

Unsymmetrical Diisocyanates. III. The Kinetics of Reactions of DEMDI

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Synopsis

In the previous investigation it was found that 3,5-diethyl-4,4'-diisocyanatodiphenylmethane (DEMDI) exhibits a marked asymmetry in the reaction with isoamyl alcohol. Since DEMDI is potentially rather cheap, and since the unsymmetrical nature of the diisocyanate is quite advantageous in certain urethane formulations, the reactions of this diisocyanate with a series of model compounds were investigated. The model compounds were chosen so as to represent the important classes of functional groups commonly reacted with diisocyanates in the preparation of polyurethanes. The compounds used were isoamyl alcohol, 2-octanol, water, 2,6-diethylaniline, 1-*n*-butyl-3-phenylurea, and 1-(4-*n*-butylphenyl)-3-(methylphenyl)-urea. The reactions were conducted in dry diglyme solvent. The extent of reaction of the isocyanate groups was followed by reaction with excess di-*n*-butylamine and back-titration with hydrochloric acid. Tetramethyl-1,3-butanediamine and dibutyltin dilaurate were used as catalysts in some runs. The results show that DEMDI has a desirably high asymmetry of reaction with alcohols or water at low temperatures. Catalysis with dibutyl dilaurate markedly increases this asymmetry. An increase in temperature generally decreases the asymmetry of DEMDI reactions, so that elevated temperatures should be avoided in prepolymer formation. The dibutyltin dilaurate is a more effective catalyst than the diamine for all of the reactions studied. The diamines are very poor catalysts for urea reactions, whereas the tin compound is quite effective.

In the previous investigation, it was found that 3,5-diethyl-4,4'-diisocyanatodiphenylmethane (DEMDI) exhibits a marked asymmetry in the reaction with isoamyl alcohol. DEMDI is potentially a rather cheap diisocyanate, and since the unsymmetrical nature of the diisocyanate is quite advantageous in certain urethane formulations, it was decided to investigate in detail the reactions of this diisocyanate with a series of model compounds. The model compounds were chosen so as to represent the important classes of functional groups commonly reacted with diisocyanates in the preparation of polyurethanes. The compounds used were isoamyl alcohol (a primary alcohol), 2-octanol (a secondary alcohol), water, 2,6-diethylaniline (an amine), 1-*n*-butyl-3-phenylurea (an aliphatic-aromatic urea), and 1-(4-*n*-butylphenyl)-3-(3-methylphenyl)urea (a bisaromatic urea).

Procedure

The procedure used is similar to that used in the previous two investigations, except that the extent of reaction was measured by means of reaction with di-*n*-butylamine and back-titration with hydrochloric acid.

Equal volumes of 0.1*M* DEMDI in dry diglyme (diglycol dimethyl ether) and 2*M* model compound in dry diglyme were mixed and placed into a constant temperature bath. Tetramethyl-1,3-butanediamine (TMBDA) and dibutyltin dilaurate were used as catalysts in some runs.

After a measured time interval at the reaction temperature, an aliquot was transferred under dry nitrogen into an Erlenmeyer flask containing an excess of 1*M* di-*n*-butylamine in diglyme. The excess dibutylamine was then titrated with 0.2 *N* hydrochloric acid in 95% ethanol, with brom phenol blue as the indicator. The amount of reacted dibutylamine which is equivalent to the unreacted isocyanate present in the aliquot sample was then calculated by comparison with a blank titration.

The apparent half-lives for reaction of the two isocyanate groups were determined by plotting the unreacted isocyanate concentration versus time on a semilog graph paper, and drawing best-fitting straight lines through the regions of about 0–20% reaction and about 50–70% reaction, respectively.

The rate constant for the reaction of the unhindered isocyanate group was calculated from the reaction rate at 0–20% reaction, it being assumed that the hindered isocyanate group was not reacting at this point. The rate constant for the reaction of the hindered isocyanate group was calcu-

TABLE I
Uncatalyzed Reactions

Reactant	Temp., °C.	$\lambda_{1/2}$, hr.	$\lambda'_{1/2}$, hr.	k_1 , l. mole ⁻¹ hr. ⁻¹	k_2 , l. mole ⁻¹ hr. ⁻¹	$\lambda'_{1/2}/$ $\lambda_{1/2}$
3-Methylbutanol-1	29.5	20	1400	0.069	0.00052	70
	60	3.8	140	0.37	0.0052	37
	100	0.98	13.6	1.53	0.058	14
2-Octanol	29.5	29	2000	0.048	0.0004	70
	60	5.6	190	0.26	0.0039	34
	100	1.2	16.3	1.2	0.048	14
Water	29.5	1.7	158	0.8	0.0046	90
	60	0.59	36	244	0.021	61
	100	0.23	8.6	6.5	0.092	37
2,6-Diethylaniline	29.5	0.25	13.7	5.6	0.053	55
	70.5	0.12	3.2	11	0.24	26
	100	0.062	1.4	24	0.56	23
1- <i>n</i> -Butyl-3-phenyl- urea	80	0.9	4.2	1.6	0.18	4.6
	100	0.54	2.7	2.6	0.27	5.0
1-(<i>p</i> -Butylphenyl)- 3- <i>m</i> -tolylurea	80	1.2	36	1.2	0.020	30
	100	0.73	13	1.91	0.056	18

TABLE II
Reactions Catalyzed by Tetramethyl-1,3-butanediamine

Reactant	Temp., °C.	Catalyst concn., M	$\lambda_{1/2}$, hr.	$\lambda'_{1/2}$, hr.	$k_{1/2}$ l. mole ⁻¹ hr. ⁻¹	$k_{2/2}$ l. mole ⁻¹ hr. ⁻¹	$\lambda_{1/2}/\lambda'_{1/2}$
3-Methylbutanol-1	29.5	0.001	0.49	13	2.8	0.056	27
	100	0.001	0.18	2.2	8.3	0.36	12
	100	0.001 ^a	0.04	0.58	40	1.36	15
2-Octanol	29.5	0.001	1.6	140	0.87	0.0052	88
	100	0.001	0.28	3.7	5.4	0.21	14
Water	29.5	0.001	1.15	48	1.2	0.0154	41
		0.002	0.85	30	1.63	0.024	36
		0.003	0.66	23	2.1	0.031	35
	100	0.005	0.5	15.6	2.8	0.047	31
		0.01	0.32	8.8	4.3	0.083	28
100	0.001	0.14	3.0	10	0.26	21	
1- <i>n</i> -Butyl-3-phenylurea	80	0.001	0.69	3.2	2.0	0.23	4.6
	100	0.001	0.45	2.1	3.1	0.36	4.6
	100	0.001 ^a	0.34	2.0	4.1	0.38	5.8
1-(<i>p-n</i> -butylphenyl)-3- <i>m</i> -tolylurea	80	0.001	0.98	30	1.42	0.024	31
	100	0.001	0.55	10.5	2.5	0.070	19

^a The catalyst was diethylenetriamine.

TABLE III
Reactions Catalyzed by Dibutyltin Dilaurate

Reactant	Temp., °C.	Catalyst concn., <i>M</i>	$\lambda_{1/2}$, hr.	$\lambda'_{1/2}$, hr.	k_1 , l. mole ⁻¹ hr. ⁻¹	k_{23} , l. mole ⁻¹ hr. ⁻¹	$\lambda'_{1/2}/\lambda_{1/2}$
3-Methylbutanol-1	29.5	0.001	0.04	7.9	30	0.092	200
	100	0.001	Fast	0.07		10	
2-Octanol	29.5	0.001	0.085	20	16.3	0.036	240
	100	0.001	Fast	0.25		3.1	
Water	29.5	0.001	0.35	0.25	4.0	0.029	71
		0.0025	0.25	13.4	5.5	0.054	54
		0.05	0.21	9.6	6.6	0.076	46
1-Butyl-3-phenylurea	100	0.001	Fast	0.26		3.0	
		0.001	Fast	0.32		2.3	
1-(<i>p</i> - <i>n</i> -Butylphenyl)- 3- <i>m</i> -tolylurea	100	0.001	Fast	1.0		0.7	

lated from the reaction rate at 50–70% reaction, it being assumed that all of the unhindered isocyanate group had reacted by this time.

The 1-*n*-butyl-3-phenylurea was prepared by the reaction of phenyl isocyanate with excess *n*-butylamine. The precipitated urea was recrystallized from ethanol and melted at 129–130°C.

The 1-(*p-n*-butylphenyl)-3-*m*-tolylurea was prepared by the reaction of *m*-tolylisocyanate with excess *p-n*-butylaniline. The gelatinous precipitate was recrystallized twice from ethanol and melted at 128–129°C.

Results

The results are given in Tables I–IV and in Figure 1. In Table I are given the reaction half-lives and rate constants for uncatalyzed reactions of DEMDI. In Table II are given the reaction half-lives and rate constants for amine-catalyzed reactions of DEMDI. In Table III are given the reaction half-lives and rate constants for dibutyltin dilaurate-catalyzed reactions of DEMDI. The $\lambda_{1/2}$ and $\lambda'_{1/2}$ are the apparent half-lives of reaction at 0–20% and 50–70% reaction, respectively. The k_1 and k_2 are the reaction rate constants calculated for the unhindered and hindered isocyanate groups, respectively.

TABLE IV
Activation Energies for the Reactions of DEMDI

Reactant	Activation energy, cal./mole				
	No catalyst		0.001M Tetramethyl- 1,3-butanediamine		0.001M Dibutyltin- dilaurate
	k_1	k_2	k_1	k_2	k_2
3-Methylbutanol-1	9,800	15,000	3,400	5,900	15,200
2-Octanol	10,400	15,500	5,800	11,800	14,200
Water	6,600	9,500	7,000	9,000	14,800
2,6-Diethylaniline	4,700	7,500			
1- <i>n</i> -Butyl-3-phenylurea	6,700	5,600	5,600	5,800	
1-(<i>p-n</i> -Butyl-phenyl)-3- <i>m</i> -tolylurea	6,600	13,400	7,600	13,900	

In Table IV are given the calculated activation energies for the various reactions of DEMDI.

In Figure 1 is shown the effect of catalyst concentration on the rate constant of the reaction of DEMDI with water at 29.5°C.

Discussion of Results

The results clearly show that DEMDI has a desirably high asymmetry of reaction with alcohols or water at low temperatures. Surprisingly, catalysis by dibutyltin dilaurate markedly increases this unsymmetry.

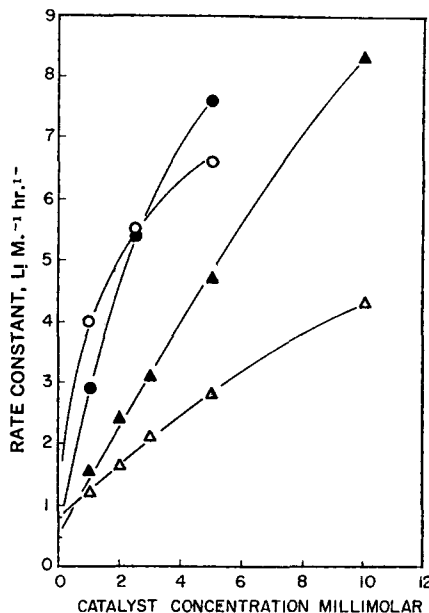


Fig. 1. Effect of catalyst on rate: (○) k_1 , dibutyltin laurate; (●) $k_2 \times 100$, dibutyltin laurate; (△) k_1 , TMBDA; (▲) $k_2 \times 100$, TMBDA.

Thus, tin catalysts should be used with DEMDI in the preparation of "ideal" urethane prepolymers.

The "ideal" prepolymers are those in which N diisocyanate molecules have reacted with one N -functional polyol. There is no coupling together of the polyol molecules caused by a diisocyanate molecule reacting twice, and thus there is no substantial increase in molecular weight during the preparation of the prepolymer. It is found that amine catalysis substantially decreases the unsymmetry of DEMDI reactions with hydroxylic materials, and should thus be avoided in prepolymer preparation.

The results show that an increase in temperature generally decreases the asymmetry of DEMDI reactions, so that elevated temperatures should be avoided in prepolymer preparation.

The dibutyltin dilaurate seems to be a more effective catalyst than the diamines for all of the reactions studied. This is particularly true in the case of the ureas. The diamines are very poor catalysts for urea reactions, whereas the tin compound is quite effective. The rate of reaction of the hindered group of DEMDI with an uncatalyzed urea is about the same at room temperature as with an alcohol. The reaction of the hindered group of DEMDI with a tin catalyzed urea at 100°C. is quite rapid, and is actually substantially faster than the reaction of the unhindered group of DEMDI with an uncatalyzed alcohol at room temperature.

It is seen from Figure 1 that the catalytic effect of tetramethylbutane-diamine is quite linear with concentration, but that the effect of the tin

catalyst is quite nonlinear. Moreover, the concentrations of tin catalyst normally used in polyurethane formulations are well into the nonlinear region. Thus, it is found at high catalyst concentrations that the amines are more active catalysts for the reaction of DEMDI with alcohols than are tin compounds.

The results obtained in this investigation are useful in the preparation and curing of polyurethane formulations using DEMDI. The results are particularly useful where it is desired to obtain "ideal" prepolymers—that is, prepolymers which consist substantially of hydroxylic compound end-capped with DEMDI, and which contain very little of the higher coupling products in which more than one hydroxylic compound residue is present.

Particular applications of DEMDI prepolymers which show promise of commercial utility are package-stable, moisture-cured polyurethane coatings and adhesives, and thermally stable prepolymers for the preparation of urethane elastomers.

Résumé

Dans la précédente étude, on avait trouvé que le 3,5-diéthyl-4,4'-diisocyanatodiphénylméthane (DEMDI) présentait une asymétrie marquée dans la réaction avec l'alcool isoamylique. Depuis que le DEMDI est virtuellement meilleur marché et depuis que la nature non symétrique du diisocyanate est tout à fait avantageuse dans certaines formulations d'uréthane, on a étudié les réactions de ce diisocyanate avec une série de composés de référence. Les composés de référence ont été choisis de telle sorte qu'ils représentent les classes importantes des groupements fonctionnels qui réagissent habituellement avec les diisocyanates dans la préparation des polyuréthanes. Les composés employés sont l'alcool isoamylique, le 2-octanol, l'eau, la 2,6-diéthylaniline, la 1-*n*-butyl-3-phénylurée et la 1-(4,4-butylphényl)-3-(méthylphényl)-urée. Ces réactions ont été effectuées dans le diglyme sec comme solvant. L'avancement de la réaction des groupes isocyanates a été suivi par réaction avec un excès de di-*n*-butylamine et par titration en retour avec l'acide chlorhydrique? La tétraméthyl-1,3-butanediamine et le dilaurate de dibutyle étain ont été employés comme catalyseurs dans certaines expériences. Les résultats montrent que le DEMDI possède une asymétrie de réaction élevée avec les alcools ou l'eau aux basses températures. La catalyse avec le dilaurate de dibutyle augmente fortement cette asymétrie. Une augmentation de température diminue généralement l'asymétrie des réactions de DEMDI, de telle sorte que des températures élevées doivent être évitées dans la formation de prépolymère. Le dilaurate de dibutyle étain est un catalyseur plus efficace que la diamine pour toutes les réactions étudiées. Les diamines sont de très faibles catalyseurs pour les réactions de l'urée, tandis que le composé de l'étain est parfaitement efficace.

Zusammenfassung

In der vorhergehenden Arbeit wurde festgestellt, dass 3,5-Diäthyl-4,4'-diisocyanatodiphenylmethan (DEMDI) eine merkliche Asymmetrie bei der Reaktion mit Isoamylalkohol aufweist. Da DEMDI in bezug auf den Preis günstig liegt und da die unsymmetrische Natur des Diisocyanats bei gewissen Urethanrezepten recht vorteilhaft ist, wurden die Reaktionen dieses Diisocyanats mit einer Reihe von Modellverbindungen untersucht. Die Modellverbindungen wurden so ausgewählt, dass sie alle wichtigen,

gewöhnlich mit Diisocyanaten bei der Darstellung von Polyurethanen zur Reaktion gebrachten funktionellen Gruppen umfassten. Folgende Verbindungen wurden verwendet: Isoamylalkohol, 2-Oktanol, Wasser, 2,6-Diäthylanilin, 1-*n*-Butyl-3-phenylharnstoff und 1-(4-*n*-Butylphenyl)-3-(methylphenyl)-harnstoff. Die Reaktionen wurden in wasserfreiem Diglyme als Lösungsmittel durchgeführt. Die Umsetzung der Isocyanatgruppen wurde durch Reaktion mit überschüssigem Di-*n*-butylamin und Rücktitration mit Chlorwasserstoffsäure bestimmt. Bei einigen Versuchen wurden Tetramethyl-1,3-butandiamin und Dibutylzinn-dilaurat als Katalysatoren verwendet. Die Ergebnisse zeigen, dass DEMDI die erwünschte hohe Asymmetrie bei der Reaktion mit Alkoholen oder Wasser bei tiefen Temperaturen besitzt. Diese Asymmetrie wird durch Katalyse mit Dibutyl-dilaurat merklich erhöht. Eine Temperaturerhöhung setzt die Asymmetrie der DEMDI-Reaktionen im allgemeinen herab, so dass bei der Bildung der Präpolymeren höhere Temperaturen vermieden werden sollten. Dibutylzinn-dilaurat ist für alle untersuchten Reaktionen ein wirksamerer Katalysator als das Diamin. Diamine sind für Harnstoffreaktionen sehr schlechte Katalysatoren, während die Zinnverbindung recht wirksam ist.

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