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Heat Capacity and Enthalpy of Formation of Trimethyl Phosphite, 2-Chloromethylbenzonitrile, and 2-Dimethylphosphonomethylbenzonitrile

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The heat capacities, C_p, of trimethyl phosphite, 2-dimethylphosphonomethylbenzonitrile, and 2-chloromethylbenzonitrile are measured with an adiabatic calorimeter, and the standard enthalpies of formation, $\Delta_f H^o$(298.15 K) (l or cr), for the three substances are determined. For this purpose, $C_p(T)$ values of trimethyl phosphite and 2-dimethylphosphonomethylbenzonitrile are measured in the temperature range from (298.15 to 350.32) K, and the $C_p(T)$ curves of 2-chloromethylbenzonitrile are also obtained for the crystal (300.35 to 329.00 K) and the liquid (337.26 to 372.45 K), respectively. The deviation of experimental heat capacities from the corresponding smoothed values lies within ± 1.5 %. A fusion transition phenomenon is found from the $C_p(T)$ curves of 2-chloromethylbenzonitrile, and the enthalpy of fusion is measured with a differential scanning calorimeter (DSC). The gas-phase standard enthalpies of formation, $\Delta_f H^o$(g, 298.15 K), of the three compounds are evaluated by the Benson group additive method. The critical temperature T_c, critical pressure P_c, and enthalpy of vaporization $\Delta_{vap}H^o$ of the compounds are also calculated by different group additive methods. On the basis of the above data, the values of $\Delta_f H^o$(l, 298.15 K) of trimethyl phosphate and 2-dimethylphosphonomethylbenzonitrile and of $\Delta_f H^o$-(cr, 298.15 K) of 2-chloromethylbenzonitrile are estimated. A thermochemical cycle including a chemical reaction is designed to examine the reliability of the values by measuring the heat of reaction. The result shows that the enthalpies of formation, $\Delta_f H^o$(298.15 K) (l or cr), for the three substances are acceptable.

Introduction

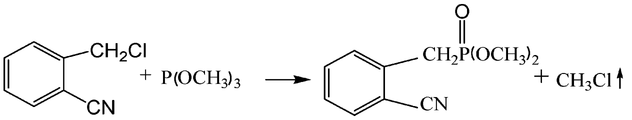
The specific heat capacity and enthalpy of substances are not only the most important thermodynamic properties but also the characteristic data concerned with the structure of a substance. They are widely used in physics and chemistry as well as in chemical engineering, energy resources, and material engineering.

2-Dimethylphosphonomethylbenzonitrile (CASRN 78022-18-1) is an important intermediate used in the synthesis of 1,4-bis(cyanostyryl)benzene (CASRN 13001-93-3) which is the fluorescent whitening agent ER (FWA ER), one of the fluorescent dyes.[1] It is synthesized from trimethyl phosphite (CASRN 121-45-9) and 2-chloromethylbenzonitrile (CASRN 612-13-5). So, it is necessary to understand the thermodynamic properties of these compounds because it will be helpful to the engineering design for producing 1,4-bis(cyanostyryl)benzene. Previous research has focused on the efficient synthesis of 1,4-bis(cyanostyryl)benzene.[1−4] The thermodynamic properties of these compounds have not been studied as far as we know. In this study, $C_p(T)$ and $\Delta_f H^o$(298.15 K) (l or cr) of trimethyl phosphite, 2-chloromethylbenzonitrile, and 2-dimethylphosphonomethylbenzonitrile are reported. An adiabatic calorimeter is used to measure the heat capacities, and different group additive methods are used to derive other thermodynamic properties such as enthalpy of formation $\Delta_f H^o$(g, 298.15 K), critical temperature T_c, critical pressure P_c, and enthalpy of vaporization $\Delta_{vap}H^o$ of the compounds.

Measurement of $C_p(T)$ for Trimethyl Phosphite, 2-Dimethylphosphonomethylbenzonitrile, and 2-Chloromethylbenzonitrile

Samples. Trimethyl phosphite and 2-chloromethylbenzonitrile are purchased from Haohua Chemical Reagent Company of Shanghai with the following purities, respectively: 99.5 % and 99 %. 2-Dimethylphosphonomethylbenzonitrile is prepared according to the procedures given in the literature[5] and purified by reduced pressure distillation. Its mass fraction purity is better than 98.5 % by gas chromatography.

The process is



2-Chloromethylbenzonitrile is heated to 423.15 K in a round-bottomed flask by an oil bath. Then, trimethyl phosphite is added slowly, and the temperature is kept at (423.15 to 433.15) K for 4 h. The product is purified by reduced pressure distillation. Its boiling point at 0.1 MPa is determined to be (552 to 553) K with a microscopic boiling point device.

Apparatus and Procedures

Adiabatic Calorimeter. The apparatus and experimental procedures used here are similar to those described in the literature.[6] Briefly, the automatic adiabatic calorimeter consisted of a sample cell, a miniature platinum resistance thermometer, an electric heater, inner and outer adiabatic shields, a Dewar vessel, a high-vacuum can, and two sets of six-junction chromel−constantan thermopiles which are installed between the calorimetric cell and the inner shield and between the inner and the outer shields. Prior to the heat capacity measurement of the sample, the heat capacities of α-aluminum oxide, the standard reference material, are measured from T = (298 to 380) K to verify the reliability of the adiabatic calorimeter. The results show that the deviation of our calibration is within ± 0.5 %.

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Table 1. Heat Capacities of Trimethyl Phosphite Liquid

T	C_p	T	C_p	T	C_p
K	$J\cdot g^{-1}\cdot K^{-1}$	K	$J\cdot g^{-1}\cdot K^{-1}$	K	$J\cdot g^{-1}\cdot K^{-1}$
299.05	1.4237	316.73	1.5206	335.89	1.6310
302.10	1.4438	319.69	1.5484	337.70	1.6457
305.10	1.4562	322.33	1.5652	340.75	1.6719
308.15	1.4762	325.90	1.5747	343.73	1.7095
310.95	1.4818	329.00	1.5870	348.05	1.7290
313.75	1.5132	331.35	1.6149		

Table 2. Heat Capacities of 2-Dimethylphosphonomethylbenzonitrile Liquid

T	C_p	T	C_p	T	C_p
K	$J\cdot g^{-1}\cdot K^{-1}$	K	$J\cdot g^{-1}\cdot K^{-1}$	K	$J\cdot g^{-1}\cdot K^{-1}$
298.15	1.8661	320.36	1.9658	339.02	2.1578
303.16	1.8781	322.75	1.9884	342.19	2.1923
308.11	1.8900	326.25	2.0179	345.14	2.2215
311.36	1.9188	329.25	2.0547	347.69	2.2495
314.55	1.9395	332.55	2.0870	350.32	2.2690
317.75	1.9521	336.54	2.1249		

Table 3. Heat Capacities of 2-Chloromethylbenzonitrile

T	C_p	T	C_p	T	C_p
K	$J\cdot g^{-1}\cdot K^{-1}$	K	$J\cdot g^{-1}\cdot K^{-1}$	K	$J\cdot g^{-1}\cdot K^{-1}$
		Crystal			
300.35	1.1321	310.95	1.1818	322.33	1.2452
303.10	1.1438	313.75	1.1832	325.90	1.2547
305.10	1.1562	316.73	1.1906	329.00	1.2870
308.15	1.1662	319.69	1.2084		
		Liquid			
337.26	2.2367	352.35	2.3193	365.85	2.3916
340.28	2.2405	355.31	2.3395	367.00	2.4156
344.05	2.2515	357.91	2.3512	370.10	2.4367
346.70	2.2678	360.55	2.3605	371.20	2.4518
349.55	2.2812	362.85	2.3789	372.45	2.4736

The heat capacity measurements are conducted by the standard procedure of intermittently heating the sample and alternately measuring the temperature. The heating rate and the temperature increments of the experimental points were generally controlled from (0.1 to 0.4) K$\cdot$min^{-1} and (1 to 4) K. The heating duration is 10 min, and the temperature drift rates of the sample cell measured in an equilibrium period are always kept within (10^{-3} to 10^{-4}) K$\cdot$min^{-1} during the acquisition of all heat capacity data. Taking into account the above factors and the effect of impurities in substances, the estimated uncertainty of heat capacity measurements is better than ± 1 %.

Differential Scanning Calorimeter (DSC). The DSC experiments are performed on a DSC 200F3 from Netzsch Instrument Inc. Both the cell constant and the temperature calibrations are obtained from the run in which a calibration material (e.g., indium) is heated through its melting point. The enthalpy of fusion and the melting point of indium are used to determine the cell constant and temperature calibrations. The samples are cooled with an average rate of about 6 K$\cdot$min^{-1}. The measurements are made using a heating rate of 2.5 K$\cdot$min^{-1}. The DSC samples have a mass between (5 and 15) mg. The determination of a melting temperature is estimated to be accurate to ± 0.1 K. The enthalpy of fusion can be determined with an accuracy of ± 0.05 kJ$\cdot$mol^{-1}.

Results and Discussion

Heat Capacity of Trimethyl Phosphite and 2-Dimethylphosphonomethylbenzonitrile. The values for heat capacities of trimethyl phosphite and 2-dimethylphosphonomethylbenzonitrile are listed in Table 1 and Table 2 and plotted in Figure 1.

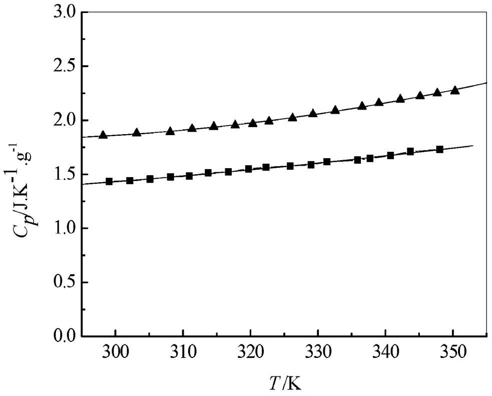


Figure 1. Heat capacities of trimethyl phosphite and 2-dimethyl phosphonomethylbenzonitrile: ■, trimethyl phosphite; ▲, 2-dimethylphosphonomethylbenzonitrile; —, values calculated by eq 1.

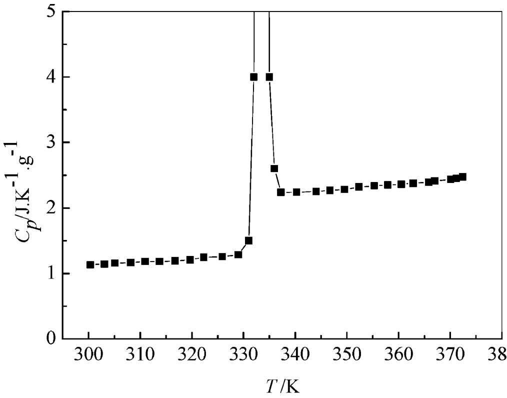


Figure 2. Heat capacities of 2-chloromethylbenzonitrile: ■, experimental results; — , values calculated by eq 1.

Heat Capacity of 2-Chloromethylbenzonitrile. 2-Chloromethylbenzonitrile is a crystal at 298.15 K and 0.1 MPa. Heat capacities of 2-chloromethylbenzonitrile are listed in Table 3 and plotted in Figure 2. The heat capacities of 2-chloromethylbenzonitrile increase with temperature in a smooth and continuous manner, without any thermal anomaly in the range from (300.35 to 329.35) K, which means that the compound is stable in this range. However, a thermal anomaly is observed in the temperature range from (329.35 to 335.15) K, which is demonstrated by an increase curve. The thermal anomaly can be ascribed to a solid−liquid-phase transition according to the melting point (334.15 K).[7]

For each sample, a polynomial function of the type

$$C_p/\mathrm{J\cdot g^{-1}\cdot K^{-1}} = a_0 + a_1\cdot T/\mathrm{K} + a_2\cdot(T/\mathrm{K})^2 \qquad (1)$$

was used to correlate the experimental values of C_p with temperature by the method of least-squares. The coefficients a_i in eq 1, the deviations of experimental results from the smoothed curve E, and the temperature range T of eq 1 are shown in Table 4. The polynomial correlation functions are then valid in the range of experimental temperatures.

Enthalpy of Fusion for 2-Chloromethylbenzonitrile. The enthalpy of fusion $\Delta_{\mathrm{fus}}H^{\mathrm{o}}$ of 2-chloromethylbenzonitrile was determined to be 20.53 kJ$\cdot$mol^{-1}, from the following equation[8]

$$\Delta_{\mathrm{fus}}H^{\mathrm{o}} = \frac{Q - m\int_{T_{\mathrm{i}}}^{T_{\mathrm{fus}}} C_p(\mathrm{cr})dT - m\int_{T_{\mathrm{fus}}}^{T_{\mathrm{f}}} C_p(\mathrm{l})dT - m\int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} C_p(0)dT}{n} \qquad (2)$$

Table 4. Parameters a_i, Deviations E, and Temperature Range T of Equation 1

sample	a_0	a_1	$a_2 \cdot 10^{-5}$	E/%	T/K
trimethyl phosphite	2.0396	−0.00909	2.35345	± 1.1	299 to 349
2-dimethylphosphonomethylbenzonitrile	8.8383	−0.05038	9.04112	± 0.8	298 to 351
2-chloromethylbenzonitrile(s)	1.0505	−0.00466	1.63299	± 1.0	300 to 329
2-chloromethylbenzonitrile(l)	9.6553	−0.00480	7.60575	± 1.5	337 to 373

where T_i is a temperature slightly lower than the initial melting temperature; T_f is a temperature slightly higher than the final melting temperature; Q is the total energy introduced into the sample cell from T_i to T_f; $C_p(0)$ is the heat capacity of the sample cell from T_i to T_f; $C_p(\mathrm{cr})$ is the heat capacity of the sample in the solid phase from T_i to T_{fus}; $C_p(\mathrm{l})$ is the heat capacity of the sample in the liquid phase from T_{fus} to T_f; m is the mass of the sample; and n is the molar amount of the sample. The enthalpy of fusion, $\Delta_{\mathrm{fus}}H^{\mathrm{o}}$, of 2-chloromethylbenzonitrile was measured to be (20.81 ± 0.05) kJ·mol^{-1} by a differential scanning calorimeter (DSC). The difference of $\Delta_{\mathrm{fus}}H^{\mathrm{o}}$ measured by the two different kinds of methods is 1.3 %.

Estimation of $\Delta_f H^o$(298.15 K) for 2-Chloromethylbenzonitrile, Trimethyl Phosphite, and 2-Dimethylphosphonomethylbenzonitrile. Because 2-chloromethylbenzonitrile is a crystal under 298.15 K and 0.1 MPa, its solid standard enthalpy of formation $\Delta_f H^{\mathrm{o}}$(cr, 298.15 K) can be expressed

$$\Delta_f H^{\mathrm{o}}(\mathrm{cr}, 298.15\ \mathrm{K}) = \Delta_f H^{\mathrm{o}}(\mathrm{g}, 298.15\ \mathrm{K}) - \Delta_{\mathrm{sub}}H^{\mathrm{o}}(298.15\ \mathrm{K}) \tag{3}$$

Here $\Delta_f H^{\mathrm{o}}$(g, 298.15 K) is the gas standard enthalpy of formation and $\Delta_{\mathrm{sub}}H^{\mathrm{o}}$(298.15 K) is the enthalpy of sublimation.

Trimethyl phosphite and 2-dimethylphosphonomethylbenzonitrile are liquids at 298.15 K and 0.1 MPa. The liquid standard enthalpy of formation $\Delta_f H^{\mathrm{o}}$(l, 298.15 K) can be estimated by eq 4.

$$\Delta_f H^{\mathrm{o}}(\mathrm{l}, 298.15\ \mathrm{K}) = \Delta_f H^{\mathrm{o}}(\mathrm{g}, 298.15\ \mathrm{K}) - \Delta_{\mathrm{vap}}H^{\mathrm{o}}(298.15\ \mathrm{K}) \tag{4}$$

The $\Delta_f H^{\mathrm{o}}$(l, 298.15 K) of trimethyl phosphite and 2-dimethylphosphonomethylbenzonitrile can be obtained, if $\Delta_f H^{\mathrm{o}}$(g, 298.15 K) and $\Delta_{\mathrm{vap}}H^{\mathrm{o}}$(298.15 K) of these two compounds are known.

Six group contribution methods on standard enthalpies of formation in the gaseous state have been used in the literature.[9] Because the Benson method allows for effects of next-nearest neighbors, it is the most useful method for complex, high molecular weight species and yields the smallest errors with only a few large deviations. In the present paper, the Benson method is selected to estimate $\Delta_f H^{\mathrm{o}}$(g, 298.15 K) of trimethyl phosphite, 2-chloromethylbenzonitrile, and 2-dimethylphosphonomethylbenzonitrile using the expression

$$\Delta_f H^{\mathrm{o}}(\mathrm{g}, 298.15\ \mathrm{K}) = \sum_j n_j \Delta_f H_j^{\mathrm{o}}(\mathrm{g}, 298.15\ \mathrm{K}) \tag{5}$$

where $\Delta_f H_j^{\mathrm{o}}$(g, 298.15 K) is the group contribution value and n_j is the number of times the contribution is required. 2-Chloromethylbenzonitrile contains four kinds of groups shown in Table 6. Three of them, $\Delta_f H_j^{\mathrm{o}}$(g, 298.15 K), can be found from the literature.[10] The $\Delta_f H_j^{\mathrm{o}}$(g, 298.15 K) of another one is determined as follows.

$\Delta_f H^o$(298.15 K) and $\Delta_f H^o$(g, 298.15 K) of 2-Chloromethylbenzonitrile. The $C-(C_B)(Cl)(H)_2$ group contribution has not been reported so far. Fortunately, the group contribution of $C-(C_B)(Br)(H)_2$ can be found in the literature (−21.4 kJ·mol^{-1}).[10] So, we can get a suitable contribution value of $C-(C_B)(Cl)(H)_2$ by comparing the group contribution differences of some groups such as $C-(Cl)(C)_3$, $C-(B_r)(C)_3$, $C_d-(Cl)(H)$, $C_d-(B_r)(H)$, $C_B-(Cl)$, and $C_B-(B_r)$ in Table 5. It is clear that the differences of group contributions tend to a value of −51.41 kJ·mol^{-1} when Br is replaced by Cl. So, the contribution value of $C-(C_B)(Cl)(H)_2$ is calculated to be −72.98 kJ·mol^{-1}.

Table 5. Differences of Group Contributions When Br Is Replaced by Cl

group	$\Delta_f H_j^{\mathrm{o}}$(g, 298.15 K) kJ·mol^{-1}	differences between two groups kJ·mol^{-1}
$C-(Cl)(C)_3$	−53.50[10]	−51.83
$C-(B_r)(C)_3$	−1.67[10]	
$C_d-(Cl)(H)$[a]	−5.02[10]	−51.00
$C_d-(B_r)(H)$	45.98[10]	
$C_B-(Cl)$[b]	−15.88[10]	−51.41
$C_B-(B_r)$	35.53[10]	

[a] C_d represents a carbon atom that is joined to another carbon atom by a double bond. [b] C_B represents the aromatic C atoms.

Table 6. Calculation of $\Delta_f H^o$(g, 298.15 K) for 2-Chloromethylbenzonitrile

group	contribution number	$\Delta_f H_j^{\mathrm{o}}$(g, 298.15 K) kJ·mol^{-1}
$C_B-(C)$	1	23.03[10]
$C_B-(H)$	4	13.79[10]
$C_B-(CN)$	1	149.64[10]
$C-(C_B)(Cl)(H)_2$	1	−72.73
ΔH_f^{o}(g, 298.15 K)		155.12

$\Delta_f H^{\mathrm{o}}$(g, 298.15 K) of 2-chloromethylbenzonitrile is estimated by the Benson method, and the value is 155.86 kJ·mol^{-1}. The calculation process is presented in Table 6.

We also estimate the value by the Joback method,[11] another broadly applicable method. The result is 159.38 kJ·mol^{-1}.The deviation between these two methods is 2.3 %, so the $\Delta_f H^{\mathrm{o}}$(g, 298.15 K) of 2-chloromethylbenzonitrile and the $\Delta_f H_j^{\mathrm{o}}$(g, 298.15 K) of group $C-(C_B)(Cl)(H)_2$ are acceptable and available. We select the value calculated by the Benson method as the gas standard enthalpy of formation for 2-chloromethylbenzonitrile.

T_c, P_c, and $\Delta_f H^o$(cr, 298.15 K) of 2-Chloromethylbenzonitrile. The calculation of $\Delta_f H^{\mathrm{o}}$(cr, 298.15 K) for 2-chloromethylbenzonitrile is followed by eq 3 in which $\Delta_{\mathrm{sub}}H^{\mathrm{o}}$ can be expressed as

$$\Delta_{\mathrm{sub}}H^{\mathrm{o}}(298.15\ \mathrm{K}) = \Delta_{\mathrm{sub}}H^{\mathrm{o}}(T_{\mathrm{fus}}) - \int_{298.15\ \mathrm{K}}^{T_{\mathrm{fus}}} [C_p(\mathrm{g}) - C_p(\mathrm{cr})]dT \tag{6}$$

In eq 6, the heat capacity difference $[C_p(\mathrm{g}) - C_p(\mathrm{cr})]$ is approximately 3R for a nonplastic crystal, and the enthalpy of sublimation at melting temperature $\Delta_{\mathrm{sub}}H^{\mathrm{o}}(T_{\mathrm{fus}})$ can be calculated as follows

$$\Delta_{\mathrm{sub}}H^{\mathrm{o}}(T_{\mathrm{fus}}) = \Delta_{\mathrm{vap}}H^{\mathrm{o}}(T_{\mathrm{fus}}) + \Delta_{\mathrm{fus}}H^{\mathrm{o}}(T_{\mathrm{fus}}) \tag{7}$$

where $\Delta_{\mathrm{vap}}H^{\mathrm{o}}(T_{\mathrm{fus}})$ and $\Delta_{\mathrm{fus}}H^{o}$ are enthalpy of vaporization and enthalpy of fusion at melting temperature, respectively.

Table 7. Structural Contributions to Calculate Δ_T in Equation 11[9] and Φ in Equation 12[9]

group	contribution number	Δ_T	Φ
$=\overset{|}{C}H$ (in ring)	4	0.011[12]	0.154[12]
$=\overset{|}{C}-$ (in ring)	2	0.011[12]	0.154[12]
$-\overset{|}{C}H_2$	1	0.020[12]	0.227[12]
$-Cl$	1	0.017[12]	0.320[12]
$-CN$	1	0.060[12]	0.360[12]
$\sum \Delta_T$		0. 163	1.831

The Watson relation[9] is used to estimate $\Delta_{vap}H^o(T)$ at T_{fus} as follows

$$\Delta_{vap}H^o(T) = \Delta_{vap}H^o(T_b)\left(\frac{1 - T/T_c}{1 - T_b/T_c}\right)^n \tag{8}$$

where T_c is critical temperature; T_b is boiling point; and $\Delta_{vap}H^o(T_b)$ is enthalpy of vaporization at T_b.

Viswanath and Kuloor[9] recommend that n can be obtained by the expression

$$n = \left(0.00264\frac{\Delta_{vap}H^o(T_b)}{RT_b} + 0.8794\right)^{10} \tag{9}$$

The value of $\Delta_{vap}H^o(T_b)$ can be estimated by Riedel's equation[9]

$$\Delta_{vap}H^o(T_b)/\text{kJ}\cdot\text{mol}^{-1} = \frac{4.18T_cT_b/\text{K}^2(5 \log P_c/\text{MPa} + 2.83)}{(0.930T_c - T_b)/\text{K}} \tag{10}$$

where P_c is critical pressure and T_c is critical temperature.

To estimate the enthalpy of vaporization of 2-chloromethylbenzonitrile at any temperature, we must know the critical temperature and critical pressure of 2-chloromethylbenzonitrile. However, there are no data on this compound. T_c can be calculated by the equation proposed by Riedel et al.: $T_c = T_b/\theta$. In this study, the Lydersen method[12] is used to estimate θ

$$\theta = 0.567 + \sum \Delta_T - \left(\sum \Delta_T\right)^2 \tag{11}$$

where $\sum \Delta_T$ is obtained by adding the contributions listed in Table 7.

The boiling point of 2-chloromethylbenzonitrile is 525.15 K.[7] Taking $\sum \Delta_T$ from eq 11, θ can be estimated as 0.703. Finally, T_c is calculated to be 746.6 K. We also estimate the value by Vowle's method,[9] another broadly applicable method. The result is 745.1 K. So 746.6 K can be selected as the critical temperature of 2-chloromethylbenzonitrile in this paper.

The Lydersen method[12] is used to calculate P_c of 2-chloromethylbenzonitrile by the expression

$$P_c = \frac{0.1M}{(\Phi + 0.34)^2} \tag{12}$$

where M is the molecular weight and Φ is an additive constant which is determined from the molecular structure.

Φ can be calculated by adding structural constants listed in Table 7.

Table 8. Calculation of Δ_fH^o(g, 298.15 K) for Trimethyl Phosphite

group	contribution number	$\Delta_fH_j^o$(g, 298.15 K) kJ·mol^{-1}
$P-(O)_3$	1	−279.22[10]
$O-(P)(C)$	3	−98.23[10]
$C-(P)(H)_3$	3	−42.13[10]
Δ_fH^o(g, 298.15 K)		−703.67

Taking Φ from eq 12, P_c is calculated to be 3.21 MPa. The value estimated by Riedel's method[10] is 3.15 MPa. The difference between these two methods is small, so the values are reliable and available to use. We choose 3.21 MPa for the critical pressure of 2-chloromethylbenzonitrile.

Taking T_c and P_c from eq 10, the value of $\Delta_{vap}H^o(T_b)$ is 52.63 kJ·mol^{-1}. With the same T_c and P_c, we can get the value of $\Delta_{vap}H^o(T_b) = 51.54$ kJ·mol^{-1} by Giacalone's method.[9]

The value 52.63 kJ·mol^{-1} is selected as the $\Delta_{vap}H^o(T_b)$ of 2-chloromethylbenzonitrile. Using eqs (9 to 6) and eq 3 successively, we can get $\Delta_{vap}H^o(T_{fus}) = 66.00$ kJ·mol^{-1}, $\Delta_{sub}H^o(T_{fus}) = 86.53$ kJ·mol^{-1}, and Δ_fH^o(cr, 298.15 K) = 70.23 kJ·mol^{-1}, respectively.

Δ_fH^o(g, 298.15 K) and Δ_fH^o(298.15 K) for Trimethyl Phosphite. The calculation process by the Benson method is shown in Table 8, and the result is compared with the literature value.

The calculation value is −703.67 kJ·mol^{-1}. The value reported in the literature[13] is −704.1 kJ·mol^{-1}, and the deviation is only 0.09 %. The calculation value of trimethyl phosphite with the Benson method is accurate.

Δ_fH^o(l, 298.15 K) of trimethyl phosphite is estimated by eq 4. The calculation procedure is similar to that of 2-chloromethylbenzonitrile. The boiling point of trimethyl phosphite is 384.15 K.[7] The critical temperature could be approximated by the Guldberg rule:[9] $T_c = 1.5T_b = 576.23$ K. In the literature,[14] T_c is found to be 576.2 K. The critical pressure is calculated to be 3.39 MPa by Herzog's method,[9] which is close to the literature value (3.45 MPa).[14] Taking T_c and P_c to eq 10, the value of $\Delta_{vap}H^o(T_b)$ is 33.69 kJ·mol^{-1}. With the same T_c and P_c, we can get the value of $\Delta_{vap}H^o(T_b) = 33.40$ kJ·mol^{-1} by Giacalone's method. The value 33.69 kJ·mol^{-1} is selected as the $\Delta_{vap}H^o(T_b)$. $\Delta_{vap}H^o$(298.15 K) is calculated to be 38.65 kJ·mol^{-1} by eqs 8 and 9. Finally, we get the Δ_fH^o(l, 298.15 K) of trimethyl phosphite of −742.34 kJ·mol^{-1}, which is close to the literature value (−741.0 kJ·mol^{-1}).[13]

Δ_fH^o(g, 298.15 K) and Δ_fH^o(298.15 K) for 2-Dimethylphosphonomethylbenzonitrile. In the estimation of Δ_fH^o(g, 298.15 K) for 2-dimethylphosphonomethylbenzonitrile, the $C-(PO)(C_B)(H)_2$ group contribution is determined by a proce-

Table 9. Differences of Group Contributions When C Is Replaced by C_B

group	$\Delta_f H_j^o$(g, 298.15 K) kJ·mol^{-1}	differences between two groups kJ·mol^{-1}
$C-(C_d)(C_B)(H)_2$	−17.93[10]	1.97
$C-(C_d)(C)(H)_2$	−19.90[10]	
$C-(C_B)(B_r)(H)_2$	−21.32[10]	1.25
$C-(C)(B_r)(H)_2$	−22.57[10]	
$C-(C_B)(I)(H)_2$	35.11[10]	1.67
$C-(C)(I)(H)_2$	33.44[10]	

Table 10. Calculation of Gas Standard Enthalpy of Formation for 2-Dimethylphosphonomethylbenzonitrile

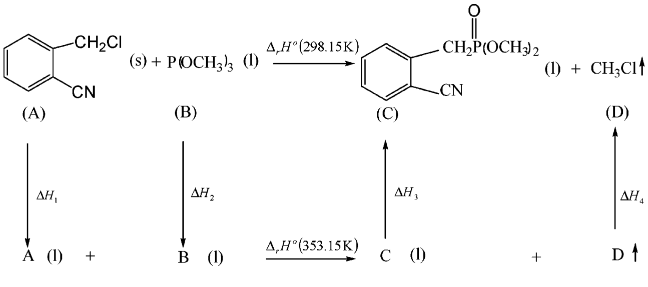
group	contribution number	$\Delta_f H_j^o$(g, 298.15 K) kJ·mol^{-1}
$C_B-(C)$	1	23.03[7]
$C_B-(H)$	4	13.79[7]
$C_B-(CN)$	1	149.64[7]
$PO-(C)(O)_2$	1	−415.91[7]
$O-(C)(PO)$	2	−170.13[7]
$C(H_3)O$	2	−42.13[7]
$C-(PO)(C_B)(H)_2$	1	−12.54
$\Delta_f H^o$(g, 298.15 K)		−625.12

dure similar to $C-(C_B)(Cl)(H)_2$. As shown in Table 9, contribution values of three pairs of groups are listed and compared. It can be seen that the differences of group contributions tend to a value (1.67 kJ·mol^{-1}) when C is replaced by C_B. The contribution value of $C-(PO)(C)(H)_2$ is −14.21 kJ·mol^{-1}, so the value of $C-(PO)(C_B)(H)_2$ is calculated to be −12.54 kJ·mol^{-1}.

The calculation for the gas standard enthalpy of formation is the same as that mentioned above for 2-dimethylphosphonomethylbenzonitrile, and the corresponding data are shown in Table 10. The gas standard enthalpy of formation is −625.12 kJ·mol^{-1} for 2-dimethylphosphonomethylbenzonitrile. This value will be manifested by experimental data in the back of this article.

In this work, the boiling point of 2-dimethylphosphonomethylbenzonitrile is measured to be (552 to 553) K with a microscopic boiling point device. With the same method as that used for trimethyl phosphite, we can get $T_c = 829.5$ K, $P_c = 2.30$ MPa, $\Delta_{vap}H^o(T_b) = 43.64$ kJ·mol^{-1}, and $\Delta_{vap}H^o$(298.15 K) = 54.69 kJ·mol^{-1}, respectively. Finally, we get the value of $\Delta_f H^o$(l, 298.15 K) (−679.80 kJ·mol^{-1}). This value cannot be checked by another prediction method as 2-chloromethylbenzonitrile and cannot be manifested by the literature value as trimethyl phosphite. So we design a thermochemical cycle to verify it.

Verification of the $\Delta_f H^o$(l, 298.15 K) for 2-Dimethylphosphonomethylbenzonitrile by Experiment. The thermochemical cycle designed for the derivation of $\Delta_f H^o$(l, 298.15 K) of 2-dimethylphosphonomethylbenzonitrile is shown as follows.



We can derive $\Delta_f H^o$(l, 298.15 K) of 2-dimethylphosphonomethylbenzonitrile from eq 13.

$$\Delta_r H^o(298.15\text{ K}) = \sum_B \nu_B \Delta_f H^o(\text{B, 298.15 K}) \qquad (13)$$

According to the Kirchhoff equation, $\Delta_r H^o$(298.15 K) can be obtained

$$\Delta_r H^o(298.15\text{ K}) = \Delta_r H^o(353.15\text{ K}) + \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 \quad (14)$$

In eq 14, ΔH_1, ΔH_2, ΔH_3, and ΔH_4 are enthalpy changes of 2-chloromethylbenzonitrile, trimethyl phosphite, 2-dimethylphosphonomethylbenzonitrile and methane chloride, and can be calculated as follows, respectively.

$$\Delta H_1 = 151.5 \times \int_{298.15\text{ K}}^{334.15\text{ K}} C_p(\text{cr})dT + \Delta_{fus}H^o(334.15\text{ K}) + 151.5 \times \int_{334.15\text{ K}}^{353.15\text{ K}} C_p(\text{l})dT = 33.65\text{ kJ·mol}^{-1} \quad (15)$$

$$\Delta H_2 = 124 \times \int_{298.15\text{ K}}^{353.15\text{ K}} C_p(\text{l})dT = 10.78\text{ kJ·mol}^{-1} \quad (16)$$

$$\Delta H_3 = 225 \times \int_{353.15\text{ K}}^{298.15\text{ K}} C_p(\text{l})dT = -24.89\text{ kJ·mol}^{-1} \quad (17)$$

$$\Delta H_4 = 50.5 \times \int_{353.15\text{ K}}^{298.15\text{ K}} C_p(\text{g})dT = -2.36\text{ kJ·mol}^{-1} \quad (18)$$

where $C_p(\text{g})/\text{J·g}^{-1}\text{·K}^{-1} = 0.2729 + 0.002025T/\text{K} - 8.04\cdot10^{-7}(T/\text{K})^2 + 6.8159\cdot10^{-11}(T/\text{K})^3$ is the heat capacity of gas methane chloride.[15]

$\Delta_r H^o$(353.15 K) is measured by a heat conduction microcalorimeter which consists of a sample cell and a reference cell. This method has been described in more detail in the literature.[16] The temperature of this calorimetric experiment is (353.15 ± 0.01) K. The sample cell has the same volume as the reference cell (16 cm^3). To prevent corrosion of the stainless steel cells, two double-layer glass tubes are put in the cells, respectively. In the sample cell, 1.0 g (± 0.0001 g) of trimethyl phosphate and 1.22 g (± 0.0001 g) of 2-chloromethylbenzonitrile are added into the inner tube and the outer tube, respectively. Then the system is heated to the required temperature. After 1 h, the inner tube is broken by a rod, and a chemical reaction between trimethyl phosphate and 2-chloromethylbenzonitrile takes place. The thermal effect is recorded automatically on a computer. According to the mass and the composition of the residue, the heat of reaction at this temperature can be calculated. The experiment is performed five times, and the results are listed in Table 11 in which m is the mass of 2-dimethylphosphonomethylbenzonitrile. The estimated uncertainty of measure is ± 0.5 %.

Finally, $\Delta_r H^o$(298.15 K) = −89.86 kJ·mol^{-1} is obtained from eq 14. $\Delta_f H^o$(298.15 K) of methane chloride is −81.96 kJ·mol^{-1}.[9] According to eq 13, $\Delta_f H^o$(298.15 K) of 2-dimethylphosphonomethylbenzonitrile is calculated to be −680.01 kJ·mol^{-1}. The deviation between experiment and calculation is 0.03 %. The result shows that the calculated values of $\Delta_f H^o$(l, 298.15 K) of trimethyl phosphate and 2-dimethylphosphonomethylbenzonitrile and of $\Delta_f H^o$(cr, 298.15 K) of 2-chloromethylbenzonitrile are reliable and available.

Summary

The heat capacities of trimethyl phosphite, 2-chloromethylbenzonitrile, and 2-dimethylphosphonomethylbenzonitrile have been measured. To calculate $\Delta_f H^o$(g, 298.15 K) of 2-chloromethylbenzonitrile and 2-dimethylphosphonomethylbenzonitrile, the enthalpy group values of $C-(C_B)(Cl)(H)_2$ and $C-(PO)(C_B)(H)_2$ for the Benson method are derived to be −72.73 kJ·mol^{-1}

Table 11. Enthalpy of Reaction at 353.15 K

no.	m / mg	$\Delta_r H^o$(353.15 K) / mJ	$\Delta_r H^o$(353.15 K) / kJ·mol^{-1}
1	10.34	−4917.71	−107.01
2	10.92	−5185.79	−106.85
3	9.85	−4674.15	−106.77
4	10.00	−4762.67	−107.16
5	11.76	−5591.49	−106.98
mean			−106.95

and −12.54 kJ·mol^{-1}, respectively. After determining T_c and P_c of the compounds, $\Delta_f H^o$(cr, 298.15K) of 2-chloromethylbenzonitrile and $\Delta_f H^o$(l, 298.15 K) for trimethyl phosphite and 2-dimethylphosphonomethylbenzonitrile were calculated to be 70.23 kJ·mol^{-1}, −742.34 kJ·mol^{-1}, and −679.80 kJ·mol^{-1}, respectively.

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