

Reaction Kinetics for Hindered Amine/Epoxydes by DSC

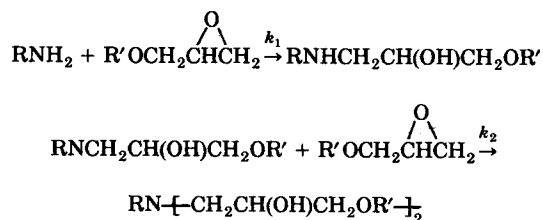
JAMES V. DUFFY, ERIC HUI, and BRUCE HARTMANN, *Naval Surface Weapons Center, Silver Spring, Maryland 20903-5000*

Synopsis

The rate constants for the reaction of two aliphatic hindered amines with phenylglycidyl ether (PGE) and the diglycidyl ether of bisphenol A (DER 332) were determined by differential scanning calorimetry (DSC). The two exothermic peaks which are present in the DSC data result from the consecutive reactions of the primary and secondary amine hydrogens and allow k_1 and k_2 to be determined. The resulting k_1/k_2 ratios obtained for these hindered amine systems are larger than the ratios previously reported for unhindered amine/epoxydes.

INTRODUCTION

Aliphatic amines are commonly used to cure polyfunctional epoxydes for use in a variety of applications. The kinetics of this reaction have been studied and reaction rate constants reported for both the primary amine hydrogen (k_1) and the secondary amine hydrogen (k_2).



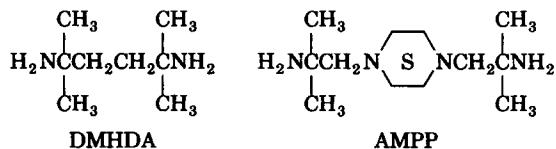
Charlesworth¹ reports rate constant ratios (k_1/k_2) for aliphatic amines to be in the range of 1.5–2. When steric hindrance is present in the amine, the reaction rates are reduced and k_1/k_2 becomes larger. Recently, the NMR reaction kinetics of the hindered amine 2,5-dimethyl-2,5-hexanediamine (DMHDA) with phenylglycidyl ether (PGE) in DMSO was reported by Rinde et al.² to have a k_1/k_2 value of 60. It was shown³ that the DMHDA/DER332 system cured in a two-step reaction such that linear polymerization occurred initially at 25°C to the total exclusion of crosslinking and the resulting resin remained stable and soluble for long periods. Furthermore, the consecutive nature of the polymerization/crosslinking reactions brought on by steric hindrance in DMHDA may produce changes in the morphology of the resin and account for the increased impact strengths and high glass transition temperatures reported. Mijorić et al.⁴ did find morphological changes between diethylene triamine and DMHDA-cured epoxy resins but report that the thermomechanical and fracture properties of these two systems are very similar in nature.

The purpose of the present work was to determine the usefulness of differential scanning calorimetry (DSC) in effectively determining the reaction kinetics of hindered amine/epoxide systems. DSC is an attractive technique because it is simple to use, data are obtained quickly, and only small quantities of resin are required. This method of obtaining kinetic information was used by Kissinger⁵ to study various minerals and later was applied by Prime⁶ to thermosetting resins.

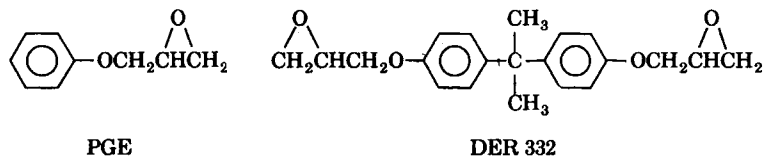
EXPERIMENTAL

Materials

The two hindered aliphatic amines used in this study were 2,5-dimethyl-2,5-hexanediamine (DMHDA) and 1,4-bis(2-amino-2-methylpropyl)piperazine (AMPP):



Each of these amines was reacted with phenylglycidyl ether (PGE) and the diglycidyl ether of bisphenol A (DER332) to give the four systems studied:



These materials were obtained from commercial sources and were used without additional purification.

The DSC experiments were carried out in a Dupont thermal analyzer Model 990 equipped with a Model 910 DSC module. The samples were weighed on a Sartorius 3704 balance and, immediately after mixing, were stored in sealed vials at room temperature under dry nitrogen. Samples were removed and placed in aluminum DSC pans which were then hermetically sealed and weighed before and after each run. Programmed rates of 1, 2, 5, 10, and 20°C/min were used. Initially, several molar concentrations were used in this study, but it was found that the 10 : 1 molar ratio of epoxide/amine gave the most reproducible results.

RESULTS AND DISCUSSION

A typical programmed DSC run using one of these hindered amine systems gives two distinct exothermic peaks (Fig. 1). The first peak is from the heat

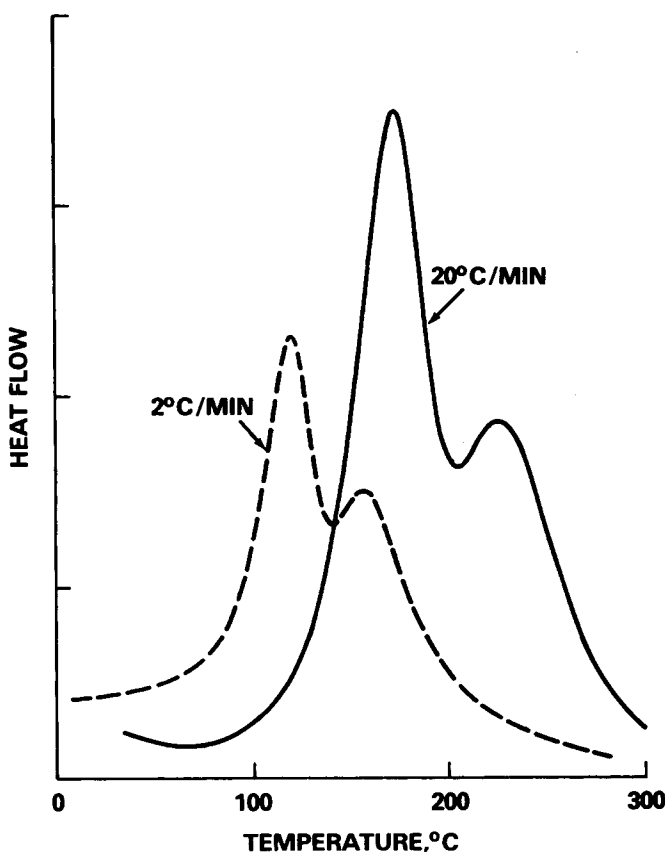


Fig. 1. Typical DSC thermograms for hindered amine/epoxide systems.

generated from the reaction of the primary amine hydrogen with epoxide (T_{p_1}) followed by the secondary amine hydrogen reaction at a higher temperature (T_{p_2}). After T_{p_1} and T_{p_2} have been determined for a given system at several heating rates, the activation energies (E_a) and frequency factors (A) for the reaction can be determined from the Kissinger equation:

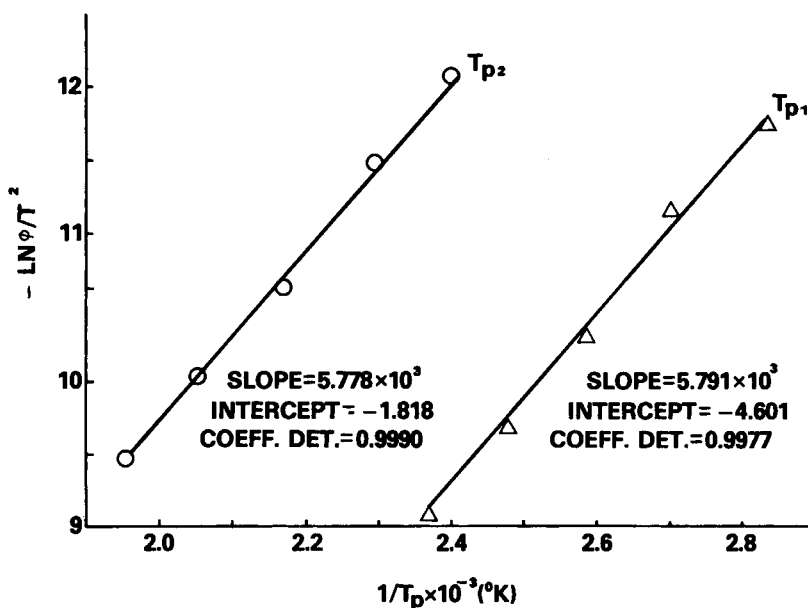
$$-\ln(\phi/T_p^2) = E_a/RT_p - \ln(AR/E_a)$$

where ϕ is the programmed heating rate, T_p is the peak exothermic temperature, E_a is the activation energy, R is the gas constant, and A is the frequency factor.

Typical experimental results for the PGE/AMPP (10:1) system are shown in Table I. When $-\ln \phi/T_p^2$ is plotted against $1/T_p$, the slope is E_a/R and the intercept is $-\ln(AR/E_a)$ (Fig. 2). For this reaction (PGE/AMPP) E_{a_1} and E_{a_2} were 11.51 and 11.48 kcal/mol, respectively, while A_1 and A_2 were 9.612×10^3 and 5.932×10^2 s⁻¹. Using these experimental values and the Arrhenius equation, it is now possible to calculate k_1 and k_2 for this reaction. These reaction rate constants together with those for the other systems studied are shown in Table II. The rate constants show good agreement

TABLE I
 DSC Results from PGE/AMPP (10:1)

ϕ (°C/min)	T_{p1} (K)	$1/T_{p1}$ ($\times 10^{-3}$)	$-\ln(\phi/T_{p1}^2)$	T_{p2} (K)	$1/T_{p2}$ ($\times 10^{-3}$)	$-\ln(\phi/T_{p2}^2)$
20	422.5	2.367	9.096	511.5	1.955	9.479
10	405.0	2.469	9.705	487.0	2.053	10.074
5	387.5	2.581	10.310	461.0	2.169	10.658
2	370.0	2.703	11.134	435.5	2.296	11.460
1	353.5	2.829	11.736	416.5	2.401	12.064


 Fig. 2. Determination of E_a and A for PGE/AMPP (10:1) using the Kissinger equation.

within each amine system and the k_1/k_2 ratios obtained for the four systems were between 9 and 16. Note that the k_1/k_2 values found here for DMHDA/PGE using DSC are lower than those reported by Rinde et al.² using NMR, which could be due in part to the difference between kinetic experiments performed on bulk systems (DSC) and those in solution (NMR).

 TABLE II
 Reaction Rates Constants for Several Aliphatic Amine/Epoxy Systems
 at 25°C

Systems	E_{a1} (kcal/mol)	E_{a2} (kcal/mol)	k_1 (s^{-1}) ($\times 10^{-5}$)	k_2 (s^{-1}) ($\times 10^{-5}$)	k_1/k_2
DMHDA/PGE	11.2	11.6	2.85	0.32	9
DMHDA/DER 332	11.2	11.5	2.93	0.25	12
AMPP/PGE	11.5	11.5	3.49	0.23	16
AMPP/DER 332	11.4	11.4	3.45	0.24	15

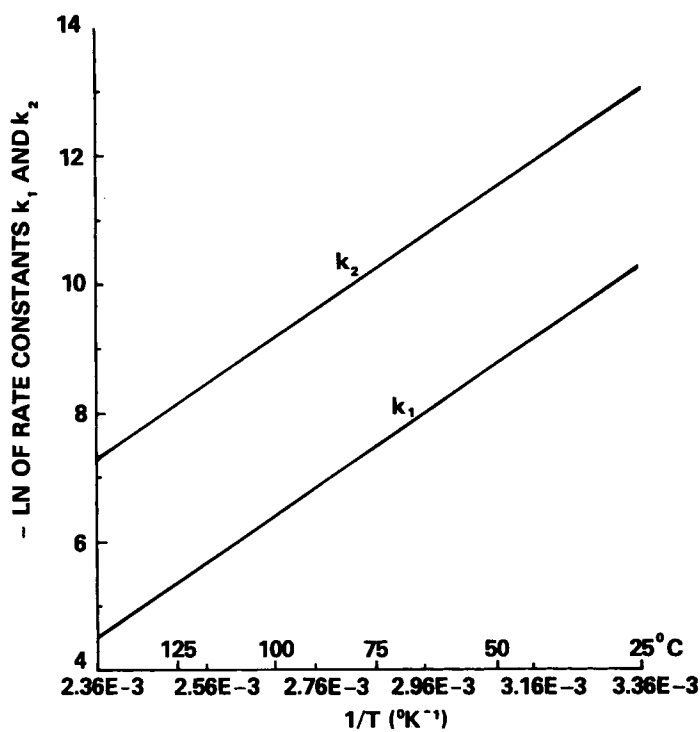


Fig. 3. Rate constants variation with temperature for PGE/AMPP (10:1).

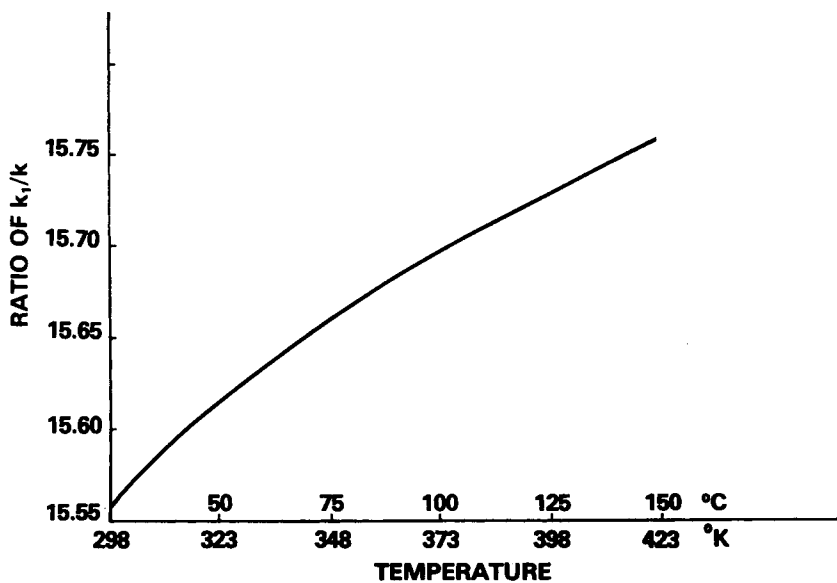


Fig. 4. Temperature dependence of the k_1/k_2 ratio for PGE/AMPP (10:1).

The temperature dependence of k_1 and k_2 for the AMPP/PGE system is shown in Figure 3. The change in the k_1/k_2 ratio with temperature for this system was calculated from the relationship:

$$k_1/k_2 = 16.3 \exp(-13/T)$$

which is obtained by ratioing the rate constant expressions obtained from the Arrhenius equation. The results obtained from this expression are plotted in Figure 4.

CONCLUSIONS

Differential scanning calorimetry (DSC) was used to obtain rate constants and activation energies for four hindered aliphatic amine/epoxide systems. The agreement in rate constants was excellent and was independent of the particular amine or epoxide selected. The k_1/k_2 ratios for these systems varied between 9 and 16 while values for activation energies were between 11.2 and 11.6 kcal/mol.

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