Microcalorimetric Study on the Oscillating System of Two-phase Reaction of Aqueous Acid with Primary Amine in Chloroform

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It has been found that the two-phase reactions of aqueous HCl, HOAc or H_3PO_4 with primary amine N_{1923} in chloroform are oscillating reactions. Their power-time curves were measured by the titration microcalorimetric method, and the induction period (t_{in}). The first oscillating period ($t_{p.1}$) and the second oscillating period ($t_{p.2}$) were determined. The apparent activating parameters and the orders of the oscillating systems were calculated and the following relationships were established: for the oscillating system of hydrochloric acid $t_{in} \propto c_{HCl}^{0.147}\exp(\frac{1.35\times10^3}{T})$, $t_{p.1} \propto c_{HCl}^{0.241}\cdot\exp(\frac{4.33\times10^3}{T})$, $t_{p.2} \propto c_{HCl}^{0.290}\exp(\frac{5.59\times10^3}{T})$; for the oscillating system of acetic acid, $t_{in} \propto c_{HOAc}^{0.883}\exp(\frac{2.32\times10^3}{T})$, $t_{p.1} \propto c_{HOAc}^{0.399}\cdot\exp(\frac{4.50\times10^3}{T})$, $t_{p.2} \propto c_{HOAc}^{0.301}\exp(\frac{5.88\times10^3}{T})$; for the oscillating system of phosphoric acid, $t_{in} \propto c_{H_3PO_4}^{1.14}\exp(\frac{7.70\times10^4}{T})$, $t_{p.1} \propto c_{H_3PO_4}^{1.42}\exp(\frac{1.14\times10^4}{T})$, $t_{p.2} \propto c_{H_3PO_4}^{1.47}\exp(\frac{1.27\times10^4}{T})$.

Keywords oscillating system, hydrochloric acid, acetic acid, phosphoric acid, primary amine N_{1923}, titration microcalorimetric method

Introduction

Since Belousov[1] found for the first time that the oxidation of citric acid by bromic acid in homogeneous system could produce an oscillating reaction system in the presence of Ce^{3+} as catalyst, much research has been done concerning the oscillating regularity.[2-7]

Primary amine N_{1923} ($RCH(NH_2)R'$, R and R′ represent alkyl of C_{9-11}, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences): content of primary amine is bigger than 99.8%, content of nitrogen is 3.61×10^{-3} mol/g and average molecular weight is 291.8. It is a good extract for acids and metals. The extractions of acetic acid,[8] citric acid[9] and hydrochloric acid[10] by N_{1923} have been reported.

We found an interesting heterogeneous oscillating phenomenon when the thermochemistry of the two-phase reactions between aqueous solutions of inorganic acid and N_{1923} in chloroform was studied. The apparent activating parameters and the orders of these oscillating systems are reported in this paper.

Experimental

Instrument

The 2277 thermal activity monitor is produced by Thermometric AB (Sweden). Four independent calorimetric units are hold in a water bath (23 L) with working temperatures between 10 and 90 ℃. The operation can be maintained at a given temperature within $\pm10^{-4}$ ℃ over 24 h. The detection limit of the monitor is 0.15 μW and the baseline stability is 0.20 μW over 24 h.

Materials

N_{1923}, the average molecular weight is 291.8. The content of primary amine is bigger than 99.8% and the content of nitrogen is 3.61×10^{-3} mol/g. HCl, HOAc and H_3PO_4 are all analytical grade. Solution 1: solution of hydrochloric acid (0.025, 0.05, 0.10, 0.20 mol/L); solution 2: solution of acetic acid (0.10, 0.20, 0.30, 0.50 mol/L); solution 3: solution of phosphoric acid (0.20, 0.30, 0.40 mol/L); solution 4: primary amine N_{1923} (0.50 mol/L) in chloroform.

Method

In the experiment, two 4 mL of ampoule units were used. One of them contained the sample solution and the other was the reference. The sample solution contained 1 mL of

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solution 1, 2 or 3 and 1 mL of solution 4, the reference contained 1 mL of acid solution and 1 mL of chloroform. The power-time curves were recorded when the amplifier of the monitor was set at 1000 μW and the stirrer shaft was set at the desired speed of 120 r/min for sample solution. When the recording pen returned to the baseline and became stabilized, the process of the oscillating system was completed.

Results and discussion

The power-time curves of the two-phase reaction of inorganic acid with N_{1923} are determined at different temperatures. The obtained values of the induction period (t_{in}), the first oscillating period ($t_{p.1}$) and the second oscillating period ($t_{p.2}$), are listed in Table 1.

The power-time curves of the reactions were also determined at different initial concentrations of acids. The results are listed in Table 2.

Taking the reaction of aqueous HCl with N_{1923} in chloroform as an example, its power-time curves at different temperatures and different initial concentrations of HCl are shown in Figs. 1 and 2, respectively.

Effects of different temperatures on the oscillating systems

The results show that the values of t_{in}, $t_{p.1}$ and $t_{p.2}$ decrease with the increasing of temperature for all the systems. From the relation of $\ln k = \ln A - \frac{E}{RT}$ (Arrhenius theory) and $\ln k = \ln \frac{1}{t} + A'$ (reported in Ref. 11), we have $\ln \frac{1}{t} = -\frac{E}{RT} + A'$. Using the obtained values of t_{in}, $t_{p.1}$ and $t_{p.2}$ at different temperatures to draw a plot of $\ln \frac{1}{t}$ vs. $\frac{1}{T}$, both E and A'' can be obtained from the following equations.

For HCl-N_{1923} oscillating system:

$$\ln \frac{1}{t_{in}} = -1.66 - \frac{1.35 \times 10^3}{T} \quad (1)$$
$r = 0.9998$ $E_{in} = 11.2$ kJ/mol

$$\ln \frac{1}{t_{p.1}} = 8.66 - \frac{4.33 \times 10^3}{T} \quad (2)$$
$r = 0.9993$ $E_{p.1} = 36.0$ kJ/mol

$$\ln \frac{1}{t_{p.2}} = 13.1 - \frac{5.59 \times 10^3}{T} \quad (3)$$
$r = 0.9999$ $E_{P.2} = 46.4$ kJ/mol

For HOAc-N_{1923} oscillating system:

$$\ln \frac{1}{t_{in}} = 1.69 - \frac{2.32 \times 10^3}{T} \quad (4)$$
$r = 0.9957$ $E_{in} = 19.3$ kJ/mol

$$\ln \frac{1}{t_{p.1}} = 9.42 - \frac{4.50 \times 10^3}{T} \quad (5)$$
$r = 0.9910$ $E_{p.1} = 37.4$ kJ/mol

$$\ln \frac{1}{t_{p.2}} = 14.3 - \frac{5.88 \times 10^3}{T} \quad (6)$$
$r = 0.9766$ $E_{P.2} = 48.9$ kJ/mol

For H_3PO_4-N_{1923} oscillating system:

Table 1 Values of t_{in}, $t_{p.1}$ and $t_{p.2}$ obtained at different temperatures[a]

T (K)	HCl-N_{1923} system			HOAc-N_{1923} system			H_3PO_4-N_{1923} system		
	t_{in} (min)	$t_{p.1}$ (min)	$t_{p.2}$ (min)	t_{in} (min)	$t_{p.1}$ (min)	$t_{p.2}$ (min)	t_{in} (min)	$t_{p.1}$ (min)	$t_{p.2}$ (min)
298	485	360	295	440	290	205	1675	655	500
303	450	280	215	385	245	175	955	285	210
308	420	220	160	350	175	125	725	190	125
313	390	180	120	300	145	80			

[a] Initial concentrations of the acids: HCl, 0.10 mol/L; HOAc, 0.30 mol/L; H_3PO_4, 0.30 mol/L.

Table 2 Values of t_{in}, $t_{p.1}$ and $t_{p.2}$ obtained at different initial concentrations of acids at 308 K

c (mol/L)	HCl-N_{1923} system			HOAc-N_{1923} system			H_3PO_4-N_{1923} system		
	t_{in} (min)	$t_{p.1}$ (min)	$t_{p.2}$ (min)	t_{in} (min)	$t_{p.1}$ (min)	$t_{p.2}$ (min)	t_{in} (min)	$t_{p.1}$ (min)	$t_{p.2}$ (min)
0.025	340	150	100						
0.05	375	180	125						
0.10	420	220	160	130	120	95			
0.20	460	245	180	220	150	110	475	105	75
0.30				350	175	125	725	190	125
0.40							1050	280	210
0.50				525	230	155			

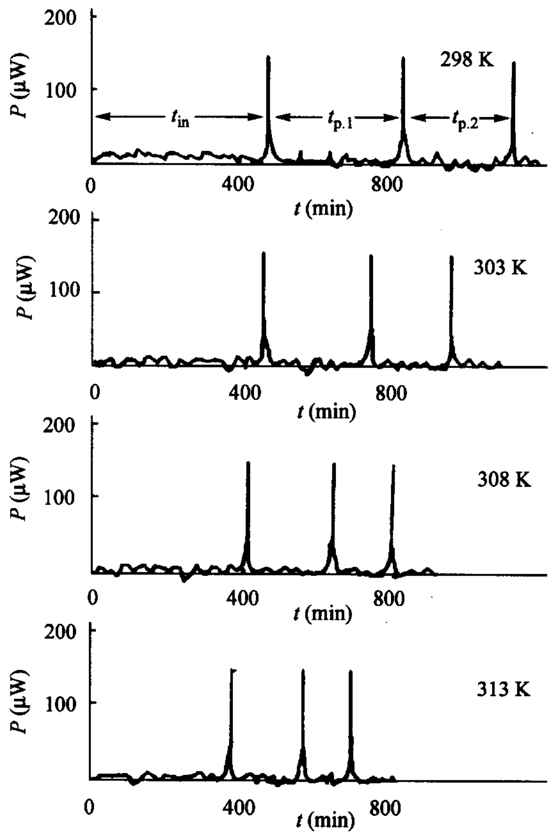

Fig. 1 Power-time curves of oscillating system of hydrochloric acid at different temperatures (c_{HCl} = 0.10 mol/L).

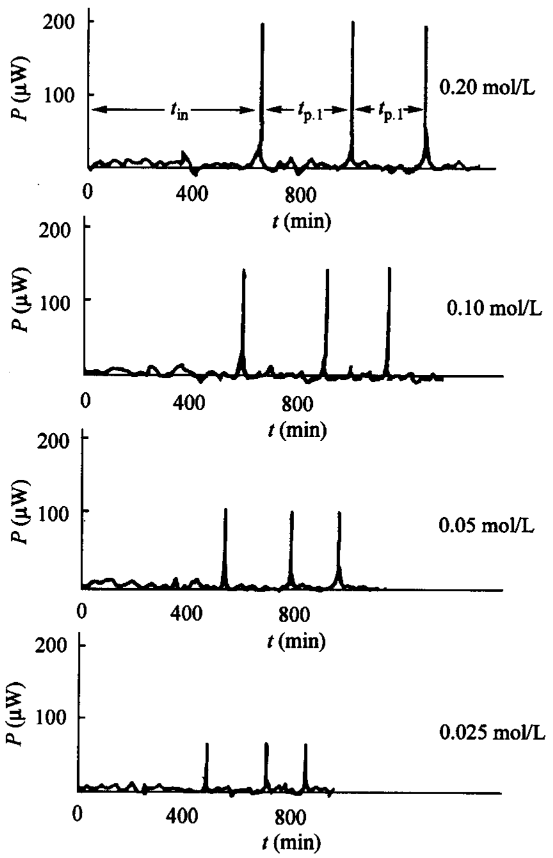

Fig. 2 Power-time curves of oscillating system of hydrochloric acid at different initial concentration of acids (308 K).

$$\ln \frac{1}{t_{in}} = 18.4 - \frac{7.70 \times 10^3}{T} \quad (7)$$

$r = 0.9829 \quad E_{in} = 64.0$ kJ/mol

$$\ln \frac{1}{t_{p.1}} = 31.8 - \frac{1.14 \times 10^4}{T} \quad (8)$$

$r = 0.9826 \quad E_{p.1} = 94.8$ kJ/mol

$$\ln \frac{1}{t_{p.2}} = 36.6 - \frac{1.27 \times 10^4}{T} \quad (9)$$

$r = 0.9909 \quad E_{P.2} = 106$ kJ/mol

Where E_{in}, $E_{p.1}$ and $E_{p.2}$ ($= E$) are apparent activating parameters.

Effects of initial concentration of acids on the oscillating systems

Analyzing the data in Table 2, it is found that there is a linear relationship between ln t_{in}, ln $t_{p.1}$ or ln $t_{p.2}$ and the logarithm of the initial concentrations of the inorganic acid. From the plots of ln t vs. ln c_{acid}, following equations and the orders of the oscillating systems (n_{in}, $n_{p.1}$ and $n_{p.2}$) can be obtained.

For HCl-N_{1923} oscillating system:

$$\ln t_{in} = 6.37 + 0.147 \ln c_{HCl} \quad (10)$$

$r = 0.9992 \quad n_{in} = 0.147$

$$\ln t_{p.1} = 5.91 + 0.241 \ln c_{HCl} \quad (11)$$

$r = 0.9929 \quad n_{p.1} = 0.241$

$$\ln t_{p.2} = 5.69 + 0.290 \ln c_{HCl} \quad (12)$$

$r = 0.9904 \quad n_{p.2} = 0.290$

For HOAc-N_{1923} oscillating system:

$$\ln t_{in} = 6.88 + 0.883 \ln c_{HOAc} \quad (13)$$

$r = 0.9971 \quad n_{in} = 0.883$

$$\ln t_{p.1} = 5.68 + 0.399 \ln c_{HOAc} \quad (14)$$

$r = 0.9914 \quad n_{p.1} = 0.339$

$$\ln t_{p.2} = 5.22 + 0.301 \ln c_{HOAc} \quad (15)$$

$r = 0.9850 \quad n_{p.2} = 0.301$

For H_3PO_4-N_{1923} oscillating system:

$$\ln t_{in} = 7.98 + 1.14 \ln c_{H_3PO_4} \quad (16)$$

$r = 0.9982 \quad n_{in} = 1.14$

$$\ln t_{p.1} = 6.94 + 1.42 \ln c_{H_3PO_4} \quad (17)$$

$r = 0.9997 \quad n_{p.1} = 1.42$

$$\ln t_{p.2} = 6.66 + 1.47 \ln c_{H_3PO_4} \quad (18)$$

$r = 0.9948 \quad n_{p.2} = 1.47$

Combining Eqs. (1)—(9) with Eqs. (10)—(18), following non-linear relationships for the oscillating systems can be established successfully.

For the oscillating system of hydrochloric acid

$$t_{in} \propto c_{HCl}^{0.147} \exp(\frac{1.35 \times 10^3}{T})$$
$$t_{p.1} \propto c_{HCl}^{0.241} \exp(\frac{4.33 \times 10^3}{T})$$
$$t_{p.2} \propto c_{HCl}^{0.290} \exp(\frac{5.59 \times 10^3}{T})$$

For the oscillating system of acetic acid

$$t_{in} \propto c_{HOAc}^{0.883} \exp(\frac{2.32 \times 10^3}{T})$$
$$t_{p.1} \propto c_{HOAc}^{0.399} \exp(\frac{4.50 \times 10^3}{T})$$
$$t_{p.2} \propto c_{HOAc}^{0.301} \exp(\frac{5.88 \times 10^3}{T})$$

For the oscillating system of phosphoric acid

$$t_{in} \propto c_{H_3PO_4}^{1.14} \exp(\frac{7.70 \times 10^4}{T})$$
$$t_{p.1} \propto c_{H_3PO_4}^{1.42} \exp(\frac{1.14 \times 10^4}{T})$$
$$t_{p.2} \propto c_{H_3PO_4}^{1.47} \exp(\frac{1.27 \times 10^4}{T})$$

Conclusions

A new oscillating system of two-phase reaction of inorganic acid aqueous solution and primary amine N_{1923} in chloroform solution was found in solvent extraction system.

The induction period (t_{in}), the first oscillating period ($t_{p.1}$) and the second oscillating period ($t_{p.2}$) of these oscillating systems were determined by their power-time curves. The obtained values of t_{in}, $t_{p.1}$ and $t_{p.2}$ were all much longer than those in homogeneous oscillating system. These decreased with increasing temperature for a definite system, and increased with increasing acidic concentration at a definite temperature.

The apparent activating parameters and the orders of the oscillating systems were obtained by graphic method. These kinetic data are very useful in studies for oscillating systems.

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