

Kinetics of Alcohol-Isocyanate Reactions with Metal Catalysts*

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Synopsis

A study has been conducted of the kinetics of the reactions of primary and secondary alcohols with phenyl isocyanate in the presence of metal catalysts. It has been determined that the type and concentration of metal catalyst, the structure of the alcohols, and the type of solvent play an important role in the reaction rates and ratios of rate constants. Catalysis by lead naphthenate increased the reaction rates of 2-methoxy-1-propanol and 1-methoxy-2-propanol more than 3-methoxy-1-propanol, whereas catalysis by dibutyltin dilaurate enhanced the reaction rates of 3-methoxy-1-propanol more than those of 2-methoxy-1-propanol and of 1-methoxy-2-propanol. Dibutyltin dilaurate has been found to impart a high ratio of $K_{\text{primary}}/K_{\text{secondary}}$, where the primary alcohol was 3-methoxy-1-propanol and the secondary alcohol was 1-methoxy-2-propanol. Determinations of mixtures in toluene solutions containing up to 75% of 3-methoxy-1-propanol were made with good accuracy.

INTRODUCTION

In a recent kinetic study of polyether diol- and polyol-diisocyanate reactions, Wissman et al.¹ found that the use of dibutyltin dilaurate as a catalyst caused a substantially larger increase in the reaction rate of ethylene oxide "capped" poly(oxypropylene) glycol (Pluronic L61, Wyandotte Chemicals Corporation) with tolylene diisocyanate when compared to the rate of the unmodified poly(oxypropylene) glycol of the same chain length. Hence it was deemed of interest to determine whether other metal catalysts might also increase differences in the reaction rates of primary and secondary alcohols with isocyanate in comparison with rate differences for uncatalyzed reactions. Previously, Siggia and Hanna² and more recently Smith³ had reported the use of 1,4-diaza[2,2,2]bicyclooctane (triethylenediamine, Dabco, Houdry Process Corporation) as a catalyst in rate studies of reactions of primary and secondary alcohols and ether alcohols with phenyl isocyanate. Smith observed that triethylenediamine increased the rate constant for the 1-butanol-phenyl isocyanate reaction at 35.5°C. to about six times that for the 2-butanol-phenyl isocyanate reaction.

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A preliminary study was made to determine the selectivity of various metal catalysts, including stannous octoate, stannous oleate, dibutyltin dilaurate, and lead naphthenate, for the alcohol- or glycol-isocyanate reactions. The effects of catalyst concentration and influence of solvents were also investigated.

In addition to polyethylene glycol, hydroxy-containing model compounds such as 1-butanol, 2-butanol, 1,4-cyclohexanediol, and 2,3-butanediol were employed in this study. 3-Methoxy-1-propanol, 2-methoxy-1-propanol, and 1-methoxy-2-propanol were also included to determine the effects of the ether groups on the reactivity of the alcohols. Because of the spread in the reaction rates of primary and secondary alcohols with dibutyltin dilaurate as a catalyst, this process was investigated as a possible method for the quantitative determination of primary and secondary alcohols. The quantitative determinations of primary and secondary alcohol groups in alcohol blends have been the subject of several recent investigations.^{2,4-8} Interest in these studies has been stimulated by the search for more accurate and quicker methods for determining the ratio of primary and secondary hydroxyl groups in polyether diols and polyols. This has been particularly true for those derived from propylene and ethylene oxide adducts of diols and polyols used in the preparation of polyurethanes for various end uses. Among the analytical methods which have shown the greatest promise are those of Siggia and Hanna^{2,4} which are based upon differential reaction rates of primary and secondary alcohols with either acetic anhydride or phenyl isocyanate. It was hoped that the catalytic process using dibutyltin dilaurate would result not only in greater speed but that it would also aid in the sensitivity of the method reported by Hanna and Siggia.⁴

EXPERIMENTAL

Materials and Purification

Solvents were dried over Linde molecular sieves, Type 4A, and distilled: toluene, b.p. 52°C./100 mm., Cellosolve acetate, b.p. 94-94.5°C./100 mm.

1-Butanol and 2-butanol were dried over sodium, fractionated, and only the middle cuts used: for 1-butanol, b.p. 53.5°C./40 mm.; for 2-butanol, b.p. 38.2°C./40 mm. Other hydroxyl-containing compounds were distilled: 3-methoxy-1-propanol, b.p. 150-151°C./739 mm.; 1-methoxy-2-propanol, b.p. 119-120°C./747 mm.

2-Methoxy-1-propanol was prepared by the following reaction sequence: Sodium lactate was converted to methyl lactate, b.p. 143-145°C. by reaction with an excess of methyl alcohol in the presence of sulfuric acid.⁹ The methyl ester was reacted with thionyl chloride in pyridine solution to form methyl-2-chloropropionate (b.p. 129-130°C.);¹⁰ the latter was converted to methyl-2-methoxypropionate (b.p. 129-131°C.) by reaction with sodium methoxide in methanol solution.¹⁰ Reduction to 2-methoxy-1-propanol (b.p. 130-131°C., n_D^{25} 1.4078) was then effected by lithium aluminum hydride in ether solution.¹¹

Polyethylene glycol, molecular weight 393 (Wyandotte Chemicals Corporation) was degassed and stripped of water (to below 0.02%). *cis*-1,4-Cyclohexanediol, m.p. 100–102°C. and 2,3-butanediol, b.p. 94–95°C./20 mm. were used.

Phenyl isocyanate, Eastman Kodak Company, white label; lead naphthenate, Ferro Chemical Corporation; dibutyltin dilaurate (T-12), stannous octoate (T-9), and stannous oleate (T-18), obtained from M & T Chemicals, Inc., were used as received without further purification.

Procedure

Solutions employing dry solvent were prepared at 30°C. to contain 0.11*N* phenyl isocyanate and 0.10*N* alcohol. Aliquots from the reaction of a solution of the hydroxyl-containing compound, catalyst, and phenyl isocyanate were analyzed for unreacted isocyanate according to ASTM Method D-1638-61T.

Data were calculated and plotted according to the classical second-order reaction rate equation for reactants at different initial concentration. In the case where mixtures of the primary and secondary alcohols were reacted, two slopes resulted. The slopes of slower reacting secondary alcohols were extrapolated to zero time, and the concentration of the primary alcohols was calculated according to the procedure recommended by Siggia and Hanna.²

RESULTS AND DISCUSSION

Data in Table I indicate that the primary alcohols 1-butanol, 3-methoxy-1-propanol, and polyethylene glycol (molecular weight 393) reacted with phenyl isocyanate at similar rates when catalyzed with dibutyltin dilaurate. An exception to this behavior of the primary alcohols was 2-methoxy-1-propanol, which reacted at less than one-third the rate. The secondary alcohols, 2-butanol and 1-methoxy-2-propanol, exhibited rates that were similar to each other. However, the 2,3-butanediol reacted at a faster rate than the other secondary alcohols, up to 50% reaction, at which point the

TABLE I
Second-Order Rate Data for Reaction of Phenyl Isocyanate
with Hydroxyl Compounds^a

Hydroxyl compounds	$K \times 10^4$, l./equiv.-sec.
1-Butanol	170
2-Butanol	15
Polyethylene glycol (M. W. 393)	151
2,3-Butanediol	100 (initial)
3-Methoxy-1-propanol	160
2-Methoxy-1-propanol	48.3
1-Methoxy-2-propanol	11.4

^a Toluene solutions at 30°C.; NCO/OH = 1.1/1; 0.5×10^{-4} mole/l. dibutyltin dilaurate catalyst.

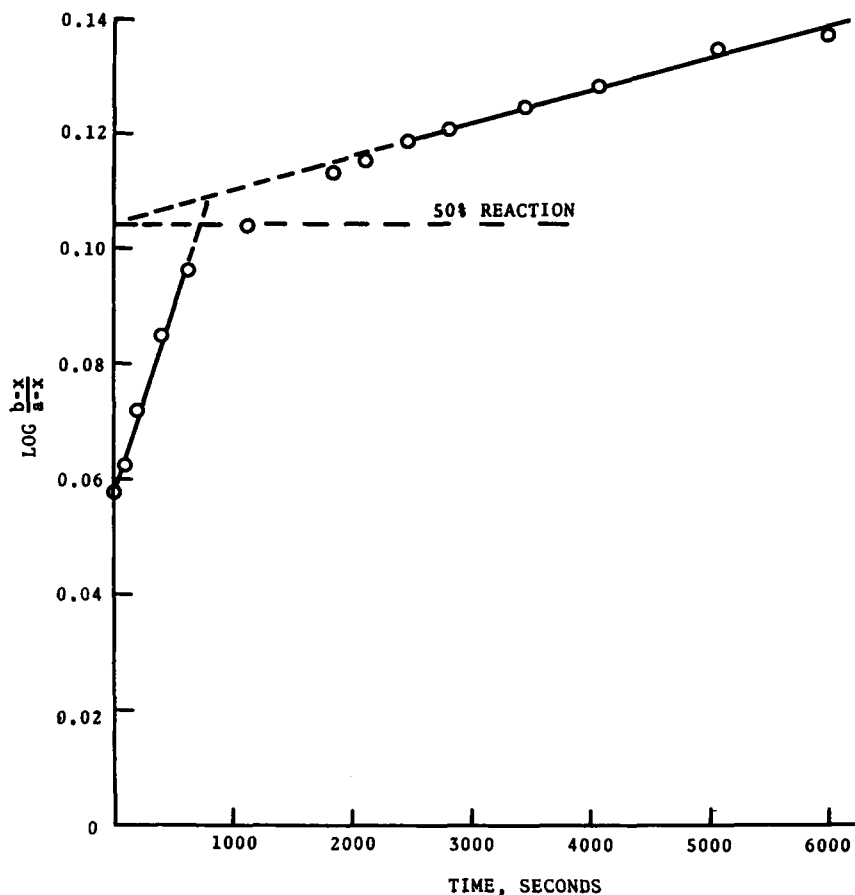


Fig. 1. Reaction of 2,3-butanediol with phenyl isocyanate at 30°C. (0.5×10^{-4} mole/l. dibutyltin dilaurate catalyst).

rate decreased greatly (Fig. 1). This was presumably due to the strong hydrogen bonding between the adjacent hydroxyl groups, resulting in an activating influence on the reaction of one hydroxyl with phenyl isocyanate.

TABLE II
Effect of Catalyst Concentration on Rate Constants of
Phenyl Isocyanate-Diol Reactions^a

Cat. concn., mole/l. $\times 10^4$	$K \times 10^4$, l./equiv.-sec.			$K_{\text{primary}}/K_{\text{secondary}}$
	Polyethylene glycol	1,4-Cyclohexane- diol		
0.5	24.1	4.8		5
1.0	37.2	5.9		6.3
1.5	54.3	11.0		5

^a Cellosolve acetate solutions at 30°C.; dibutyltin dilaurate catalyst.

TABLE III
Catalysis of Phenyl Isocyanate-Alcohol Reactions*

Catalyst	$K \times 10^4$, l./equiv. sec.		$K \times 10^4$ l./equiv.-sec.						K_A/K_C	K_B/K_C
	1-Butanol	2-Butanol	(A)			(B)		(C)		
			3-Methoxy 1-propanol	3-Methoxy 2-propanol	3-Methoxy 1-propanol	2-Methoxy 1-propanol	1-Methoxy 2-propanol			
None	0.9	0.3			0.5	0.4	0.2	1.2	2.5	2.0
Dibutyltin dilaurate	290.0	24.2	3.0	12.0	262.0	75.7	15.2	3.5	17.2	4.9
Stannous octoate	12.0	3.4	3.5	3.5	60.3	—	48.5	—	1.2	—
Stannous oleate	6.9	2.0	3.5	3.5	40.4	—	41.4	—	1.0	—
Lead naphthenate	6.3	0.9	7.0	7.0	32.0	106.5	68.0	0.3	0.5	1.6

* Toluene solutions at 30°C.; 1×10^{-4} mole/l. catalysts.

Further reaction proceeded at a greatly reduced rate, presumably due to steric hindrance.

Table II shows the effect of increasing catalyst concentration on the reaction rate of primary (polyethylene glycol) and secondary (1,4-cyclohexanediol) glycols in Cellosolve acetate solution. The rate constants increased for both types of hydroxyl and the ratio of $K_{\text{primary}}/K_{\text{secondary}}$ remained nearly constant at the various catalyst concentrations.

The catalytic effects of various metal salts on the rates of phenyl isocyanate-alcohol reactions are shown in Table III. As expected, the uncatalyzed reactions of the primary alcohols, 1-butanol, 3-methoxy-1-propanol, and 2-methoxy-1-propanol exhibited higher rates than the secondary alcohols, 2-butanol and 1-methoxy-2-propanol.

Dibutyltin dilaurate caused a significantly larger increase in the reaction rates of the primary alcohols than the secondary alcohols. Thus, the ratio of rate constants for primary/secondary was raised from 3 to 12 for the butanols, from 2.5 to 17.2 for K_A/K_C , and 2.0 to 4.9 for K_B/K_C , where A, B, and C refer to 3-methoxy-1-propanol, 2-methoxy-1-propanol, and 1-methoxy-2-propanol, respectively. The ratio of rate constants for the primary alcohols K_A/K_B increased from 1.2 (uncatalyzed) to 3.5 (dibutyltin dilaurate-catalyzed). The other three catalysts (stannous octoate, stannous oleate, and lead naphthenate) caused significantly greater increases in the rates of the methoxypropanols than the butanols, indicating the activating effect of the methoxy group in the presence of these catalysts. In the case of lead naphthenate, higher rates resulted for the secondary 1-methoxy-2-propanol and the primary 2-methoxy-1-propanol as compared to the primary 3-methoxy-1-propanol. The effect of the proximity of the methoxy group to hydroxyls is thus demonstrated. Confirmation of this effect of lead naphthenate was obtained by the reaction of the methoxypropanols at various catalyst concentrations. The data in Table IV again show the 1-methoxy-2-propanol and 2-methoxy-1-propanol to give higher rates than the 3-methoxy-1-propanol. Thus, the effect of the position of the methoxy group on the reaction catalyzed by lead naphthenate in toluene solution was again exhibited.

TABLE IV
Influence of Lead Naphthenate Concentration on
Rate Constants of Phenyl Isocyanate-Methoxypropanol Reactions^a

Lead naphthenate concn., mole/l. $\times 10^4$	$K \times 10^4$, l./equiv. sec.			K_A/K_B	K_A/K_C	K_B/K_C
	(A) 3-Methoxy- 1-propanol	(B) 2-Methoxy- 1-propanol	(C) 1-Methoxy- 2-propanol			
0.5	14.2	63.4	58.3	0.2	0.2	1.1
1.0	32.0	106.5	68.0	0.3	0.5	1.6
1.5	42.6	120.1	77.0	0.4	0.6	1.6

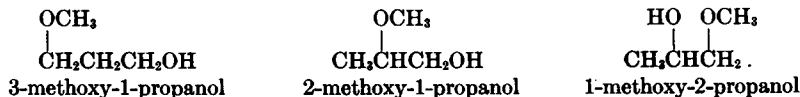
^a Toluene solutions at 30°C.

TABLE V
Effect of Dibutyltin Dilaurate on Rate Constants
of Phenyl Isocyanate-Methoxypropanol Reactions^a

Cat. concn., mole/l. × 10 ⁴	K × 10 ⁴ , l./equiv. sec.			K _A /K _B	K _A /K _C	K _B /K _C
	(A) 3-Methoxy- 1-propanol	(B) 2-Methoxy- 1-propanol	(C) 1-Methoxy- 2-propanol			
0.5	162.0	48.3	11.2	3.4	14.6	4.3
1.0	262.0	75.7	15.2	3.5	17.2	4.9
1.5	340.0	85.5	20.5	4.0	16.9	4.2

^a Toluene solutions at 30°C.

The effect of the position of the methoxy group on reactions catalyzed by dibutyltin dilaurate in toluene solution is shown in Table V. Both 2-methoxy-1-propanol and 1-methoxy-2-propanol exhibited lower rates when catalyzed with dibutyltin dilaurate than they did when catalyzed by lead naphthenate, while 3-methoxy-1-propanol reacted at faster rates when catalyzed by dibutyltin dilaurate. It is apparent that the effects of alcohol structure on rates were different in reactions catalyzed by either metal salt. The proximity of the methoxy group to the hydroxyl group in 1-methoxy-2-propanol and 2-methoxy-1-propanol, as well as the position of the methyl group, appear to have the



most important influence on these rates. Differences in reaction mechanisms caused by these two catalysts are being investigated.

Lower reaction rates were obtained for all three methoxypropanols when catalyzed by dibutyltin dilaurate in Cellosolve acetate than in toluene solution (Table VI). It is probable that the more polar Cellosolve acetate was able to deactivate the hydroxyl groups by its ability to form complexes.

TABLE VI
Effect of Dibutyltin Dilaurate Concentration on Rate Constants
of Phenyl Isocyanate-Methoxypropanol Reactions^a

Cat. concn., mole/l. × 10 ⁴	K × 10 ⁴ , l./equiv. sec.			K _A /K _B	K _A /K _C	K _B /K _C
	(A) 3-Methoxy- 1-propanol	(B) 2-Methoxy- 1-propanol	(C) 1-Methoxy- 2-propanol			
0.5	45.2	4.3	7.5	10.1	6.0	0.6
1.0	77.1	11.5	13.4	7.0	5.8	0.9
1.5	108.2	14.7	21.5	7.4	5.1	0.7

^a Cellosolve acetate solutions at 30°C.

The data in Table IV and V make it apparent that dibutyltin dilaurate was the most effective of the catalysts investigated for differentiating between the primary and secondary alcohols, 3-methoxy-1-propanol and 1-methoxy-2-propanol, by reaction with phenyl isocyanate. The kinetic method of Siggia and Hanna² was utilized to determine the composition of synthetic mixtures of these methoxypropanols. The results obtained (Table VII) illustrate that mixtures of 5–75% primary alcohol can be determined with accuracy.

TABLE VII
Determination of Mixtures of 3-Methoxy-1-propanol
and 1-Methoxy-2-propanol^a

Cat. concn., mole/l. $\times 10^4$	Primary hydroxyl, %	
	Present	Found
0.5	45.0	44.7
0.5	75.0	75.2
0.5	50.0	49.5
1.0	5.0	4.5
1.0	10.0	10.8
1.0	25.0	24.8
1.0	50.0	49.8
1.0	75.0	75.3
1.0	80.0	76.0

^a Toluene solutions at 30°C.

The infrared determination of isocyanate as modified by Floutz^{1,12} can be used instead of the titration method to obtain isocyanate concentrations.

It appears that dibutyltin dilaurate is a good catalyst for the quantitative determination of primary and secondary hydroxyl groups in alcohol blends where the differential reaction rates with phenyl isocyanate are sufficiently large, as exemplified by 3-methoxy-1-propanol in the presence of 1-methoxy-2-propanol.

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Résumé

On a étudié la cinétique des réactions des alcools primaires et secondaires avec l'isocyanate de phényle en présence de catalyseurs métalliques. On a trouvé que le type et la concentration du catalyseur métallique, la structure des alcools et le type de solvant jouent un rôle important sur les vitesses de réaction, et sur les rapports des constantes de vitesse. La catalyse par le naphthénate de plomb augmente plus fortement les vitesses de réaction du 2-méthoxy-1-propanol et du 1-méthoxy-2-propanol que celles du 3-méthoxy-1-propanol, tandis que la catalyse par le dilaurate de dibutylétain augmente plus fortement les vitesses de réaction du 3-méthoxy-1-propanol que celles du 2-méthoxy-1-propanol et du 1-méthoxy-2-propanol. On a trouvé que le dilaurate de dibutylétain donne une valeur élevée pour le rapport $K_{\text{primaire}}/K_{\text{secondaire}}$ dans le cas où l'alcool primaire était le 3-méthoxy-1-propanol et l'alcool secondaire le 1-méthoxy-2-propanol. Des déterminations effectuées sur des mélanges de solutions dans le toluène, contenant jusqu'à 75% de 3-méthoxy-1-propanol, ont été effectuées avec une bonne précision.

Zusammenfassung

Eine Untersuchung der Kinetik der Reaktion von primären und sekundären Alkoholen mit Phenylisocyanat in Gegenwart von Metallkatalysatoren wurde durchgeführt. Typ und Konzentration des Metallkatalysators, die Struktur des Alkohols und der Lösungsmitteltyp spielen für die Reaktionsgeschwindigkeit und das Verhältnis der Geschwindigkeitskonstanten eine wichtige Rolle. Katalyse durch Bleinaphthenat erhöhte die Reaktionsgeschwindigkeit von 2-Methoxy-1-propanol und 1-Methoxy-2-propanol stärker als von 3-Methoxy-1-propanol, während Katalyse durch Dibutylzinnlaurat die Reaktionsgeschwindigkeit von 3-Methoxy-1-propanol mehr als diejenige von 2-Methoxy-1-propanol und 1-Methoxy-2-propanol hinaufsetzt. Es wurde gefunden, dass Dibutylzinnlaurat für 3-Methoxy-1-propanol als primären Alkohol und 1-Methoxy-2-propanol als sekundären Alkohol zu einem hohen Verhältnis $K_{\text{primär}}/K_{\text{sekundär}}$ führt. Mischungen, die in Toluollösung bis zu 75% 3-Methoxy-1-propanol enthielten, konnten mit guter Genauigkeit bestimmt werden.

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