Thermochimica Acta, 77 (1984) 367–373
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE CATALYSED REACTION OF ISOCYANATE AND EPOXIDE GROUPS: A STUDY USING DIFFERENTIAL SCANNING CALORIMETRY

MIGUEL URIBE * and KENNETH A. HODD

Department of Materials Technology, Brunel University, Uxbridge UB8 3PH (Gt. Britain)

(Received 24 January 1984)

ABSTRACT

Using differential scanning calorimetry (DSC) and IR spectroscopy the catalysed reactions of phenylglycidylether and 4,4′-diisocyanatodiphenylene methane (MDI) have been studied. The initial reaction with both the catalysts used, tetraethylammonium bromide (R4NBr) and ethylmethylimidazole (EMI), has the trimerisation of the isocyanate which occurs at 150–175 °C and this was a more strongly promoted event at room temperature by EMI. The second reaction observed in the DSC thermograms was between isocyanate and epoxide to form oxazolidone. Again EMI was the more efficient catalyst. The heat of MDI trimerisation was found to be -155.6 kJ mol^{-1}, whilst the heat of oxazolidone formation was -141.9 kJ mol^{-1}.

INTRODUCTION

The reaction of the isocyanate and the epoxide group to produce an oxazolidone ring (I) has been the subject of recent attention [1–3] and is of interest as a resin curing process.

(I)

R' = e.g., PhNCO

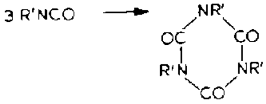
The formation of the oxazolidone is strongly exothermic and the rate and extent of its formation is influenced by the choice of catalyst, for which alkaline chlorides [4], quarternary ammonium halide [5,6], alkaline butoxides [7] and imidazole [1] have been reported. Competitive with the formation of (I) is the trimerisation of isocyanate to form isocyanurate (II) which is also

---

* Present address: E.S.I.Q.I.E., Instituto Politécnico Nacional, Mexico City, DF. CP07360, Mexico.

0040-6031/84/$03.00

markedly exothermic and catalysed by the compounds to which reference has been made.



(II)

R' = e.g., PhNCO

In this communication a study of the catalysed formation of (**I**) and (**II**) using differential scanning calorimetry (DSC) to follow the reaction of phenyl glycidyl ether (PGE) and 4,4'-diisocyanatodiphenylene methane (MDI) is reported.

EXPERIMENTAL

Materials

Phenyl glycidyl ether (Fluka), was used as supplied, epoxy number 146 ± 2. 4,4'-Diisocyanatodiphenylene methane (BDH), was used as supplied. Tetraethylammonium bromide (R4NBr) 98% purity (BDH), $T_m = 285$–$287\,^\circ C$. 2-Ethyl-4-methylimidazole (EMI) 97% purity (Aldrich), $T_v = 292$–$295\,^\circ C$.

Instrumental analysis

Differential scanning calorimetry

Thermograms (77–327 °C at 5 or 20 °C min^{-1}) were obtained using ~ 5-mg samples in crimped aluminium pans, under N_2, in a Perkin-Elmer DSC-2B and associated TADS 3500. Indium was used as standard (6.79 cal g^{-1}).

Reaction samples were prepared by blending 0.02 mol PGE, and 0.01 mol MDI together with 1.4% of catalyst (on the weight of MDI). Thermograms of blends were obtained immediately upon mixing and following periods of storage at ambient temperature (~ 23 °C) of 1 to about 650 h (four sets at different times of storage were run).

Infrared spectrometry

Spectra were obtained using a 1% dispersion of sample in KBr and presenting the resulting disc to a Perkin-Elmer 683 IR spectrophotometer.

As a guide to the reaction the following absorption bands were observed: 2250 cm^{-1} isocyanate; 1750 cm^{-1} oxazolidone; 1700 cm^{-1} isocyanurate; and 910 cm^{-1} epoxide.

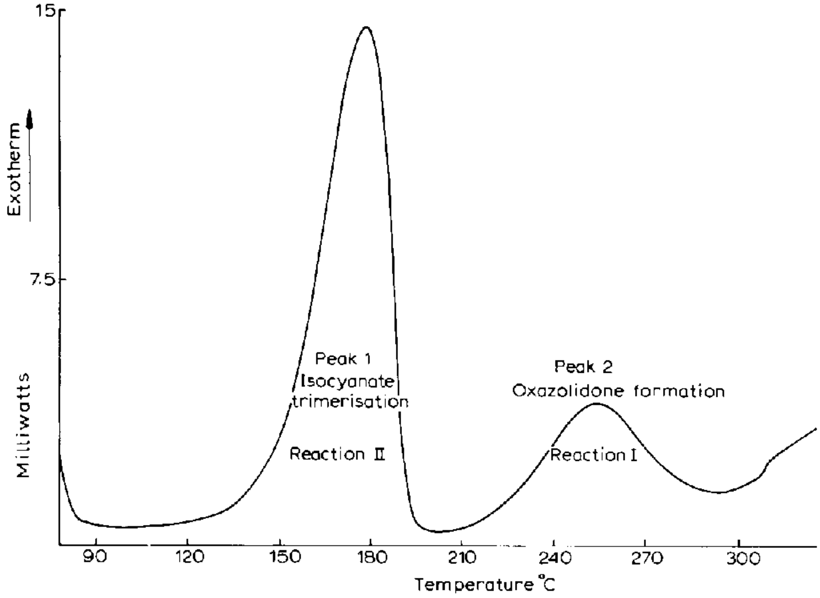


Fig. 1. DSC thermogram of the reaction of phenylglycidylether and 4-4′-diisocyanatodiphenylene methane with tetraethylammonium bromide as catalyst.

RESULTS AND DISCUSSION

A typical DSC thermogram for the PGE/MDI reaction in the presence of R4NBr (Fig. 1) exhibits two strong exotherms, the first at 175 °C and a second at 251 °C. The IR spectra of the PGE/MDI mixture before the first DSC peak, between the first and second DSC peaks and after the second DSC peak clearly indicates the origins of the two exotherms (Table 1). From Table 1 it is evident that the first peak is attributable to the trimerisation of

TABLE 1

Infrared absorption peaks of the reaction products of phenylglycidylether and 4,4′-diisocyanatodiphenylene methane from the DSC study using tetraethylammonium bromide (R4NBr) or ethylmethylimidazole (EMI) as catalyst

Frequency (cm^{-1})	R4NBr			EMI	
	Before peak 1	After peak 1	After peak 2	Before peak 1	After peak 2
2250	Very strong	Strong	None	Weak	None
1750	Weak	Strong	Strong	Weak	Strong
1700	Very strong	Strong	Strong	Strong	Weak
910	Strong	Strong	Very weak	Strong	Very weak

TABLE 2

Isocyanurate (II) and oxazolidone (I), forming reaction peak temperatures and peak areas from the DSC thermograms of the catalysed reaction of phenylglycidylether and 4,4′-diisocyanatodiphenylene methane

	Catalyst	
	R4NBr	EMI
Trimerisation (**II**) *Peak 1*		
Peak temperature (°C)	175	147
Peak area (J g^{-1}) [a]	622 ± 22	333 ± 47
Oxazolidone formation (**I**) *Peak 2*		
Peak temperature (°C)	251	177
Peak area (J g^{-1}) [b]	80 ± 5	258 ± 8

[a] Per gram of isocyanate.

[b] Per gram of PGE/MDI 2:1 mixture.

isocyanate (**II**) whilst the second is due to oxazolidone formation (**I**). A similar picture emerges when EMI is substituted for R4NBr as catalyst. This replacement alters the DSC thermograms in detail but not in the gross features; thus, twin exothermic peaks having the same attribution as previously determined are observed, however both peaks are displaced to lower temperatures and the size of the peaks is altered (Table 2) with the oxazolidone peak area increasing between three- and fourfold.

Additionally, a comparison of the DSC thermograms of the trimerisation of MDI in the presence and absence of PGE provides strong support for the suggestion first made by Jones and Savill [8] that epoxides promote reaction **II**. With PGE the heat of reaction of trimerisation was 155.6 kJ mol^{-1} whilst without PGE it was 14.1 kJ mol^{-1}. Additionally the peak temperature of trimerisation was reduced by the presence of PGE from 218 to 175°C. Both factors clearly indicate a more complete reaction.

Comparison of the results of the catalysed reactions indicates that both R4NBr and EMI are powerful catalysts for isocyanate trimerisation (**II**) but that EMI is much the superior catalyst for the formation of oxazolidone (**I**). Indeed, reaction (**II**) is so strongly promoted by R4NBr and EMI that it occurs at ambient temperature upon storage of catalyst/PGE/MDI mixtures. Reaction (**I**), formation of oxaxolidone, does not, however, occur to any significant extent upon storage as may be judged from Table 3, which gives the residual peak areas for reactions (**I**) and (**II**) after storage of mixtures, by DSC.

The apparent kinetic parameters of reactions (**I**) and (**II**) were obtained using the Perkin-Elmer TADS kinetics analysis software. Rate of reaction, K_0 l s^{-1} activation energy, E_A kJ mol^{-1} and reaction order, n, may be derived according to the following equations.

TABLE 3

DSC thermogram exotherms (J g^{-1}) attributable to reactions (**I**) and (**II**) after storage of blends of phenylglycidyl ether, 4-4′-diisocyanatodiphenylene methane and catalyst

Storage time at 23 °C (h)	Catalyst			
	R4NBr [a]		EMI [b]	
	Trimerisation (**II**) [c]	Oxazolidone (**I**) [d]	Trimerisation (**II**) [c]	Oxazolidone (**I**) [d]
		average		average
1–4	435 ± 22	80 ± 5	333 ± 47	258 ± 8
24	393 ± 13	from 1	32	from 1 to
		to 480 h	–	96 h
48	346 ± 2		–	
72	335 ± 2		–	
96	173		–	
192	24		–	
360	12		–	
480	8.2		–	

[a] Heating rate 20 °C min^{-1}.

[b] Heating rate 5 °C min^{-1}.

[c] Per gram of isocyanate.

[d] Per gram of PGE/MDI 2 : 1 mixture.

The rate of the reaction often is assumed to have the form

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = K(1-\alpha)^n$$

where α = degree of chemical conversion obtained by the partial heat at time, t: $\alpha = \Delta H_{\mathrm{partial}}/\Delta H$

$$K = K_0 \exp(-E_A/RT)(1-\alpha)^n$$

This equation can be reduced to a linear form by taking the natural logarithm

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \ln K_0 - E_A/RT + n\ln(1-\alpha)$$

A multilinear regression is performed by using

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}t},\quad 1/T\qquad \text{and } \ln(1-\alpha)$$

The apparent kinetic parameters of reactions (**II**) and (**I**) and the results are collected in Table 4.

A number of conclusions may be drawn from the data collected in Tables 1–4.

First, that peak 1 in the DSC thermogram is attributable to the trimerisation of MDI to form an isocyanurate. This is contrary to the DTA study of

TABLE 4

Apparent kinetic parameters of isocyanurate and oxazolidone formation derived by analysis of DSC peak areas

Catalyst					
Peak 1: trimerisation of isocyanate to isocyanurate (**II**)			Peak 2: oxazolidone formation (**I**)		
ln K_0 l s^{-1}	E_A kJ mol^{-1}	N	ln k_0 l s^{-1}	E_A kJ mol^{-1}	N
1.4% R4NBr on MDI					
28.15 ± 0.6	113.9 ± 2.46	0.8	39.5 ± 0.85	183.2 ± 3.95	1.6
1.4% EMI on MDI					
5.27 ± 0.11	36.1 ± 0.77	0.6	27.9 ± 0.6	128.9 ± 2.78	1.1

Gromakov et al. [9] of oxazolidone formation. They reported the observation of only one peak. It does appear, however, that although trimerisation is accompanied by a low conversion of epoxy and isocyanate to oxazolidone, the major part of this latter process occurs at much higher temperatures.

Second, that whilst both R4NBr and EMI are effective catalysts for reaction (**II**), the trimerisation, EMI is the most effective, indeed it is so effective that reaction (**II**) was probably partially completed before the DSC thermogram at zero time was obtained. This may explain the discrepancies in the kinetic parameters for reaction (**II**) given in Table 4. A calculation of the heat of formation of the trimer of MDI for the R4NBr-catalysed reaction yields a value of -155.6 kJ mol^{-1}, this factor remains unreported but the figure may be compared with the value -194.6 kJ mol^{-1} for the trimerisation of phenyl isocyanate [2]. Additionally, the order of reaction obtained of 0.8 is in close agreement with what the first-order process trimerisation is expected to be.

Third, EMI is also found to be a very powerful promoter of the formation of oxazolidone as is evidenced by the greater peak areas observed in DSC thermograms for reaction (**I**) catalysed by EMI compared to those catalysed by R4NBr. The reduction in peak 2 temperature for EMI-catalysed reactions confirms this conclusion.

Fourth, the kinetic parameters derived for the oxazolidone-forming reaction (**I**) are not to be regarded as accurate owing to difficulties in identifying precisely the baseline between peaks 1 and 2. The heat of oxazolidone formation derived from the EMI catalysed reaction is -141.9 kJ mol^{-1} comparison with -44 kJ mol^{-1} when the reaction is catalysed by R4NBr.

ACKNOWLEDGEMENTS

One of the authors (M.U.) gratefully acknowledges financial support for part of this work from Brunel University (BRIEF) and from the S.E.R.C.

REFERENCES

1 N. Kinjo, S. Numata and T. Koyana, J. Appl. Polym. Sci., 28 (1983) 1729.
2 G. Woods, Flexible Polyurethane Foams, Applied Science Publishers, London, 1982, p. 5.
3 V. Steinbach and W. Roth, Plaste Kautsch., 30 (1) (1983) 34.
4 Herwek and Whitmore, J. Polym. Sci., Part A, 8 (1970) 2759.
5 G. Speranza, J. Org. Chem., 23 (1958) 1922.
6 S.R. Sandler, F. Berg and G. Kitazawa, J. Appl. Polym. Sci., 9 (1965) 1994.
7 R. Di Leone, J. Am. Soc. Preprints 9, (1), (1968) 642.
8 J.I. Jones and N.G. Savill, J. Chem. Soc., 4 (1957) 4392.
9 N.S. Gromakov, V.G. Hozin and V.A. Voskvesevsky in H. Chihara (Ed.), Thermal Analysis, Heyden, London, 1977, pp. 279–282.