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Optimizing Urethane Synthesis by Studying the Kinetics of Reactions Between a Model Alcohol and Isocyanates in Various Solvents

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Summary

The rates of the reactions between the model alcohol 2,4,4-trimethyl-1-pentanol (TMPO) and the isocyanates 4,4'-diphenylmethane diisocyanate (MDI) and triphenylmethane triisocyanate (TTI) have been studied in various solvents i.e., p-xylene, p-xylene/N,N-dimethylformamide (DMF) 75/25, and tetrahydrofuran (THF)), in the temperature range from 24° to 68°C. The rates of the reactions between TMPO plus isocyanates was similar to that of 1-butanol plus isocyanates. The reactivities of the two -NCO groups in MDI and the three -NCO groups in TTI are virtually identical. The rate of the TMPO/TTI reaction is slightly higher and its activation energy is slightly lower than that of the TMPO/MDI reaction. The fastest rates have been obtained in the binary solvent system p-xylene/DMF.

Introduction

The syntheses of new linear and branched polyisobutylene-based polyurethanes have recently been reported (1,2). The syntheses became feasible with the availability of linear polyisobutylene (PIB) diols (3) and three-arm star triols (4) carrying exactly 2.0 and 3.0 primary hydroxy end groups, respectively. In the course of our fundamental investigations in this field we became interested in exploring the effect of experimental conditions on the reaction between these PIB-alcohols and isocyanates.

This paper concerns an investigation of the kinetics of the reaction between TMPO, a model alcohol that exactly mimics the end group of hydroxy-telechelic polyisobutylenes $HOCH_2CH(CH_3)CH_2\sim\!\sim\!\sim PIB\sim\!\sim\!\sim CH_2CH(CH_3)CH_2OH$ and the isocyanates MDI and TTI, $CH_2(C_6H_4NCO)_2$ and $CH(C_6H_4NCO)_3$, in various solvents at various temperatures. The results of these investigations were to provide guidance for selecting optimum conditions for the synthesis of PIB-based polyurethane thermoplastic elastomers and model networks.

Experimental

Materials: 4,4'-Diphenylmethane diisocyanate (MDI) (Mobay) was vacuum distilled before use. Triphenylmethane triisocyanate (TTI) (Mobay), 20% solution in methylene chloride, was purified by precipitating into dry *n*-pentane to remove insoluble oligomers, then fractionated under high vacuum only the middle fraction being collected. The distillate was a light yellow viscous liquid which crystallized upon storage under dry nitrogen. According to di-n-butylamine/HCl tritration (5) the product was 99.99% pure. The synthesis of 2,4,4-trimethyl-1-pentanol (TMPO) has been described (3). Xylene and N,N-Di-Dimethylformamide (DMF) (Fisher Scientific) were refluxed under dry nitrogen over calcium hydride, and freshly distilled into amber bottles before use (6,7). Tetrahydrofuran (THF) (Fisher Scientific) was refluxed over lithium aluminum hydride under dry nitrogen and distilled before use. Di-n-butylamine Aldrich) was used as received and an ∿0.25 N di-n-butylamine solution in THF was prepared and titrated with 0.1 N HCl. Standard 0.1 N HCl was prepared by diluting Fisher certified concentrated HCl solution in a volumetric flask with distilled water. Indicator solution was prepared by dissolving 0.1g bromcresol green (Aldrich) in 1.5 ml 0.1 N NaOH solution, then diluted to 100 ml with distilled water.

Rate Measurements

Isocyanate solutions were prepared in 50 ml volumetric flasks and transferred to three-neck round bottom flasks equipped with magnetic stirrer, condenser, nitrogen inlet tube, and gas bubbler in a dry box filled with dry nitrogen gas. The flasks were heated to a desired temperature and TMPO was added. Samples of 2 ml aliquots were removed at desired time intervals, and the amount of unreacted isocyanate was determined by di-*n*-butylamine/HCl titration (5) as follows: The aliquot was added to a culture tube containing an excess of di-*n*-butylamine in THF, and the pipet was rinsed with 2 ml THF into the same culture tube. The tube was capped with a Teflon-lined cap, shaked, and placed into boiling water for 10 min. After cooling to room temperature, one drop of indicator solution was added and the excess of di-*n*-butylamine was back-titrated with 0.1 N HCl.

Polyisobutylene-based polyurethane networks have been prepared by the use of THF solvent, however, it was found that the reaction between hydroxy-telechelic polyisobutylene and MDI or TTI was very long (two weeks) in this solvent (2). We have carried out similar experiments with our model alcohol TMP and found relatively low rates in THF in the 24 to 60°C range. Figures 1 and 2 illustrate the data, and the first part in Table 1 shows the corresponding numerical data. Further, the rate of reaction between TMPO and MDI in THF was about 150 times lower than that between 1-butanol and MDI in xylene, i.e., 1.6×10^{-6} versus 1.9×10^{-4} ℓ mole^{-1} sec^{-1}. The reaction in THF is sluggish even at higher temperatures (see E_a values in Table 1). The relatively slow reactions obtained in THF may be due to hydrogen bonding between THF and the reactants (8).

The TMPO/MDI reaction is faster in p-xylene than in THF, thus steric compression in TMPO is not a rate-limiting parameter. Figures 3 and 4 show the rate data obtained using xylene as solvent and Table 1 shows the rate constants and activation energy.

The linearity of the plots (absence of breaks in the lines) suggests that the two NCO groups possess equal reactivities. Similar observations have been made by others(9,10).

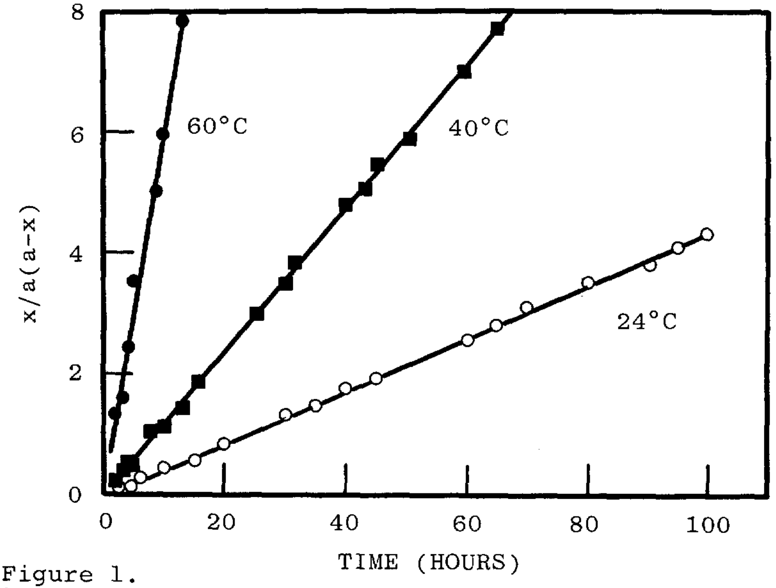


Figure 1.
Second Order Plots for Reaction of MDI with TMPO in Tetrahydrofuran at $[NCO]_o = [OH]_o$.

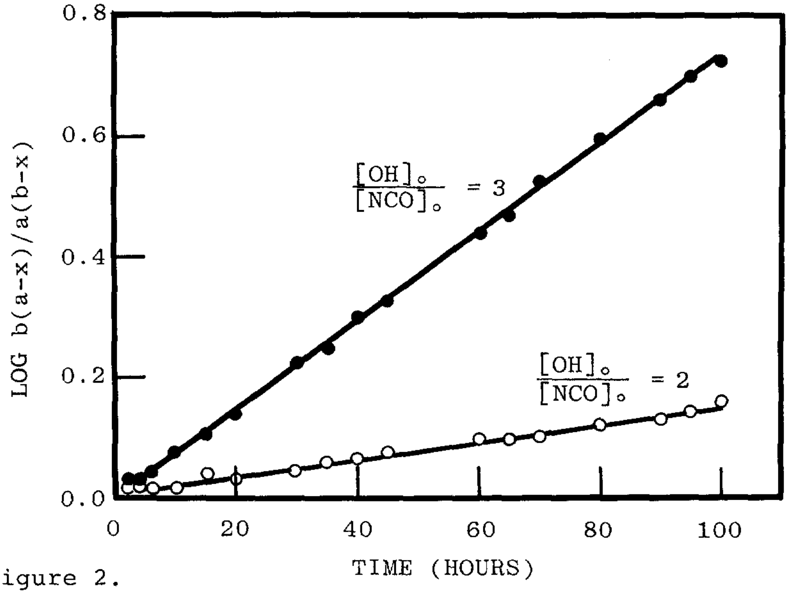


Figure 2.
Second Order Plots for Reaction of 4,4'-Diphenylmethane Diisocyanate (MDI) with 2,4,4-Trimethyl-1-pentanol (TMPO) in Tetrahydrofuran at 24°C.

Table 1

REACTION OF 2,4,4-TRIMETHYL-1-PENTANOL WITH 4,4'-DIPHENYLMETHANE DIISOCYANATE

$[\mathrm{NCOL}]_o$	$\frac{[\mathrm{OH}]_o}{[\mathrm{NCO}]_o}$	Temp.	$k \times 10^4$	Ea*
mole/1		°C	1/mole sec	kcal/mole
IN TETRAHYDROFURAN				
0.222	3	24	0.106	26.7
0.222	3	24	0.045	
0.222	1	24	0.012	
0.240	1	40	0.33	
0.235	1	60	1.67	
IN XYLENE				
0.22	3	24	2.82	10.9
0.22	2	24	2.37	
0.22	1	24	1.60	
0.245	1	42.5	4.30	
0.245	1	63	13.73	
MIXTURE OF XYLENE AND N,N-DIMETHYLFORMAMIDE (75/25 v/v)				
0.24	1	24	13.89	8.14
0.24	1	38	23.15	
0.24	1	68.5	82.01	

*Ea was calculated based on the data obtained at $[\mathrm{NCO}]_o = [\mathrm{OH}]_o$

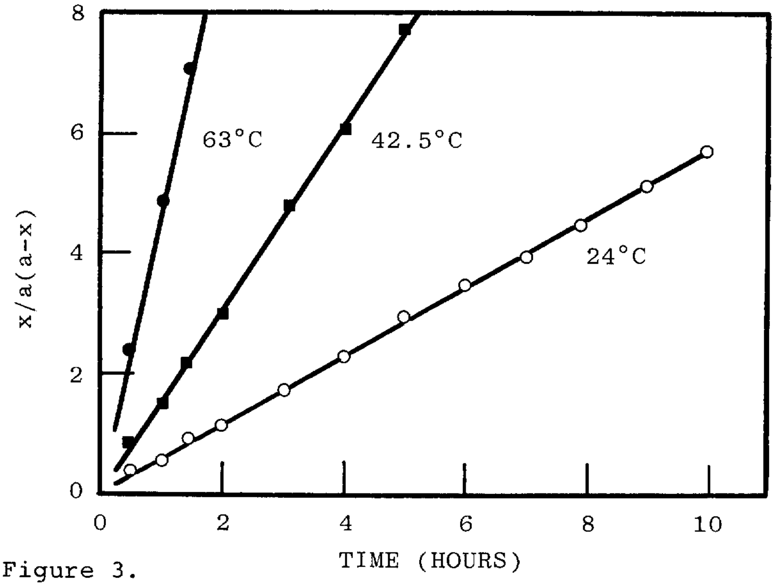


Figure 3.
Second Order Plots for Reaction of MDI with TMPO in Xylene at $[NCO]_o = [OH]_o$.

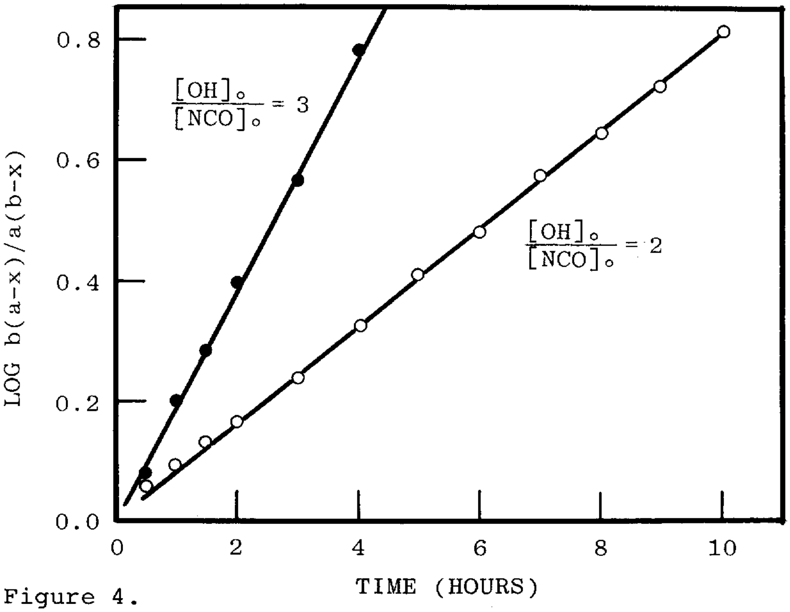
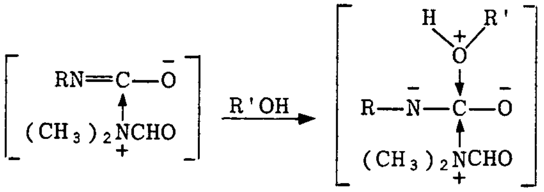


Figure 4.
Second Order Plots for Reaction of MDI with TMPO in Xylene at 24°C.

Significantly, the E_a for the TMPO/MDI reaction is virtually identical to that published for the 1-butanol/MDI system (10.9 and 9.6 kcal $mole^{-1}$) (9,11). Figure 5 shows the rate dependence upon alcohol concentration for the TMPO/MDI reaction and further illustrates that the reactivities of TMPO and 1-butanol are very similar.

Similar results have been obtained with the TMPO/TTI system by the use of xylene as shown by the data in Figure 6 and Table 2. Again, the linearity of the plots indicates that the reactivities of the three -NCO groups in TTI are identical. It is of interest that the rate of the TMPO plus TTI reaction is somewhat faster and the activation energy lower than that of the TMP plus MDI reaction.

Finally the rate of urethane formation between TMPO and MDI was investigated in the mixed solvent p-xylene/DMF (75/25 v/v). This solvent system provides homogeneous mixes for hydroxy-telechelic polyisobutylenes, isocyanates, and 1,4-butanediol. Figure 7 shows the rate plots at various temperatures and the lower part of Table 2 the corresponding numerical values. Evidently the rates are highest and the activation energy lowest in the presence of DMF. This rate accelerating effect may be due to DMF catalyzing urethane formation, or to the formation of an activated intermediate between DMF and isocyanates prior to reaction with the alcohol (12):



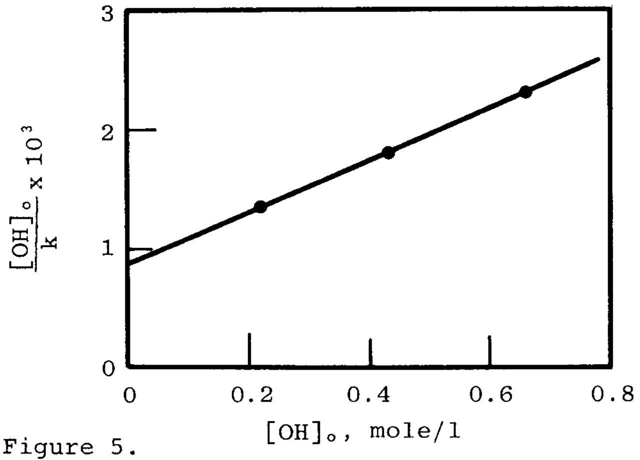


Figure 5.
Rate Dependence upon Alcohol Concentration for Reaction of MDI with TMPO in Xylene at 24°C.

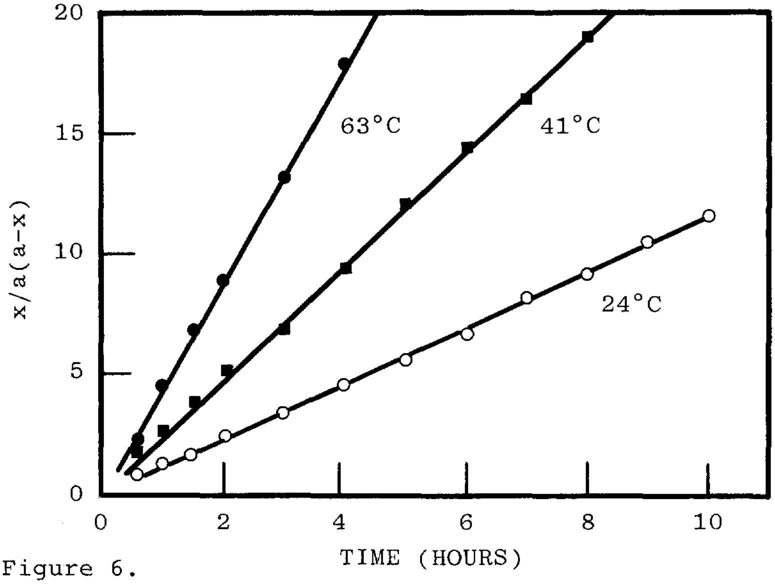


Figure 6.
Second Order Plots for Reaction of Trimethylmethane Triisocyanate (TTI) with 2,4,4-Trimethyl-1-pentanol (TMPO) in Xylene at $[NCO]_o = [OH]_o$.

Table 2

REACTION OF 2,4,4-TRIMETHYL-1-PENTANOL WITH TRIPHENYLMETHANE TRIISOCYANATE IN XYLENE

Temperature °C	$k \times 10^4$ l/mole sec	Ea kcal/mole
24	3.20	
41	6.65	6.9
63	12.46	

$[NCO]_o = [OH]_o = 0.2543$ mole/l

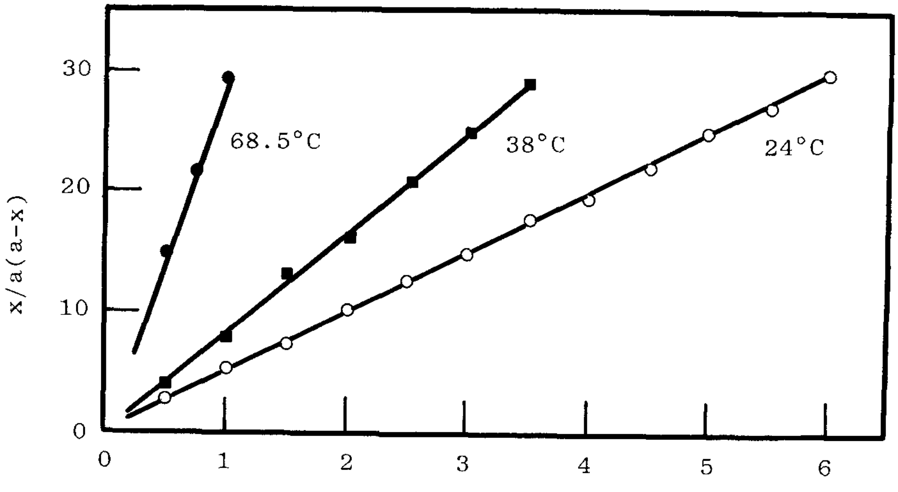


Figure 7.
Second Order Plots for Reaction of MDI with TMPO in the mixture of Xylene/N,N-Dimethylformamide = 75/25 (v/v).

Acknowledgement

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