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DIFFERENTIAL SCANNING CALORIMETRY STUDY OF REACTIONS OF PHENYL GLYCIDYL ETHER WITH PHOSPHORIC ACID

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The reactions of phenyl glycidyl ether *(PGE)* with phosphoric acid in three molar ratios have been studied by means of DSC alone. The results obtained from isothermal measurements are as follows: $\Delta H = -91.0$ kJ/mole PGE (1 : 1 molar ratio); $\Delta H = -100.5$ kJ/mole PGE (1 : $\frac{2}{3}$ molar ratio).

The DSC curves obtained from dynamic experiments are multipeaked and give ΔH values higher than those obtained from isothermal measurements. These results can be explained by taking into account the acid concentration, the different reactivities of the hydrogens of the phosphoric acid and the possibility that secondary reactions occur.

The extent of curing of epoxide resins in the presence of amines is generally evaluated [1] on the basis of the enthalpy variation, as measured by DSC, for the reaction of phenyl glycidyl ether with *n*-butylamine: $\Delta H = -105.6$ kJ/E.M.M. [2].

Analogous values for the reaction of an epoxide with inorganic polybasic acids are not to be found.

The aim of this work was to study, by means of DSC only, the reaction of phosphoric acid with a simple epoxide compound, such as phenyl glycidyl ether.

Experimental

The following reactants were used:
phenyl glycidyl ether 95% (Fluka);
orthophosphoric acid 99% (Carlo Erba).
These were used without further purification.

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DSC curves were obtained on a DSC-2 Perkin-Elmer instrument equipped with the Perkin-Elmer Thermal Analysis Data Station 3600. Samples of 1-3 mg phosphoric acid were weighed in aluminium pans and the epoxide was then added from a microsyringe. The pans were closed with covers in which a small hole had been made.

The instrument was preset at 308 K and the sample was either heated to 773 K at 20 deg/min (dynamic test) or rapidly heated (160 deg/min) to a pre-determined temperature (isothermal test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output. All experiments were carried out in nitrogen atmosphere.

Results

The obtained data were analyzed by assuming that the evolved heat is proportional to the extent of reaction.

Mixtures having PGE : H_3PO_4 molar ratios of 1 : 1, 1 : 2/3 and 1 : 1/3 were used. Isothermal and dynamic experiments were performed within the temperature range 308-773 K.

Figure 1 shows the dynamic DSC curve of pure H_3PO_4. Figures 2a, 2b and 2c present typical DSC curves obtained in dynamic experiments at the studied molar ratios. Figure 3 illustrates the enthalpic pattern at 558 K of a 1 : 1 PGE/H_3PO_4 mixture.

The exothermic peak from 321 to 406 K in the DSC curve of H_3PO_4 is also found in all the dynamic DSC curves for all the studied mixtures, without regard to their composition.

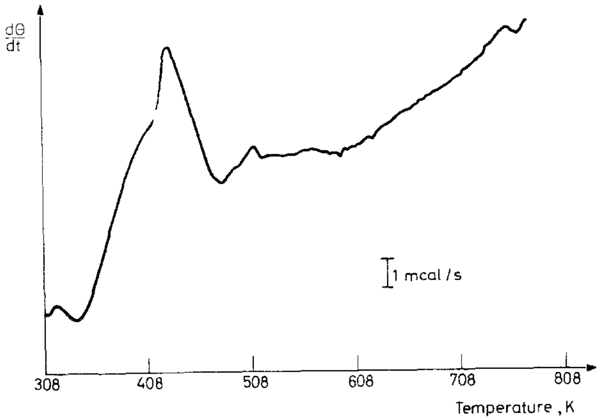


Fig. 1 Typical DSC curve obtained in dynamic experiment of H_3PO_4

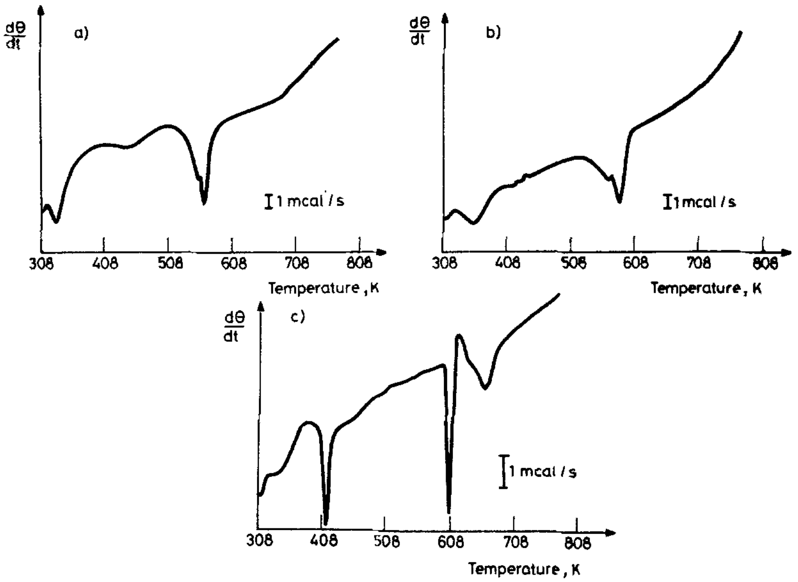


Fig. 2 Typical DSC curves obtained in dynamic experiments of PGE/H_3PO_4 molar mixtures: a) 1 : 1; b) 1 : 2/3; c) 1 : 1/3

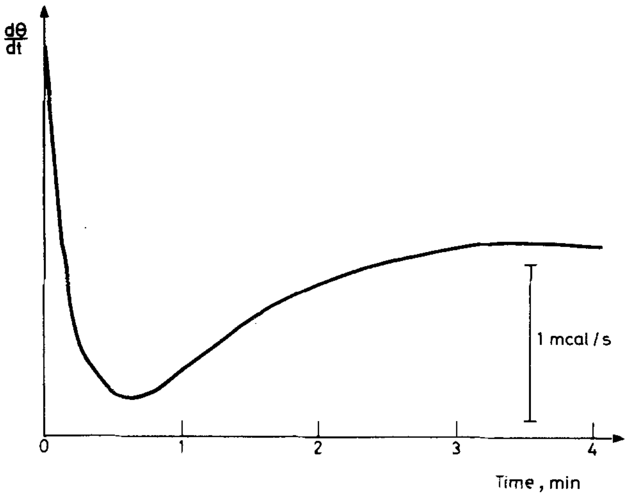


Fig. 3 Typical DSC curve obtained in isothermal experiment at 558 K of a 1 : 1 PGE/H_3PO_4 molar mixture

Table 1 Results from DSC analysis of H_3PO_4 and of the reactions between PGE and H_3PO_4. Range of scanned temperature: 308–773 K. Heating rate: 20 deg/min

Reagents molar ratio	1st peak		2nd peak		3rd peak		4th peak		Total ΔH (2nd + 3rd + 4th) kJ/mole PGE
	temperature range, K	ΔH^a kJ/mole	temperature range, K	ΔH^a kJ/mole	temperature range, K	ΔH^a kJ/mole	temperature range, K	ΔH^a kJ/mole	
H_3PO_4	321–406	−38.5	416–475	+38.8					
PGE + H_3PO_4 1 : 1	318–362	−41.0	395–499	−26.3	513–598	−121.7			−148.0
PGE + H_3PO_4 1 : 2/3	326–396	−38.3	514–606	−112.9					−112.9
PGE + H_3PO_4 1 : 1/3	320–372	−15.5	396–431	−22.1	594–617	−45.7	631–676	−21.5	−89.3

[a] For all samples, but H_3PO_4, ΔH is kJ/mole PGE

A ΔH value increasing with the H_3PO_4 content of the examined mixtures corresponds to this peak.

Table 1 gives the results obtained from dynamic measurements and the value of the total enthalpy variation obtained by adding the ΔH values of all the peaks, except that attributed to phosphoric acid. The isothermal experiments are dealt with in Table 2.

Table 2 Results from DSC analysis of reactions between PGE and H_3PO_4. Isothermal experiments

PGE:H_3PO_4 molar ratio	Temperature K	ΔH kJ/mole PGE	Peak time min.
1:1	518	−35.7	8.0
1:1	523	−39.4	3.7
1:1	533	−38.2	3.4
1:1	543	−91.3	7.3
1:1	563	−90.7	2.1
1:2/3	553	−102.4	3.1
1:2/3	578	−104.9	2.5
1:2/3	583	−94.3	2.3
1:1/3	543	−16.8	14.2
1:1/3	553	−29.1	0.9
1:1/3	603	−45.4	0.9

There are two exothermic peaks that characterize the dynamic DSC curves for 1:1 molar mixtures; these fall within the temperature ranges 395–499 K ($\Delta H = -26.3$ kJ/mole PGE) and 513–598 K ($\Delta H = -121.7$ kJ/mole PGE). The isothermal DSC curves also revealed the existence of different enthalpy variations in relation to the temperature selected for the measurement. Experiments carried out at 518 K and 533 K gave ΔH values of −35.7 and −38.2 kJ/mole PGE, respectively. Experiments carried out at 543 K and 563 K yielded enthalpy variations of about −91 kJ/mole PGE. The isothermal tests gave reproducible results starting from 518 K only.

In the case of 1:2/3 PGE/H_3PO_4 mixtures, the DSC curves obtained from dynamic or from isothermal experiments exhibited only one exothermic peak, in comparable temperature ranges. The ΔH measured in dynamic tests was −112.9 kJ/mole PGE and refers to the exothermic peak in the temperature range 514 K to 606 K, whereas the isothermal measurements at selected temperatures from 553 K to 583 K gave a ΔH of from −94.3 to −104.9 kJ/mole PGE.

The study of mixtures containing the reagents in the 1 : 1/3 molar ratio yielded dynamic DSC curves characterized by three exothermic peaks that appear in a very broad temperature range, from 396 K to 676 K. Isothermal experiments at 543 K, 553 K and 603 K led to increasing enthalpy variations, with a maximum value of −45.4 kJ/mole PGE. This value is much lower than that found by adding the peaks obtained in dynamic measurements. In this case we observed no exothermic peak when isothermal measurements were carried out at temperatures lower than 543 K.

Discussion

The results obtained from isothermal measurements show that the reaction ΔH of 1 : 1 and 1 : 2/3 molar mixtures reaches a maximum and a fairly steady value at temperatures not lower than 543 K.

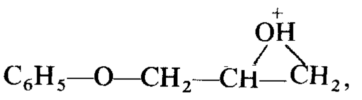
The average ΔH values measured in isothermal tests over 533 K for 1 : 1 ($\Delta H = -91.0$ kJ/mole PGE) and 1 : 2/3 ($\Delta H = -100.5$ kJ/mole PGE) molar mixtures are comparable to that of −105.6 kJ/E.M.M. found for the reaction PGE-*n*-butylamine [2].

At temperatures equal to or higher than 543 K, the 1 : 1/3 molar mixtures gave ΔH values much lower than those found for the other studied mixtures. This behaviour can be explained qualitatively if we consider that the phosphoric acid concentration is very low in these mixtures in comparison with the others studied. Moreover, the hydrogens of the phosphoric and/or pyrophosphoric acid that forms at the temperature of the measurement are characterized by very different dissociation constants [3]:

$$H_3PO_4: K_1 = 7.1\times 10^{-3};\ K_2 = 6.3\times 10^{-8};\ K_3 = 4.4\times 10^{-13}.$$

$$H_4P_2O_7: K_1 \simeq 10^{-1};\ K_2 \simeq 1.5\times 10^{-2};\ K_3 = 2.7\times 10^{-7};\ K_4 = 2.4\times 10^{-10}.$$

In fact, therefore, the quantity of highly acid hydrogens is lower than that corresponding to a 1 : 1 molar ratio of acid hydrogen/epoxide. The great acidity difference of the hydrogens present in the two acids suggests a different reactivity with the epoxide group to give the protoned compound



the formation of which is generally believed to be the first step in the acid-epoxide reactions [4].

The total ΔH values obtained via dynamic measurements are always higher than those from isothermal tests. In particular, the 1 : 1/3 molar mixtures gave total ΔH values $\simeq -90$ kJ/mole PGE, i.e. a value double that found in the isothermal test at 603 K. It is very probable that the higher temperatures reached in dynamic measurements promote not only the reaction of the less acid hydrogens, but also reactions of rearrangement and/or scission of the ether bond [5, 6].

Conclusions

The enthalpy variation obtained from isothermal DSC curves for the reaction of PGE with phosphoric acid is −91.0 kJ/mole PGE (1 : 1 molar ratio) or −100.5 kJ/mole PGE (1 : 1/3 molar ratio).

The higher values obtained from dynamic measurements are probably to be attributed to the occurrence of secondary reactions. The presence of several peaks in the corresponding DSC curves can be related to the different reactivities with the epoxide group of the hydrogens present in the phosphoric acid and/or in the pyrophosphoric acid that forms due to the heating.

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Zusammenfassung — Die Reaktion von Phenylglycidyläther *(PGE)* mit Phosphorsäure wurde bei drei verschiedenen molaren Verhältnissen allein mittels DSC untersucht. Isotherme Messungen ergaben folgende Werte: $\Delta H = -91.0$ kJ/mol PGE (molares Verhältnis 1 : 1); $\Delta H = -100.5$ kJ/mol PGE (molares Verhältnis 3 : 2). Die bei dynamischen Experimenten erhaltenen DSC-Kurven weisen viele Peaks auf und ergeben ΔH-Werte, die größer als die durch isotherme Messungen erhaltenen sind. Diese Ergebnisse können erklärt werden, wenn die Säurekonzentration, die unterschiedliche Reaktivität der Wasserstoffatome der Phosphorsäure und die Möglichkeit des Verlaufs sekundärer Reaktionen in Rechnung gestellt werden.

Резюме — Методом ДСК изучена реакция глицидофенилового эфира (ГФЭ) с фосфорной кислотой (ФК) при трех различных молярных соотношениях. На основе изотермических измерений смесей с молярным соотношением ГФЭ : ФК равным 1:1 и 1:2/3, вычислены значения ΔH, равные соответственно −91.0 и −100.5 кдж·моль$^{-1}$. Кривые ДСК, измеренные в динамических условиях, состояли из многих пиков и давали значения ΔH более высокие по сравнению с изотермическими измерениями. Полученные результаты могут быть объяснены, принимая во внимание концентрацию кислоты, различную реакционную способность водородов фосфорной кислоты и возможность протекания вторичных реакций.