determination of As$_2$O$_3$(aq) consumed by reaction with Cl$_2$(g) corresponds to an error of 0.004 per cent of the final result (standard molar energy of combustion of CTP; item 100). The contribution from the pre-oxidation of As$_2$O$_3$(aq) was calculated by assuming that the pre-oxidation was interrupted by the formation of a large amount of HCl in the bomb solution.[11] About 1 per cent of As$_2$O$_3$(aq) was consumed by the pre-oxidation and its contribution was about 0.01 per cent of the total standard energy change (item 95).

The second significant side reaction is the formation of nitric acid, the correction relating to the reaction: HNO$_3$(aq) = (1/2)N$_2$(g) + (5/2)O$_2$(g) + (1/2)H$_2$O(l). The mole fraction of N$_2$ found as nitric acid in the final bomb solutions was about 0.2.

The contribution from this reaction amounts to nearly 0.1 per cent of total standard energy change (item 95) and a possible error of 1 per cent in the determination of nitric acid leads to an error of 0.004 per cent in the final result (item 100), which is barely significant. This uncertainty would be attributable mostly to the incomplete separation of $NO_3^-$(aq) and $AsO_4^{3-}$(aq) peaks in the original chromatogram. In the present study, the mole ratio $n(HNO_3)/n\{C_5H_3N(Cl)(CCl_3)\}$ is rather low owing to the low nitrogen content of CTP, in spite of high temperatures during combustion caused by the use of the paraffin oil. A more efficient column for the separation of ion-chromatographic peaks of $NO_3^-$(aq) and $AsO_4^{3-}$(aq) is required when the mole ratio $n(HNO_3)/n(C_pH_qO_rN_sCl_t)$ for a compound $C_pH_qO_rN_sCl_t$ studied is higher than that in the present study. The amount of $HNO_2$ was about 0.002 mmol in every experiment. This is a rather small amount in spite of the presence of arsenious oxide in the final bomb solution, its contribution being negligibly small as compared with the total standard energy change.

Au(III) and Pd(II) in the final bomb solution would be formed by the corrosion with chlorine at high temperatures of the internal fittings of the bomb and/or the solder used to produce them. The sum of contributions from Pt(IV), Au(III), and Pd(II) to the final result amounted to 0.03 per cent. The present methods for the determination of amounts of $HNO_3$ and of the noble metals are sensitive and convenient, and require a small amount of final bomb solution. Hence, they would be successfully applied to micro-bomb combustion calorimetry of organic chlorine compounds.

In this study, a composite computation form based on those for CHOCl,[6] and CHON,[5] compounds was used to calculate the standard molar energy of combustion from experimental and auxiliary quantities. Possible systematic error introduced by the present treatment to the energy of solution of carbon dioxide in the final bomb solution (item 87) may be evaluated as follows: Nitric acid contributes to item 87 through both the solubility constant (item 54, which depends on the amount of nitric acid in the solution as shown in item 51) and the molar energy of solution of carbon dioxide (item 71b). In the present experiments, the contributions of nitric acid to $K(CO_2)$ (item 51) and to $\Delta_{sol}U''(CO_2)$ (item 71b) are 0.07 per cent and 0.12 per cent of each total, respectively. Hence, the overall contribution of nitric acid to $\Delta_{sol}U(CO_2)$ (item 87) is about 0.19 per cent, while the contribution of $\Delta_{sol}U(CO_2)$ to the total standard energy change $\Delta_cU^\circ$(sub) (item 95) was 0.13 per cent. Consequently, even when the contributions from nitric acid in both of items 51 and 71b were 100 per cent in error simultaneously, their combined effect on the final result $\Delta_cU_m^\circ$(compound) (item 100) would be less than 0.001 per cent of the total, which is quite insignificant. Possible systematic error in the energy of solution of oxygen to the final bomb solution is even less significant.

Derived standard molar thermodynamic quantities are $\Delta_cU_m^\circ$(cr) $= -(2830.8 \pm 1.6)$ kJ·mol$^{-1}$, $\Delta_cH_m^\circ$(cr) $= -(2828.9 \pm 1.6)$ kJ·mol$^{-1}$, and $\Delta_fH_m^\circ$(cr) $= -(55.4 \pm 1.8)$ kJ·mol$^{-1}$, where uncertainties are twice the final overall standard deviations of the mean.[14] CODATA key values[15,16] were used to derive the standard enthalpy of formation. No other value was found in the literature for 2-chloro-6-(trichloromethyl)pyridine.

## REFERENCES

1. Tan, Z. C.; Ye, J. C.; Yin, A. X.; Chen, S. X.; Wang, W. B. *Kexue Tongbao* **1987**, 32, 240.
2. Tan, Z. C.; Sorai, M.; Suga, H. *Scientia Sinica, series B*, in the press.
3. Laynez, J.; Ringnér, B.; Sunner, S. *J. Chem. Thermodynamics* **1970**, 2, 603.
4. Zimmer, M. F.; Baroody, E. E.; Schwartz, M.; McAllister, M. P. *J. Chem. Eng. Data* **1964**, 9, 527.
5. Hubbard, W. N.; Scott, D. W.; Waddington, G. *Experimental Thermochemistry, Vol. 1*. Rossini, F. D.: editor. Interscience: New York. **1956**, Chap. 5.
6. Hu, A. T.; Sinke, G. C.; Månsson, M.; Ringnér, B. *J. Chem. Thermodynamics* **1972**, 4, 283.
7. Sakiyama, M.; Nakano, T.; Seki, S. *Bull. Chem. Soc. Jpn* **1975**, 48, 1705.
8. Nishiyama, K.; Sakiyama, M.; Seki, S.; Horita, H.; Otsubo, T.; Misumi, S. *Bull. Chem. Soc. Jpn* **1980**, 53, 869.
9. Nagano, Y.; Sakiyama, M.; Fujiwara, T.; Kondo, Y. *J. Phys. Chem.* **1988**, 92, 5823.
10. Inagaki, S.; Murata, S.; Sakiyama, M. *Bull. Chem. Soc. Jpn* **1982**, 55, 2808.
11. Stridh, G. *J. Chem. Thermodynamics* **1975**, 7, 703.
12. Wagman, W. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *The NBS Tables of Chemical Thermodynamic Properties, J. Phys. Chem. Ref. Data* **1982**, 11, Supplement No. 2.
13. *Pure Appl. Chem.* **1979**, 51, 405.
14. Olofsson, G. *Experimental Thermodynamics, Vol. 1. Combustion Calorimetry*. Sunner, S.; Månsson, M.: editors. Pergamon: Oxford. **1979**. Chap. 6.
15. CODATA Committee on Key Values for Thermodynamics, *J. Chem. Thermodynamics* **1978**, 10, 903.
16. Parker, V. B.; Wagman, D. D.; Garvin, D. *Selected Thermochemical Data Compatible with the CODATA Recommendations, NBSIR* 75–968, U.S. Department of Commerce: Washington. **1976**.