Kinetics of Polyether Polyols—Diisocyanate Reactions

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Synopsis

The reaction rates for the uncatalyzed as well as the dibutyltin dilaurate-catalyzed reactions between polyether polyols and tolylene diisocyanate (80/20 mixture of 2,4 and 2,6 isomers) are reported. Titration and infrared absorption methods were used for the determination of the residual isocyanate content, to follow the progress of the reactions. At equivalent reactant concentrations, the rate constants were found to be essentially independent of the chain length and the functionality of the polyether polyols studied. The reaction rates of polyether polyols containing terminal primary hydroxyl groups (e.g., Pluronic polyols) were greater than those of polyols with secondary hydroxyl groups and were greatly accelerated in the presence of the tin catalyst.

INTRODUCTION

The kinetics of the isocyanate–alcohol or glycol reaction has been extensively investigated.[1-11] Until recently, however, comparatively little information has been published on the reaction rates of polyether polyol-isocyanate reactions. Rauterkus and co-workers[12] investigated the reaction of oligomethylene glycols and oligooxyethylene glycols with phenyl isocyanate. The reactivity of the hydroxyl group was found to be independent of the chain length of the oligomer and of the difference in the structure of the oligomethylene and oligooxyethylene chains. Smith[13] reported the reaction rates of some polyether polyols with phenyl isocyanate and the 80/20 mixture of the 2,4 and 2,6 isomers of tolylene diisocyanate employing tertiary amines and metal salt catalysts. The present kinetic study of the reactions between polyether polyols and tolylene diisocyanate attempts to determine the influence of the following factors: (*1*) the chain length of the polyether polyols; (*2*) the functionality of the polyether polyols; (*3*) primary versus secondary hydroxyl in the polyether polyols.

The reaction rates were determined by measuring the disappearance of isocyanate by spectrophotometric and titration methods.

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EXPERIMENTAL

Materials

Table I lists properties of the commercially available polyether polyols used in this study. The catalyst, dibutyltin dilaurate, was obtained from M & T Chemicals, Inc. The tolylene diisocyanate employed had an isomer content of 78.9% 2,4 and 21.1% 2,6, and an NCO content of 48.20%.

TABLE I
Polyether Polyols

Identification	Mol. wt.	Equiv. wt.	Hydroxyl no.	Water, %
Poly(oxypropylene) adducts of:				
Propylene glycol	1960	980	57.1	0.02
Propylene glycol	1050	525	106.7	0.02
Propylene glycol	775	388	144.8	0.01
1,1,1-*Tris*(hydroxymethyl)propane	2871	957	58.5	0.02
Glycerol	2916	972	57.7	0.01
Pentaerythritol	4152	1038	54.1	0.02
α-Methylglucoside	3952	988	56.7	0.02
Poly(oxypropylene) poly(oxyethylene) glycol (Pluronic L61)[a]	2010	1005	55.7	0.02

[a] Reg. U. S. Trademark, Wyandotte Chemicals Corp.

Procedure

Polyether polyol (1 equiv.) was reacted in bulk with 2 equiv. of tolylene diisocyanate (80/20 mixture of 2,4 and 2,6 isomers). A 1% solution of dibutyltin dilaurate was prepared in toluene dried over calcium hydride. For a kinetic run involving a catalyst, 0.005% (7.9×10^{-5} moles) of dibutyltin dilaurate was employed based on the weight of reactants. This catalyst had previously been employed by Damusis and co-workers[14] in kinetic studies involving the polyether polyol–isocyanate reactions. The reaction rate was followed by analysis of the isocyanate group and the hydroxyl concentration was deduced from the isocyanate concentration. The minor effects of competing reactions, which may consume isocyanate under the reaction conditions prevailing in these experiments, were neglected.

1. Titration Method for the Determination of Isocyanate Content. Samples were withdrawn from the reaction at regular time intervals and immediately quenched in a solution of excess di-*n*-butylamine. Unreacted isocyanate was determined by back-titrating the excess amine with $1N$ hydrochloric acid with bromphenol blue as the indicator.

2. Infrared Absorption Method for the Determination of Isocyanate Content. The method by Bailey and co-workers[3] for the determination of isocyanate, as modified by Floutz,[15] was employed for the spectrophotometric measurement of reaction rates. The intensity of the absorption

band at 4.5 μ, assigned to the NCO stretching vibration, was measured with a Baird Model B infrared spectrophotometer.   At regular intervals 2 g. samples were withdrawn from the reaction flask and quenched in 70 g. of dry toluene.   The absorbance of this solution was determined using a 0.08 mm sodium chloride cell with matching cell filled with toluene as the reference.   The half-life value for a reaction was expressed as the time required for 25% depletion of isocyanate (or 50% reaction of hydroxyl).   The absorbance corresponding to the point of half-reaction was determined from a standard toluene solution containing 75% of the original number of equivalents of tolylene diisocyanate present in the reaction.

The reaction rate constants were calculated for a second-order reaction from the formula:

$$K = 1/at_{1/2}$$

where K is the reaction rate constant (liters per equivalent-seconds); a is the concentration of reactants, where the initial concentrations are the same (equivalents per liter) (assuming that only one isocyanate group on tolylene diisocyanate is reacting with each hydroxyl group of the polyether
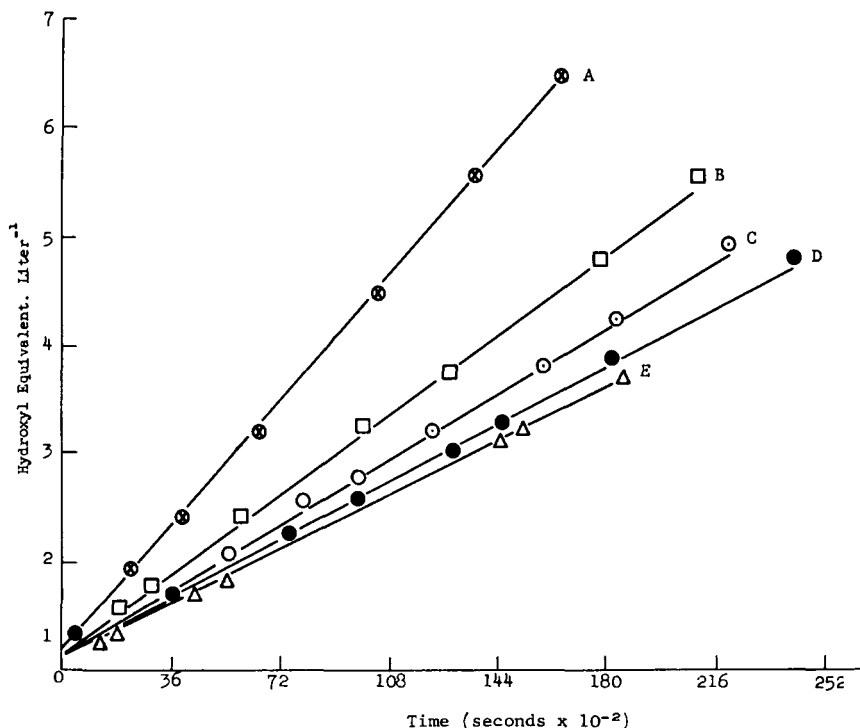

Fig. 1. Second-order plots for the reaction of polyether polyols with tolylene diisocyanate at 50°C. based on equal reactant concentrations (catalyst 0.005% dibutyltin dilaurate); poly(oxypropylene) adducts of: (A) pentaerythritol; (B) 1,1,1-tris(hydroxymethyl)propane; (C) propylene glycol; (D) glycerol; (E) α-methyl glucoside.

due to the greater reactivity of the isocyanate group in the 4-position); and $t_{1/2}$ is the half-life as determined by infrared absorption (seconds).

RESULTS

The results obtained for the dibutyltin dilaurate-catalyzed reactions of polyether polyols with tolylene diisocyanate at 50°C. are plotted in Figure 1 in terms of second-order reactions. The kinetic data for the reactions between the polyether polyols and tolylene diisocyanate, employing dibutyl-

TABLE II
Comparison of Reaction Rates Obtained from the Infrared
Method and the Titration Method
(Catalyst: Dibutyltin Dilaurate, 0.005%)

Polyol	Temp., °C.	Initial concn., equiv./l.	$t_{1/2}$, sec.		$K \times 10^4$, l./equiv. sec.	
			Titration	Infrared	Titration	Infrared
Poly(oxypropylene) adducts of:						
Pentaerythritol	40	0.848	7,200	7,380	1.64	1.60
1,1,1-*Tris*(hydroxy-methyl)propane	40	0.910	11,640	11,280	0.95	0.98
Propylene glycol	40	0.891	12,840	12,420	0.87	0.90
Propylene glycol (no catalyst)	50	0.891	13,320	13,140	0.84	0.85
Poly(oxypropylene) poly(oxyethylene) glycol (Pluronic L61)	20	0.873	1,740	1,620	6.58	7.07

TABLE III
Rate Constants and Activation Energies for the Reactions
between Polyether Polyols and Tolylene Diisocyanate
(Catalyst: Dibutyltin Dilaurate, 0.005%)

Polyol	Av. equiv. wt.	$K \times 10^4$ l./equiv. sec.					Activation energy kcal./mole
		60°C.	50°C.	40°C.	30°C.	20°C.	
Poly(oxypropylene) adducts of:							
Pentaerythritol	1038	6.67	3.27	1.64			14.1
1,1,1-*Tris*(hydroxy-methyl)propane	957	3.86	2.02	0.94			13.6
Propylene glycol	980	3.29	1.71	0.87			13.0
Glycerol	972	2.89	1.54	0.81			12.6
α-Methyl glucoside	988	2.68	1.36	0.72			13.0
Poly(oxypropylene) poly(oxyethylene) glycol (Pluronic L61)	1005			27.1	13.3	6.58	13.0

TABLE IV
Rate Constants for the Uncatalyzed Reactions of Poly(oxypropylene)
Glycols and Tolylene Diisocyanate at 50°C.

Identification	Initial hydroxyl, equiv./l.	$K \times 10^4$, l./equiv. sec.
Poly(oxypropylene) glycol (equiv. wt. 980)	0.89	1.0
Poly(oxypropylene) glycol (equiv. wt. 525) (plus dry toluene)[a]	0.89	0.7
Poly(oxypropylene) glycol (equiv. wt. 388) (plus dry toluene)[a]	0.89	0.8
Poly(oxypropylene) glycol (equiv. wt. 525)	1.49	1.3
Poly(oxypropylene) glycol (equiv. wt. 388)	1.88	1.3

[a] The polyether polyols were diluted with toluene so that polyols of different equivalent weights could be compared.

TABLE V
Rate Constants for the Uncatalyzed and Dibutyltin Dilaurate (0.005%)-
Catalyzed Reactions of Polyether Polyols with Tolylene Diisocyanate

Polyol	Catalysis	Av. equiv. wt.	$K \times 10^4$, l./equiv.-sec.		
			60°C.	50°C.	40°C.
Poly(oxypropylene) adducts of:					
Pentaerythritol	Catalyzed	1038	6.67		
	Uncatalyzed	1038	1.68		
1,1,1-Tris(hydroxymethyl)-propane	Catalyzed	957	3.86		
	Uncatalyzed	957	1.86		
Propylene glycol	Catalyzed	980	3.29	1.71	0.87
	Uncatalyzed	980	1.73	0.84	0.40
Glycerol	Catalyzed	972	2.89		
	Uncatalyzed	972	1.59		
Poly(oxypropylene) poly(oxyethylene) glycol (Pluronic L61)	Catalyzed	1005			27.10
	Uncatalyzed	1005		1.52	0.78

tin dilaurate as the catalyst, are listed in Tables II, III, and V. Table II demonstrates a good correlation between the titration method and the spectrophotometric method of measuring the disappearance of isocyanate. The rate constants at several temperatures and the activation energies for the reactions between polyether polyols of different functionality and TDI in the presence of the tin catalyst are given in Table III. Table IV lists the effect of chain length on reaction rates for uncatalyzed poly(oxypropylene) glycols at 50°C. Catalyzed and uncatalyzed reaction rates are compared in Table V.

DISCUSSION

All reactions reported in this paper were carried out by reacting 1 equiv. of a polyether polyol with 2 equiv. of an 80/20 mixture of 2,4- and 2,6-tolylene diisocyanate. Since the p-isocyanate group is approximately eight times more reactive than the o-isocyanate group,[6,9,10] the favored path is the initial combination of the p-isocyanate group with each hydroxyl group of the polyether. The data taken from the titration method were applied, therefore, to a second-order reaction of equal initial reactant concentrations.

Since both the titration and the spectrophotometric methods have been used independently, it was of interest to compare the results of these two methods. Good agreement was found between the data obtained by the two methods as noted in Table II.

It is apparent from Figure 1 and Table III that rate constants and activation energies derived from the reactions between the polyethers and tolylene diisocyanate in close approximation are independent of the functionality of the starting glycol or polyhydric alcohol. The pentaerythritol-based polyol exhibited a somewhat faster rate, but this may be due to the presence of some residual primary hydroxyl groups in the poly(oxypropylene) adduct of pentaerythritol.

Table IV demonstrates the independence of the chain length of the polymer glycols on the reaction rate constants. When polyethers differing in chain length (different equivalent weight) were reacted with tolylene diisocyanate, the numerical values of the rate constants shown do not exhibit significant differences. These findings are in good agreement with the work of Rauterkus and co-workers,[12] who showed that the reactivity of the terminal hydroxyl groups was independent of the chain length of the oligomer and of the difference in the structure of the oligomethylene and oligooxyethylene glycols in the reaction with phenyl isocyanate. Deviations in the constants noted in Table IV are primarily due to slight variations in the alkali metal content in the glycols. It has been found, as would be expected, that the rate constants increase with increasing alkali metal content.[16]

Table V shows the catalyzed and uncatalyzed rate constants for the reaction between various polyethers and tolylene diisocyanate. Included in this study was the Pluronic L61 polyol containing primary hydroxyl groups. The rates of the uncatalyzed reactions for the latter were found to be twice that of the polyethers containing predominantly secondary hydroxyl groups. Dyer and co-workers[5] found in the comparison of rates between primary and secondary butanols with phenyl isocyanate that the primary alcohol reacted three times as fast as the secondary alcohol. The somewhat lower reaction rate for the Pluronic polyol can be ascribed to the fact that all of the polyol was not completely terminated with primary hydroxyl groups, but contained some secondary hydroxyl groups. The dibutyltin dilaurate-catalyzed reaction of tolylene diisocyanate with polyols containing secondary hydroxyl groups (at the catalyst concentration selected)

proceeded at twice the rate of the uncatalyzed reaction, with the exception of the pentaerythritol-based polyether which exhibited a fourfold rate increase, presumably due to the presence of some residual primary hydroxyl groups present in the pentaerythritol base.   It is interesting to note that the catalyzed reaction between the Pluronic polyol and tolylene diisocyanate increased the rate constant 35 times as compared to the uncatalyzed reaction.   This somewhat surprising observation is the subject of a continuing investigation.

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Résumé

On donne les vitesses de réaction pour les réactions non catalysées aussi bien que pour celles catalysées par le dilaurate de dibutyle étain entre les polyéther-polyols et le diisocyanate de tolylène (mélange 80:20 des isomères 2,4 et 2,6).   Afin de suivre l'avancement des réactions on a utilisé la titration et l'analyse infra-rouge pour déterminer la quantité d'isocyanate résiduel.   En employant des concentrations équivalentes en réactifs on a trouvé que les constantes de vitesse sont essentiellement indépendantes de la longueur de la chaîne et de la fonctionnalité des polyéther-polyols étudiés.   Les vitesses de réaction des polyéther polyols contenant des groupements terminaux hydroxyles primaires (e.g., a. polyols pluroniques) sont plus grandesque celles des polyols contenant des groupements hydroxyles secondaires et sont fortement accélérées en présence d'étain comme catalyseur.

Zusammenfassung

Die Reaktionsgeschwindigkeit der nichtkatalysierten und der Dibutylzinndilaurat-katalysierten Reaktion zwischen Polyätherpolyolen und Toluylendiisocyanat (80:20-Mischung von 2,4- und 2,6-Isomeren) wird mitgeteilt. Um das Fortschreiten der Reaktion zu verfolgen, wurden zur Bestimmung des restlichen Isocyanatgehaltes Titration und Infrarotabsorptionsmethoden verwendet. Unter Verwendung äquivalenter Reaktantkonzentrationen ist die Geschwindigkeitskonstante im wesentlichen von der Kettenlänge und der Funktionalität der untersuchten Polyätherpolyole unabhängig. Die Reaktionsgeschwindigkeit der Polyätherpolyole mit endständigen primären Hydroxylgruppen (z.B. Pluronpolyole) ist grösser als die der Polyole mit sekundären Hydroxylgruppen, und sie wurde durch Anwesenheit von Zinnkatalysatoren sehr vergrössert.