Thermochimica Acta, 132 (1988) 161–164
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

ENTHALPY OF MALEIC ANHYDRIDE POLYMERIZATION IN THE PRESENCE OF PYRIDINE

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(Received 22 December 1987)

ABSTRACT

The polymerization of maleic anhydride in the presence of pyridine was studied by means of differential scanning calorimetry with isothermal tests at 328 K. The ΔH value increases with the percentage of the base. The enthalpy of the polymerization reaction of maleic anhydride in the presence of a large excess of pyridine (93.6 kJ per mol MA) was obtained by extrapolation.

INTRODUCTION

Several previous studies [1–5] have described the results of studies on the anionic polymerization of maleic anhydride in the presence of organic bases such as pyridine, triphenylphosphine and so on. The results show that the conversion of this monomer increases with the base concentration, the basicity of the initiator and the reaction temperature. In the presence of pyridine the reaction occurs with the production of CO_2 and the formation of oligomers of maleic anhydride which include pyridine in their structure [6]. Generally data on the variation in enthalpy of this polymerization reaction (greatly exothermic) are not reported.

The aim of this investigation was to study, by DSC, the polymerization reaction of maleic anhydride in the absence of a solvent, and in the presence of pyridine.

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EXPERIMENTAL

Materials

Maleic anhydride (MA), > 99% purity; pyridine (Py), > 99.8% purity; acetone-d_6, > 99.95% atom D were obtained from Fluka.

Procedure

DSC curves were obtained on a Perkin–Elmer DSC-2 instrument equipped with a Perkin–Elmer thermal analysis data station 3600. Samples of 2–5 mg MA were weighed in aluminium pans and Py was added using a microsyringe. The pans were sealed hermetically with covers. The instrument was preset at 308 K and the sample was rapidly heated (320 K min^{-1}) to 328 K (isothermal test). Indium was used as the standard for calibrating the temperature axis and the enthalpy output.

The course of the reaction in acetone solution was estimated using NMR spectroscopy directly on the solution in the NMR tube. ^{1}H NMR spectra were recorded at 298 K on a Varian XL200 FT instrument.

RESULTS

Figure 1 shows that the reaction enthalpy increases with a reduction in the molar ratio $R = [\text{MA}]/[\text{Py}]$. The study was carried out at 328 K and was

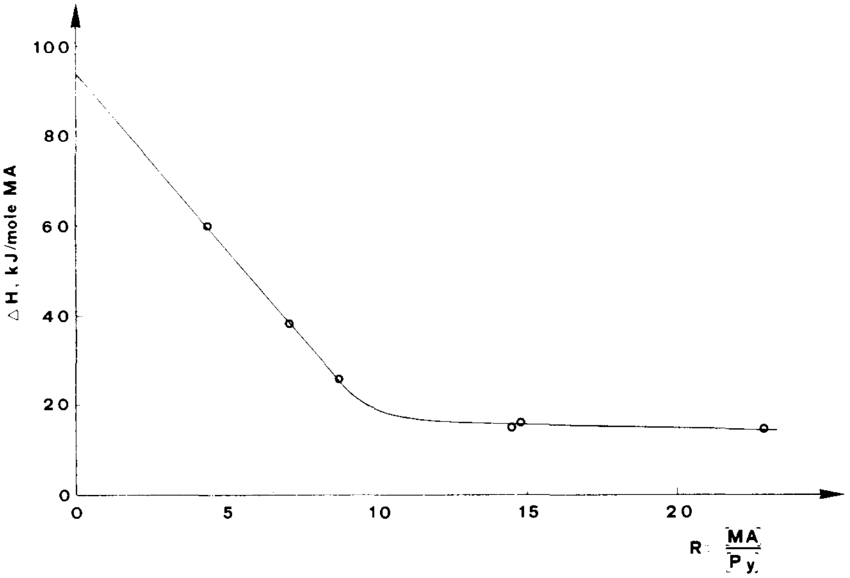

Fig. 1. Change in the reaction enthalpy with molar ratio $R = [\text{MA}]/[\text{Py}]$. Reaction temperature, 328 K.

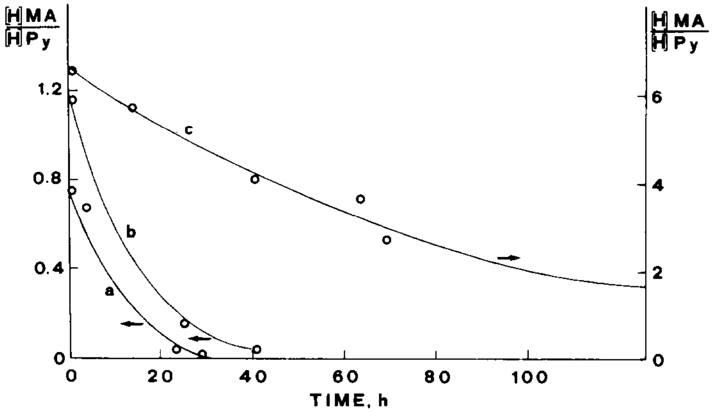

Fig. 2. Change in the ratio [H]MA/[H]Py at 298 K with time for various molar ratios R [MA]/[Py]. Curve a, $R = 0.81$; curve b, $R = 1.63$; curve c, $R = 7.9$.

restricted to mixtures containing 15.4% by weight of Py ($R = 4.4$). Mixtures containing a larger amount of the base give DSC curves from which correct ΔH values cannot be measured, since the reaction starts before the pre-determined temperature has been reacted.

The three points at $R = 8.8$, 7.1 and 4.4 fall on a straight line and, by extrapolation to zero MA concentration, the ΔH value for the reaction in the presence of a large excess of Py can be obtained. This value is 93.6 kJ per mol MA.

Figure 2 shows the MA conversion at 298 K versus reaction time when performing the reaction directly in an NMR tube and employing deuterated acetone solutions of MA and Py at the indicated molar ratios. The progress

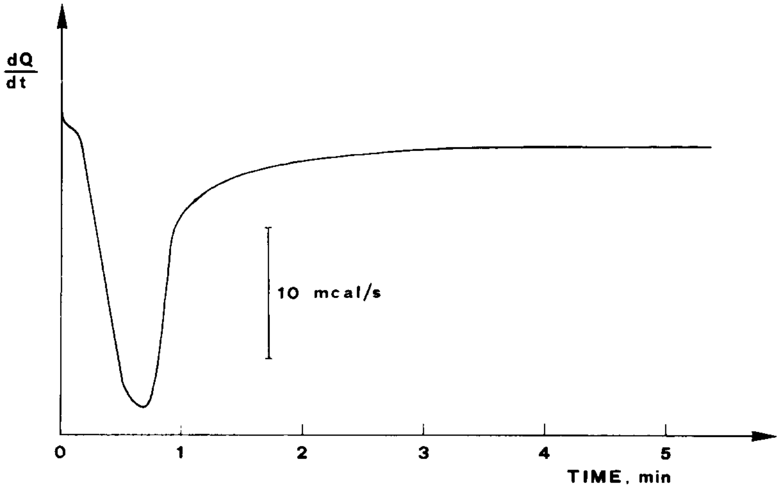

Fig. 3. Typical DSC curve at 328 K of a mixture MA–Py with $R = [MA]/[Py] = 4.4$.

of the reaction was followed by measuring the change with time of the integral of the signals from the maleic protons divided by the integral of the signals from the pyridine protons.

Figure 3 presents a typical DSC curve of an MA–Py mixture with $R = 4.4$ obtained in the isothermal experiment at 328 K.

DISCUSSION AND CONCLUSIONS

Figure 1 shows that the ΔH value increases with the Py concentration in the reaction mixture. Moreover, the conversion–time curves obtained by means of NMR spectroscopy (Fig. 2), indicate that the MA conversion is proportional to the base concentration. These results agree with those found by Sahn [7] for the bulk polymerization of MA in the presence of triphenylphosphine. The mechanism of the bulk polymerization of MA initiated by an organic base is probably the same as that of the solution polymerization.

The dependence of MA conversion on Py concentration can be explained by the direct participation of pyridine in the processes of decarboxylation and chain interruption, in addition to its function as polymerization initiator.

The ΔH value of 93.6 kJ per mol MA, obtained by extrapolating the curve in Fig. 1 to zero MA concentration, is probably a result of the sum of the ΔH values for the formation of a starting complex MA–Py [3], the polymerization reaction and the reactions of decarboxylation and chain interruption. The value of 93.6 kJ per mol MA is the greatest variation in enthalpy that is obtained when MA reacts in the presence of a large excess of Py.

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