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Research for the thermochemical properties of the formation reaction of 2-chloroethylideneaminocarbamic acid ethylester

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Abstract

The enthalpy of reaction of the 2-chloroethylideneaminocarbamic acid ethylester formation from chloroacetaldehyde and hydrazinoformic acid ethylester in ethanol at the temperature of 298.15 K has been determined by a microcalorimeter. Experimental results gave the enthalpy of formation $\Delta_r H_m^\theta = (-16.07 \pm 0.079)\,\mathrm{kJ\,mol^{-1}}$, the reaction order of this reaction $n = 1$; the rate constant $k = 1.190 \times 10^{-3}\,\mathrm{s^{-1}}$ and the free energy of activation $\Delta G_{\neq}^{\theta} = 89.718\,\mathrm{kJ\,mol^{-1}}$. The result indicates that the reaction takes place easily at room temperature. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: 2-Chloroethylideneaminocarbamic acid ethylester; Enthalpy of reaction; Calorimetry property

1. Introduction

2-Chloroethylideneaminocarbamic acid ethylester is a very important intermediate used in the synthesis of new plant growth regulators [1]. Its synthetic method and melting point have been reported [2]. However, the thermochemical properties and thermokinetics of the reaction mentioned in the title have not been reported. In this paper, the enthalpy of the reaction was measured by a microcalorimeter. The reaction thermokinetics and the fundamental parameters for the reaction, including the rate constant (k), the reaction order (n) and the free energy of activation ($\Delta G_{\neq}^{\theta}$) were calculated from the reaction enthalpy. These important parameters will provide a scientific basis for process of synthesis.

2. Experimental

2.1. Materials

Hydrazinoformic acid ethylester (kept in a desiccator) was prepared based on the literature [3]. Then it was recrystalized three times. The result purity was bigger than 99.95%, analyzed by GC. Chloroacetaldehyde and ethanol were AR grade from Fluka Chemie and Xi'an Chemical Company, respectively.

2.2. Experimental equipment and conditions

The reaction thermokinetics were studied by a microcalorimeter; RD496-III (Southwest Institutes of Electronic Engineering of China), which was equipped with two 1.6 ml vessels (Fig. 1). When the microcalorimeter reached thermal equilibrium, the glass rod of the sample and the reference vessel were pushed down simultaneously and the samples

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were mixed. The microcalorimeter was calibrated by Joule effect and its sensitivity was 63.994± 0.042 μV mV^{-1} at the temperature of 298.15± 0.005 K. It was verified by measuring the enthalpy of a super pure crystalline KCl in deionzed water at 298.15 K. The experimental value of $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\theta}$ of (17.238 ± 0.048) kJ mol^{-1} was in good agreement with that of $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\theta}$ (17.241 ± 0.018) kJ mol^{-1} reported in the literature [4]. This indicated that the device used in this work was reliable. Analytic equipment used: PE-2400 elemental analyzer; BRUKER EQ UNINOX-550 IR spectrophotometer with KBr disks, WC-1 melting point apparatus (Si Chuan University of China).

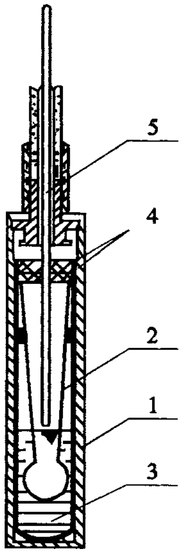
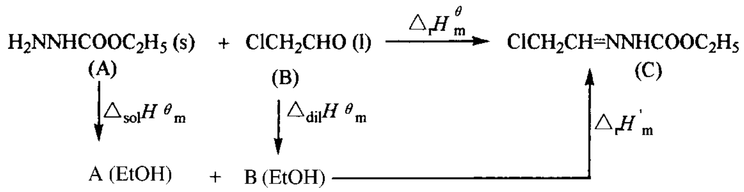


Fig. 1. Device used for the study of the reaction: (1) calorimetric cell; (2) adding tube containing chloroacetaldehyde; (3) adding tube containing hydrazinoformic acid ethylester; (4) silicone rubber cover; (5) glass rod (on depressing the rod, the bottom of the tube 2 is broken). The two solutions mix together in the tubes 2 and 3.

3. Results

3.1. Determination of the formation reaction enthalpy

Initial mixtures of starting materials 'A' and 'B' were prepared using ethanol. Since 'A' was soluble in ethanol, there was a heat of solution $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\theta}$ for 'A' and 'B' diluted, there was a heat of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}^{\theta}$ for 'B'. We designed a thermochemical cycle as follows:



Therefore, $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} = \Delta_{\mathrm{dil}}H_{\mathrm{m}}^{\theta} + \Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\theta} + \Delta_{\mathrm{r}}H_{\mathrm{m}}'$. The values of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}^{\theta}$, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\theta}$ and $\Delta_{\mathrm{r}}H_{\mathrm{m}}'$ are listed in Table 1.

$$\begin{aligned}\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\theta} &= [(-2.633 \pm 0.014) + (7.061 \pm 0.045) \\ &\quad + (-20.502 \pm 0.064)]\,\mathrm{kJ\,mol^{-1}} \\ &= (-16.074 \pm 0.079)\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

3.2. Thermokinetic parameters of the reaction in the liquid phase

The typical thermokinetic (TK) curve of the formation reaction at 298.15 K is showed in Fig. 2. The original data obtained from the TK curve are listed in Table 2. The formation reaction was an exothermal reaction. The reaction order (n) and the rate constant (k) were obtained from Eq. (1) by treating the experimental data as follows:

$$\ln\left(\frac{1}{H_0}\frac{\mathrm{d}H}{\mathrm{d}t}\right) = \ln k + n\ln\left(1 - \frac{H_t}{H_0}\right) \tag{1}$$

where H_0 is the total reaction heat (corresponding to the total area under the TK curve), H_t the reaction heat at a certain time (corresponding to the partial area under the TK curve) and $\mathrm{d}H_t/\mathrm{d}t$ the exothermic rate at time t. The calculated results are $n = 1$, $k = 1.190 \times 10^{-3}\,\mathrm{s}^{-1}$ and $r = 0.9971$. The free

Table 1
Experimental data of the $\Delta_{dil}H_m^\theta$, $\Delta_{sol}H_m^\theta$ and $\Delta_r H'_m$

S. no.	Mass (g)	$\Delta_{dil}H_m^\theta$ (mJ)	Mass (g)	$\Delta_{sol}H_m^\theta$ (mJ)	Mass (g)	$\Delta_r H'_m$ (mJ)
1	0.05230	−1758.731	0.03116	2100.584	0.05227	−6126.198
2	0.05227	−1750.286	0.03121	2114.332	0.05230	−6140.345
3	0.05236	−1767.427	0.03118	2106.831	0.05225	−6122.546
4	0.05220	−1744.656	0.03120	2112.067	0.05240	−6164.931
5	0.05232	−1761.505	0.03127	2137.604	0.05241	−6167.883
6	0.05223	−1746.366	0.03124	2125.790	0.05229	−6135.766
Mean	−1754.829 ± 9.102 or (−2.633 ± 0.014) kJ mol^{-1}		2116.201 ± 13.434 or (7.061 ± 0.045) kJ mol^{-1}		−6140.345 ± 19.288 or (−20.502 ± 0.064) kJ mol^{-1}	

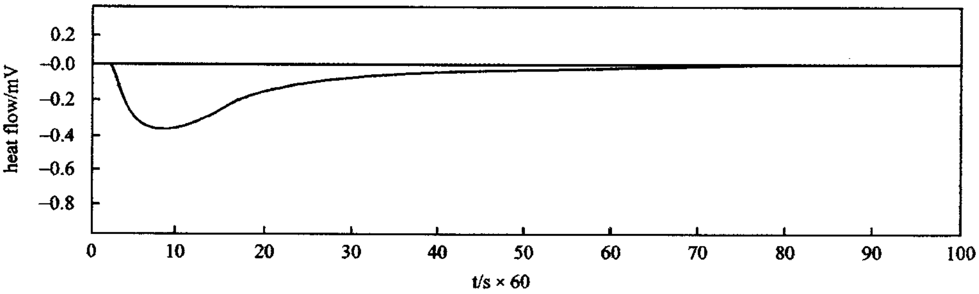


Fig. 2. Typical thermokinetic curve of the reaction studied.

energy of activation $\Delta G^\theta_{\neq}$ was obtained from Eq. (2) as follows:

$$\Delta G^\theta_{\neq} = RT\ln\left(\frac{RT}{Nhk}\right) \qquad (2)$$

where R is the gas constant, T the absolute temperature, $\Delta G^\theta_{\neq}$ the free energy of activation, N the Avogadro number and h is the Planck's constant. The calculated result is $\Delta G^\theta_{\neq} = 89.718\,\text{kJ mol}^{-1}$.

Table 2
Thermokinetic data of the reaction[a]

t (s)	$(\mathrm{d}H/\mathrm{d}t)_i \times 10^3$ (J s^{-1})	H_i/H_0
450	5.318	0.341
600	4.530	0.462
750	3.736	0.562
900	3.050	0.644
1200	2.010	0.765
1500	1.350	0.844
1800	0.933	0.897
2100	0.653	0.932
2400	0.481	0.956
2700	0.370	0.972

[a] $H_0 = -6140.345$ mJ g^{-1}.

3.3. Evaluation test of the reaction product

The final reaction solutions containing the product were combined and the solvent was removed under low pressure. The product precipitated from the residue. It showed the following characteristics after recrystallized three times: mp 120–121°C [2]. Experimental analysis: $C_5H_9O_2N_2Cl$: Calc.: C, 36.47; H, 5.47; N, 17.02%. Found: C, 36.49; H, 5.50; N, 17.05%. IR: 1547 cm^{-1} (the characteristic peak of the compound with C=N group).

Acknowledgements

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