THERMODYNAMICS OF PHENYL GLYCIDYL ETHER AND ITS REACTIONS WITH DIPHENYLCARBODIIMIDE AND PHENYL ISOCYANATE WITH THE FORMATION OF IMINOOXAZOLIDINE AND OXAZOLIDINONE IN THE 0-330 K RANGE

UDC 536.631:542.91:547.787

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Polymers containing iminooxazolidine and oxazolidine rings as structural elements have higher thermal stability and heat resistance, and also improved physicomechanical parameters [1]. These polymers are obtained by the reaction of oligoepoxides with carbodiimides and isocyanates [2, 3]. The authors of [4, 5] studied the kinetic regularities and measured the enthalpy of the reaction of diphenylcarbodiimide and phenyl isocyanate with phenyl glycidyl ether (PGE). The enthalpies of combustion and formation of PGE are given in [6], and the data on the calorimetric study of the thermodynamic properties of diphenylcarbodiimide, phenyl isocyanate, iminooxazolidine and oxazolidinone are published in [7-9].

In the present article we report the results of calorimetric studies on the thermodynamic properties of PGE and thermodynamic parameters of processes (1) and (2) for the 0-330 K range of temperatures.

EXPERIMENTAL

Phenyl glycidyl ether was dried over calcined $MgSO_4$ and distilled in vacuo, bp 366 K (200 Pa). By using the calorimetric method, from the melting point depression it was found that the overall content of impurities in the sample studied was 0.7 mole %.

To measure the heat capacity of PGE, we used an adiabatic vacuum calorimeter; its construction and method of operation are similar to those described in [10]. The metrological verification of the calorimeter showed that with the apparatus and its experimental procedure used, the C_p^0 of compounds in the solid and liquid states can be obtained with an accuracy of ±1% in the range of 14-30 K, 0.5% in the 30-50 K range, and 0.3% at T > 50 K. The heat capacity of PGE was measured in the range of 14-330 K. The weight of the sample studied was $5.0592 \cdot 10^{-3}$ kg.

In 39 series of measurements 161 experimental values of C_p^0 were obtained. The C_p^0 values obtained were graphically averaged by means of the corresponding large scale graphs. The experimental values of C_p^0 and the averaging curves of $C_p^0 = f(T)$ of PGE are shown in Fig. 1.

RESULTS AND DISCUSSION

When liquid PGE is cooled it becomes supercooled and vitrefies. On subsequent heating during the measurement of C_D^0 (the ABCD curve) its devitrication was observed, and at a

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Fig. 1. Heat capacity of phenyl glycidyl ether: OMF of crystalline ABC - of vitreous; CDK - of supercooled liquid; KE of liquid PGE.

temperature ~15 K above the glass transition point (T_g^0) , a spontaneous and complete crystallization took place. The heat capacity of the crystalline PGE is described by the OMF curve. The break in the C_p^0 vs T graph is due to the fusion of the PGE crystals. With slow gradual cooling of liquid PGE, it was possible to measure the C_p^0 of a supercooled liquid to a temperature ~20 K lower than T_f^0 . The glass transition temperature $T_g = 189 \pm 1$ K was determined from the dependence of entropy $S^0(T)$ of vitreous PGE on T by the method in [11]. Increase in the heat capacity of devitrification $\Delta C_p^0(T_g^0) = 109 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$ was found graphically (the BC section in Fig. 1). The entropy of vitreous PGE at T = 0 K was calculated from the data on $C_p^0 = f(T)$ of PGE in a vitreous crystalline and liquid states, and also from the data on the temperature and enthalpy of its fusion: $S_g^0(0) = 11.6 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$, and the difference between its zero enthalpies in the vitreous and crystalline states $H_0^0(0) - H_{CT}^0(0) = 7.8 \text{ kJ} \cdot \text{mole}^{-1}$. The calculations were carried out using equations given in [12]

$$S_{g}^{0}(0) = \int_{0}^{T_{f}^{0}} (C_{p,cr}^{0} - C_{p,a}^{0}) d \ln T + \Delta S_{f}^{0} \text{ and}$$
$$H_{g}^{0}(0) - H_{cr}^{0}(0) = \int_{0}^{T_{f}^{0}} (C_{p,cr}^{0} - C_{p,a}^{0}) dT + \Delta H_{f}^{0}$$

In the above equations, $C_{p,cr}^0$ and $C_{p,a}$ are the temperature dependences of the heat capacity of PGE in crystalline (cr) and amorphous (a) - vitreous supercooled liquid states; ΔH_f^0 and ΔS_f^0 are the enthalpy and entropy of fusion. The enthalpy of fusion was measured by the method of continuous input of energy in three experiments. The entropy of fusion was calculated from the values of the enthalpy and the melting point temperature. The thermodynamic parameters of fusion of phenylglycidyl ether are: T_f^0 276.79 ± 0.2 K, ΔH_f^0 = 17.32 ± 0.16 kJ·mole⁻¹, ΔS_f^0 = 62.57 ± 0.58 J·mole⁻¹·K⁻¹, ΔC_p^0 (T_f^0) = 88.2 J·mole⁻¹·K⁻¹. The melting point was determined from the data on the calorimetric measurements of equilibrium melting points T_F^0 depending on the fraction of the melt F according to the method of Rossini [13]. The graph of T_F^0 vs F⁻¹ dependence is a straight line, which is interpreted well by the equation

$$T_F^0 = T_0^0 - F^{-1} (T_0^0 - T_1^0)$$

At $F^{-1} = 1$, $T_1^0 = 276.54$ K the melting point of the sample studied was obtained, while at $F^{-1} = 0$, $T_0^0 = 276.79$ K, the thermodynamically equilibrium melting point temperature of a 100% pure PGE was obtained. The melting point depression $\Delta T_f = T_0^0 - T_1^0 = 0.25$ K is due to the presence of impurities. The overall content of impurities in the PGE sample studied $X_2 = 0.007$ mole was calculated from the equation

$$-\ln (1 - X_2) = A \cdot \Delta T_f^{0} (1 + B \cdot \Delta T_f^{0} + \ldots)$$

In this equation A and B are the first and second cryoscopic constants; they were calculated from our calorimetric data according to equations

$$A = \Delta H_{f}^{0} / RT_{f}^{2} = 0.02719 \text{ K}^{-1}$$
$$B = T_{f}^{-1} - \Delta C_{p}^{0} (T_{f}^{0}) / 2 \cdot \Delta H_{f}^{0} = 0.00107 \text{ K}^{-1}$$

$01.325 \text{ kPa}, M (C_9 H_{10} O_2) = 150.177$							
Т, К	C_p^0 , J-mole ⁻¹ . K ⁻¹	$H^{0}(T) - H^{0}(0),$ kJ.mole ⁻¹	S ⁰ (T) - S ⁰ (0),* J·mole ⁻¹ ·K ⁻¹	-[G ⁰ (T) - H ⁰ (0)] kJ·mole ⁻¹			
		Vitreous	state				
5 10 15 20 25 30 40 50 60 80 100 150 189	$\begin{array}{c} 0.2237\\ 1.760\\ 5.023\\ 8.980\\ 14.18\\ 21.84\\ 40.51\\ 54.90\\ 64.80\\ 75.71\\ 85.69\\ 111.9\\ 183.2 \end{array}$	$\begin{array}{c} 0,0003\\ 0,0045\\ 0,0209\\ 0,0559\\ 0,1129\\ 0,2017\\ 0,5159\\ 0,9959\\ 1,598\\ 3,013\\ 4.626\\ 9,572\\ 14,35\end{array}$	$\begin{array}{c} 0.0760\\ 0.6003\\ 1.893\\ 3.880\\ 6.402\\ 9.617\\ 18,53\\ 29,18\\ 40,13\\ 60,41\\ 78,36\\ 118,1\\ 146,3 \end{array}$	$\begin{array}{c} 0,00008\\ 0,0015\\ 0,0074\\ 0,0216\\ 0,0471\\ 0,0868\\ 0.2253\\ 0,4632\\ 0,8099\\ 1,820\\ 3,211\\ 8,146\\ 13,31 \end{array}$			
		Supercooled	liquid				
200 250 276,7 9	244,4 259,6 268,8	16,98 29,61 36,68	159,9 216,2 243,0	14,99 24,43 30,58			
	•	Crystalline	state				
5 10 15 20 25 30 40 50 60 80 100 150 200 250 276,79	$\begin{array}{c} 0,1540\\ 1,239\\ 3,613\\ 6,598\\ 10,64\\ 16,72\\ 32,27\\ 45,43\\ 55,62\\ 69,68\\ 83,88\\ 109,7\\ 135,8\\ 164,9\\ 180,9\\ \end{array}$	$\begin{array}{c} 0,0002\\ 0,0031\\ 0,0149\\ 0,0403\\ 0,0827\\ 0,1499\\ 0,3959\\ 0,7862\\ 1,294\\ 2.554\\ 4,088\\ 8,949\\ 15,06\\ 22,57\\ 27,20\\ \end{array}$	$\begin{array}{c} 0,0521\\ 0,4181\\ 1,339\\ 2,784\\ 4,658\\ 7,096\\ 14,07\\ 22,72\\ 31.95\\ 49,98\\ 67.04\\ 106.1\\ 141.1\\ 174.5\\ 192,1\\ \end{array}$	$\begin{array}{c} 0.00006\\ 0.0010\\ 0.0052\\ 0.0153\\ 0.0337\\ 0.0629\\ 0.1667\\ 0.3498\\ 0.6230\\ 1.444\\ 2.615\\ 6.966\\ 13.16\\ 21.05\\ 25.96\end{array}$			
		Liq	uid				
276,79 298,15 300 330	269,1 276.0 277,0 284,4	44,52 50,34 50,85 59,27	254,6 274,9 276,6 303,3	25,96 31,62 32,13 40,83			

TABLE 1. Thermodynamic Functions of Phenyl Glycidyl Ether p = 101.325 kPa, M (C₂H₁,O₂) = 150.177

*For the vitreous PGE $S^{\circ}(0) = 11.6 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$; for PGE in the crystalline state $S^{\circ}(0) = 0$

Here R is the universal gas constant, ΔC_p^0 (T_f^0) is increase in the heat capacity of PGE on its transition from a crystalline state into a liquid state at T_f^0 (found graphically, the KF section).

To calculate the thermodynamic functions $C_p^0 = f(T)$ of PGE, extrapolation was made from 14 to 0 K according to the equation

$$C_{\rm p}^{0} = 3D \frac{103.7}{T}$$

where D is the symbol of the Debye heat capacity function; by using the above numerical parameters, the equation describes the experimental values of C_p^0 of PGE in the range of 14-18 K with an accuracy within ±1%. In the calculations of the functions, it was assumed that at T < 14 K, this equation reproduces C_p^0 of PGE with the same accuracy.

The values of the function $H^0(T) - H^0(0)$, $S^0(T)$ were calculated by numerical integration with respect to curves of $C_p^0 = f(T)$ and $C_p^0 = f(\ln T)$, and $-[G^0(T) - H^0(0)]$, for the 0-330 K range, from the Gibbs-Helmholtz equation. The values of the functions are given in Table 1.

The thermodynamic parameters of the formation of PGE in the liquid state were calculated from the literature data on the enthalpy of formation of PGE [6] and the data in Table 1. They are equal to: $-\Delta H^0 = 182.0 \pm 2.1 \text{ kJ} \cdot \text{mole}^{-1}$, $-\Delta S_{\text{fm}}^0 = 634.3 \pm 1.4 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$, $\Delta G_{\text{f}}^0 = 7.1 \pm 2.5 \text{ kJ} \cdot \text{mole}^{-1}$.

TABLE 2. Thermodynamic Parameters of the Reaction of Phenyl Glycidyl Ether with Diphenylcarbodiimide and Phenyl Isocyanate p = 101.325 kPa

Τ, Κ	Physical state of reagents	-ΔH ⁰ ,kJ/ mole ⁻¹	$-\Delta S^0, J \cdot mole^{-1} \cdot K^{-1}$	$-\Delta G^0$, kJ/ mole ⁻¹			
Reaction (1)							
0 100 200 250 298,15 330	cr, cr; cr cr, cr; cr cr, cr; cr cr, cr; cr l, l; cr l, l; cr	129 130 133 134 174 180	0 9,8 30,0 37,3 179 196	129 129 127 125 121 115			
Reaction (2)							
0 100 200 250 298,15 330	cr, cr cr, cr; cr cr, cr; cr l, cr; cr l, l; cr l, l; cr	154 156 159 174 196,7 201	0 23,3 43,5 108 190 204	154 153 150 147 140 134			

The above values of the enthalpy of formation ΔH_{fm}^{0} , entropy of formation ΔS_{fm}^{0} and the Gibbs energy of formation ΔG_{fm}^{0} correspond to the following process at T = 298.15 K and p = 101.325 kPa

9C (gr) + 5 H₂ (g) + O₂ (g)
$$\rightarrow$$
 C₉H₁₀O₂ ($\&$)

The entropy of formation ΔS_{fm}^0 was calculated from the absolute values of the entropy of liquid PGE (Table 1), and also of the entropy of carbon in the form of graphite (gr) and gaseous H₂ and O₂ taken from [14]. The Gibbs energy of formation was calculated from the Gibbs-Helm-holtz equation.

Table 2 shows the thermodynamic parameters of processes (1) and (2). The enthalpy ΔH^0 of the processes at standard temperature and pressure was calculated from the enthalpy of formation of the reagents taken from the literature [6-9], and at other temperatures according to the Kirchhoff formula. The entropy of formation was calculated from the absolute values of the entropy of the reagents using the data from Table 1 and [7-9]. The Gibbs energy was calculated from the ΔH^0 and ΔS^0 values.

Table 2 shows that the Gibbs energy of reactions (1) and (2) is negative over the whole range of temperatures studied. Hence these processes are thermodynamically permissible. If the numerical values of ΔG^0 are taken into account, we can conclude that the equilibrium is practically completely shifted in the direction of formation of iminooxazolidine and oxazolidinone. With increase in temperature, ΔG^0 decreases in absolute value due to increase in the entropy factor $T \cdot \Delta S^0$.

The process has an upper limiting temperature. Its graphical evaluation from the dependence $\Delta H^0 = f(T)$ and $T \cdot \Delta S^0 = f(T)$ leads to a value greatly exceeding the temperature of the beginning of the thermal degradation of the reagents. The authors of [5] determined the enthalpies of reactions, (1) and (2) at 450 K in o-dichlorobenzene. For (1), $\Delta H^0 = -168.2 \pm$ 5.4 kJ·mole⁻¹, and for reaction (2), $\Delta H^0 = -176.6 \pm 3.8 \text{ kJ·mole}^{-1}$. The value of enthalpies of these processes that we obtained differ somewhat from the data in [5]. This is explained by different states of the phases of the materials studied: we studied the starting and final products in the liquid and crystalline states, while in [5] their solutions in o-dichlorobenzene were studied.

CONCLUSIONS

1. The temperature dependence of the heat capacity of phenyl glycidyl ether in vitreous, crystalline, supercooled liquid and liquid states was studied in an adiabatic vacuum calorimeter in the 14-330°K range with an error of ~0.3 %. The temperature, enthalpy and entropy of fusion, as well the glass transition temperature were determined.

2. The thermodynamic functions $H^0(T) - H^0(0)$, $S^0(T)$, $G^0(T) - H^0(0)$ were calculated for the range of 0-330 K; the zero entropy and the difference between the zero enthalpies of a vitreous and crystalline phenyl glycidyl ether were calculated; the thermodynamic parameters of its formation at a standard pressure and T = 298.15 K were calculated.

3. The enthalpy, entropy, and Gibbs energy of the reaction of phenyl glycidyl ether with diphenylcarbodiimide and phenylisocyanate were calculated. It was found that these processes are thermodynamically permissible over the whole temperature range studied and have an upper limiting temperature.

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THERMODYNAMIC PARAMETERS OF FREE RADICAL-DIMER EQUILIBRIA IN PHENYLINDANDIONE DERIVATIVES

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The present work relates to a study of equilibria between 2,2'-bis[R-2-(p-dimethylaminophenyl)indan-1,3-dionel (I) and the corresponding 2-arylindan-1,3-dione-2-yl radical (II)



Chernogolovka Branch, Institute of Chemical Physics, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1237-1243, June, 1988. Original article submitted January 13, 1987.