

Kinetic Investigations of Trimethylolpropane–Diisocyanate Reactions

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ABSTRACT: Trimethylolpropane (TMP) is frequently used as a trifunctional branching and chain-extending agent in polyurethane production. This article deals with the analysis of the reactivities of the three primary hydroxyl groups of TMP during reactions with two exemplary diisocyanates: aromatic diphenylmethane-4,4'-diisocyanate and aliphatic *m*-tetramethylxylylene diisocyanate. The method of examination is online attenuated total reflection/Fourier transform infrared spectroscopy. With this method, reactions in progress can be monitored simultaneously. It is shown that the addition of an isocyanate (here phenyl isocyanate) to the alcohol affects the rate of subsequent reactions. The higher

the substitution degree is, the smaller the rate constant is of the reaction between the remaining free hydroxyl groups and the diisocyanates. This effect is largely determined by the type of diisocyanate. For reactions with very reactive aromatic diisocyanates, steric hindrance plays a significant role. For aliphatic diisocyanates, the substitution shows only minor effects because of the slowly reacting isocyanate groups. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 4090–4097, 2006

Key words: branched; kinetics (polym.); polyurethanes

INTRODUCTION

For the production of polyurethanes, multifunctional polyols are built in the polymer chains as branching and chain-extending agents. In this case, the nature of the polyols, among other experimental conditions such as the temperature, composition of the reactants, and polarity of the solvent, has substantial influence on the formation of different polymeric structures and, therefore, on the physical properties of the final polyurethane. In this way, alcohols with two functional groups develop linear structures. In the case of higher functionalities, branching, crosslinking, or both affect the workability and processability of the polymer. Trimethylolpropane (TMP) is one of the alcohols used industrially for polyurethane production.

To influence the structure of polyurethane during its production, a precise knowledge of the kinetics of the reactions between the hydroxyl and isocyanate compounds is required. In the past, many aspects of these reactions have been examined. On the one hand, the reactivities of the isocyanate compounds in use have been analyzed: It is known that both isocyanate groups of one diisocyanate, such as TDI, can show different reactivities.^{1,2} The reaction

behavior between aliphatic and aromatic isocyanates in reactions with polyols has been examined as well.³ These studies show that aromatic isocyanate compounds react considerably faster than aliphatic ones because of possible resonance stabilization. On the other hand, the reactions have been analyzed with respect to the reactivities of the hydroxyl compounds (e.g., the reactions of polyols, such as 1,2-propylene glycol and polyether polyol, with isocyanates). In this connection, comparisons of the reactivities of the primary and secondary hydroxyl groups have been of interest.^{4–8} Secondary hydroxyl groups have lower reaction rates than primary hydroxyl groups in reactions with different isocyanate compounds. The reactions between polyol and isocyanate with respect to the different chain lengths of the alcohols have also been investigated.^{7,9} However, the question of the reactivity of different primary hydroxyl groups of one polyol remains; TMP is used as a relevant example.

In the case of the esterification of TMP with azelaic acid and *o*-phthalic anhydride, Pétaud et al.¹⁰ found that with increasing esterification of TMP, steric hindrance increased too. Further experiments¹¹ showed that these steric hindrances influenced the reactivities of the three hydroxyl groups.

This work discusses examinations and results of the reactions of TMP hydroxyl groups with diisocyanate compounds. It is shown that the addition of an isocyanate to the hydroxyl groups results in steric hin-

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drance and therefore decreasing reaction rates for consecutive urethane formation.

The alcohol monomers used were TMP, phenyl carbamic acid 2,2-bishydroxymethyl butyl ester [i.e., monosubstituted trimethylolpropane (msTMP)], and phenyl carbamic acid 2-hydroxymethyl-2-phenylcarbamoyloxymethyl butyl ester [i.e., disubstituted trimethylolpropane (dsTMP)]. All of them were handled in solution. The reaction partners were the diisocyanates: aromatic diphenylmethane-4,4'-diisocyanate (MDI) and aliphatic *m*-tetramethylxylylene diisocyanate (TMXDI), both of which are used industrially. The kinetics of these reactions were ascertained by means of online attenuated total reflection/Fourier transform infrared (ATR-FTIR) spectroscopy. This noninvasive method made it possible to monitor the course of the reaction during the entire process.

EXPERIMENTAL

Materials

TMP, the solvent isobutyl methyl ketone (MIBK), phenyl isocyanate, and diphenylmethane diisocyanate (MDI) were received from Merck. MDI was a mixture of isomers. It consisted of 59.9% diphenylmethane-4,4'-diisocyanate, 4.9% isomeric diphenylmethane diisocyanates, and 30.1% triisocyanates. The remaining 5% formed higher functional MDIs. TMXDI was made available by BASF. To examine the reaction rates of the diisocyanates with the three hydroxyl groups of TMP separately, msTMP and dsTMP were first synthesized from TMP and phenyl isocyanate with different compositions of the educts. The products were separated and cleaned by means of column chromatography. The products were proved by ¹H-NMR measurements.

msTMP

¹H-NMR (400 MHz, DMSO-*d*₆, δ): 9.49 (s, 1H, —NH), 7.47 (d, 2H, —*H*_{arom.,ortho}), 7.27 (t, 2H, —*H*_{arom.,meta}), 6.97 (t, 1H, —*H*_{arom.,para}), 4.41 (t, 2H, 2x —OH), 3.94 (s, 2H, —CH₂—O—), 3.33 (d, 4H, —CH₂—OH), 1.32 (m, 2H, —CH₂—CH₃), 0.84 ppm (t, 3H, —CH₃). ¹³C-NMR (400 MHz, DMSO-*d*₆, δ): 154.2 (C-7), 139.6 (C-8), 129.0 (C-10,10'), 122.6 (C-11), 118.5 (C-9,9'), 64.8 (C-6), 61.3 (C-4,5), 43.1 (C-3), 21.9 (C-2), 7.8 ppm (C-1).

dsTMP

¹H-NMR (400 MHz, DMSO-*d*₆, δ): 9.59 (s, 2H, —NH), 7.47 (d, 4H, —*H*_{arom.,ortho}), 7.27 (t, 4H, —*H*_{arom.,meta}), 6.98 (t, 2H, —*H*_{arom.,para}), 4.70 (t, 1H, —OH), 4.04 (s, 4H, 2x —CH₂—O—), 3.42 (d, 2H, —CH₂—OH), 1.44 (m, 2H, —CH₂—CH₃), 0.89 ppm (t, 3H, —CH₃). ¹³C-NMR (400 MHz, DMSO-*d*₆, δ): 153.9 (C-7, C-12), 139.5

(C-8, C-13), 129.1 (C-10,10', C-15,15'), 122.7 (C-11, C-16), 118.5 (C-9,9', C-14,14'), 64.4 (C-4, C-6), 60.8 (C-5), 42.3 (C-3), 22.3 (C-2), 7.8 ppm (C-1).

The reactions carried out for the kinetic examination are represented schematically in Figure 1.

Spectroscopic analysis

Concentration measurements were performed with a ReactIR 1000 ATR-FTIR spectrometer from Applied Systems (Mettler-Toledo). It was equipped with a mercury-cadmium-tellurium detector. The detector was cooled with liquid nitrogen over the entire measuring time. The program ReactIR, version 2.21, was used for the evaluation of the IR spectra obtained on the basis of the Lambert-Beer law.

The reactions of the alcohols (TMP, msTMP, and dsTMP) with the diisocyanates (MDI and TMXDI) were carried out in a double-walled, 50-mL, glass reactor. In both series of experiments [70 (2.3 mol/L) and 30 (5.2 mol/L) percentage parts of alcohol (ppa) in the solution], the alcohols and solvent were charged into the reactor and heated to the reaction temperature. Intensive mixing and isothermal reaction conditions during the entire reaction course were ensured with a magnetic stirrer and a controlled heating circulator. The measuring probe of the IR spectrometer was immersed into the reaction solution perpendicularly through the neck of the reactor. Reactions were started with the injection of the diisocyanates (the molar ratio of alcohol to diisocyanate was in all experiments 15:1).

Spectrometric measurements began synchronously, and a spectrum was recorded every minute for the first 15 min. Subsequently, a spectrum was recorded every 3 min until the end of reaction. Each spectrum was averaged on the basis of 64 scans over the wavenumber field from 650 to 4000 cm⁻¹ (resolution = ±4 cm⁻¹).

The area of the isocyanate signal was monitored during all spectral scans. It decreased exponentially with the processing time. In the reactions with MDI, reaction times in the range of 30 min to 6 h were necessary to consume the diisocyanate completely. With TMXDI, the range was 2–15 h. Figure 2 shows a cascade of spectra of an experiment with TMXDI. An exponential decrease of the isocyanate peak area with increasing reaction time is apparent.

All three alcohols (TMP, msTMP, and dsTMP) at 30 ppa were converted with MDI at a minimum of three different temperature levels. Because the boiling point of the solvent MIBK is approximately 118°C, the reaction temperature of 115°C could not be exceeded. Thus, only TMP and msTMP could be converted with MDI and TMXDI at 70 ppa. To bring dsTMP into solution, higher temperatures would have been necessary.

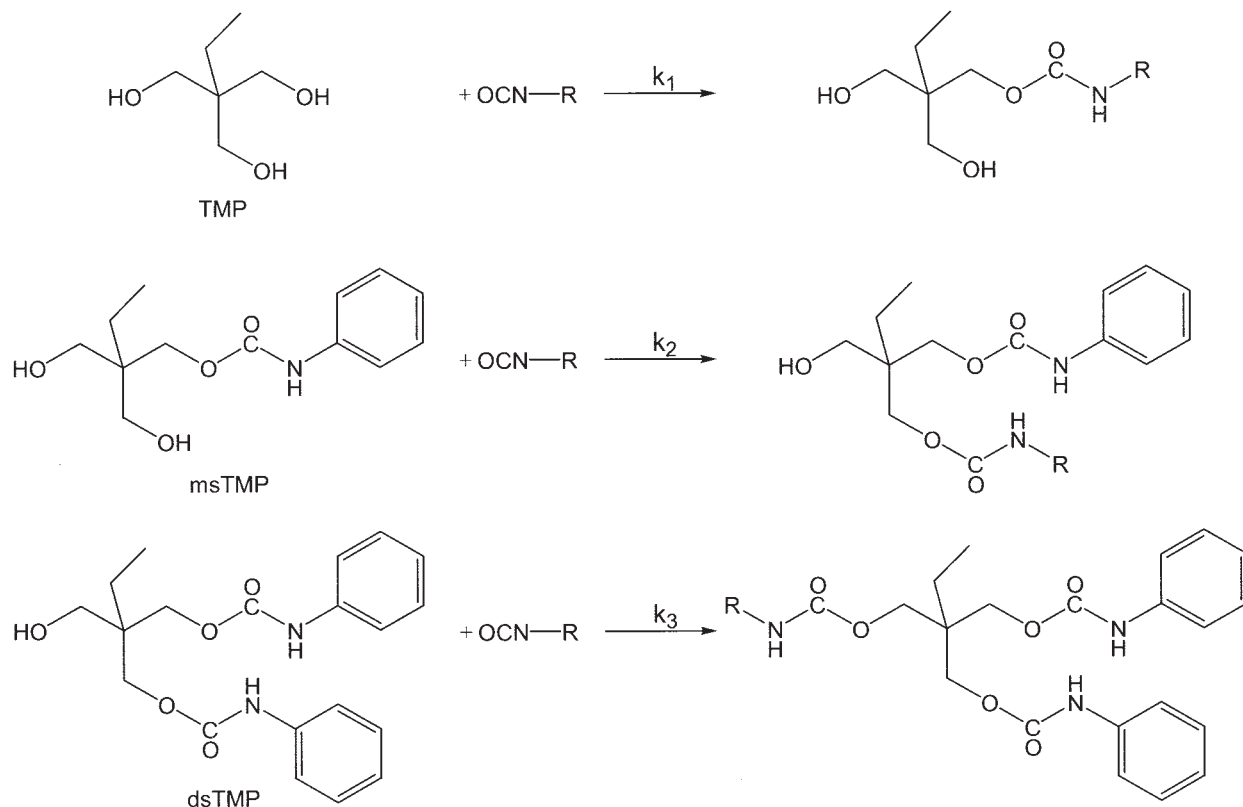


Figure 1 Schematic reactions.

RESULTS AND DISCUSSION

Analysis of the spectroscopic data

In the case of ATR-FTIR spectroscopy, the incident IR radiation that enters the sample is not directed through the sample as it is with normal absorption spectroscopy. The radiation traverses only a very short route through the sample. There it is partially absorbed and partially reflected. The reflected radiation returns to the detector and is recorded. The absorption is proportional to the concentration of the reactants according to the Lambert-Beer law:

$$A \propto \epsilon c \quad (1)$$

where A is the absorption, ϵ is the molar absorption coefficient (a material constant not depending on the concentration), and c is the concentration of the reactant.

The radiation that has been absorbed by the IR-active groups can thus be calculated from the reflected radiation. The absorption range of interest for the kinetic analysis is that of the isocyanate. It occurs between 2200 and 2350 cm^{-1} . The greatest area of the NCO absorption peak is found at the injection of the diisocyanates. This area at the beginning of the measurement is equated with the concentration of the NCO groups. Although the reaction is progressing,

the portion of NCO groups in the reaction mixture is decreasing exponentially. Consequently, the concentration of the NCO groups can be computed for every measurement point with respect to its peak area.

For the reaction between an alcohol and a diisocyanate without a catalyst, a second-order rate law is in effect:

$$r = -\frac{d[\text{NCO}]}{dt} = k[\text{NCO}][\text{OH}] \quad (2)$$

Because of the availability of alcohol in a large surplus (the molar ratio of alcohol to diisocyanate is 15:1), the OH concentration can be assumed to be quasiconstant. Consequently, a pseudo-first-order rate law results:

$$r = -\frac{d[\text{NCO}]}{dt} = K[\text{NCO}], \quad K = k[\text{OH}] \quad (3)$$

With the assumption of a constant-volume batch reactor and a constant concentration of hydroxy groups, the integration of eq. (3) gives

$$\ln \frac{[\text{NCO}]}{[\text{NCO}]_0} = -k[\text{OH}]t \quad (4)$$

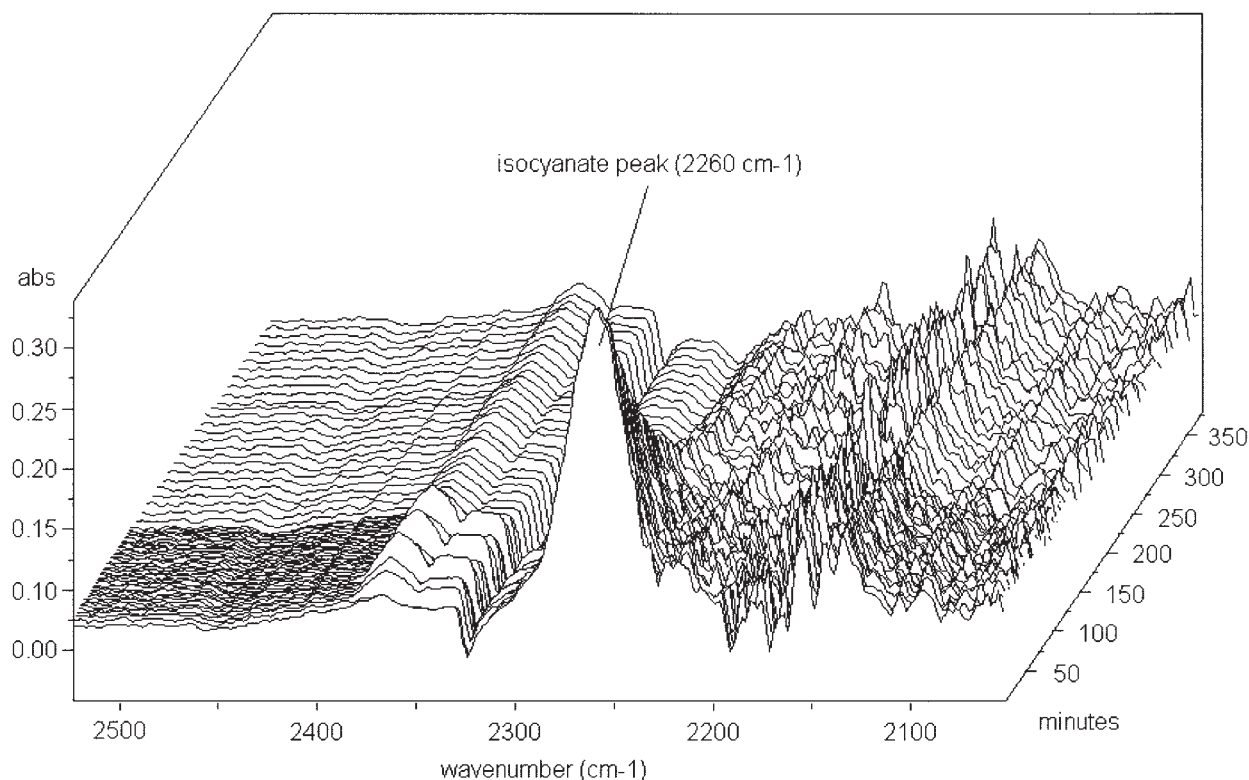


Figure 2 Cascade of the spectra of an experiment with TMXDI.

The rate constants (k) of the respective reactions can be calculated from linear least-squares analysis (shown later in Fig. 4). The reactions of the alcohols with the diisocyanates were carried out at least three different temperatures. Thus, the dependence on the temperatures of the reactions can be estimated. With the Arrhenius relationship [eq. (5)], the activation energy (E_a) values of the reactions can be obtained:

$$k = k_{\infty} e^{-E_a/RT} \quad (5)$$

By means of the E_a values and the pre-exponential factors (k_{∞}), rate constants can be calculated for temperatures not analyzed experimentally.

Reactions of alcohols with TMXDI

Known reactions with TMXDI already show that these reactions pass relatively slowly because of the aliphatic character of TMXDI. For this reason, the ppa value in the solvent was chosen to be as high as possible (70).

The reactions were also carried out at higher temperatures. The conversions of TMP with TMXDI between 80 and 115°C show a regular rise in the reaction rate with increasing temperature. Figure 3 shows the

concentration profiles over the reaction time for the experiments with TMP and TMXDI (the concentrations were standardized to one). In Figure 4, the logarithms of the concentrations as functions of time (pseudo-first-order) are represented. A reaction period of approximately 150–800 min is to be recognized in these experiments.

The reactions of msTMP and TMXDI were completed at temperatures between 100 and 115°C because msTMP could not be brought into solution below 100°C with 70 ppa. Because of the various results, it was necessary to carry out at least two reactions at each temperature. The obtained k , E_a , and k_{∞} values for the experiments with TMXDI are represented in Table I.

At 70 ppa, dsTMP solubilizes only at approximately 110°C. The injection of the diisocyanates at room temperature forces the alcohol out of participation because of the low temperature, so an IR spectroscopy measurement is impossible. For this reason, no data are available for the experiments with dsTMP and TMXDI.

Table I shows that the reactions of TMP with TMXDI pass slightly faster than the reactions of msTMP with TMXDI. The difference is relatively small here because the reaction rate is already limited by the slowly reacting TMXDI. The influence of the substituent on msTMP does not gain in significance.

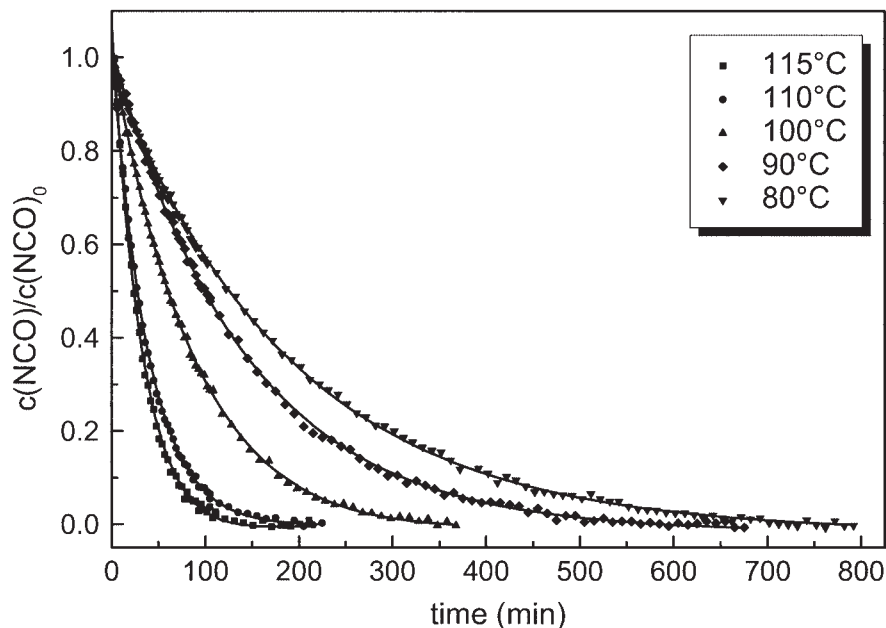


Figure 3 Exponential decrease of the TMXDI concentrations.

Reactions of alcohols with MDI

MDI reactions were examined with 70 ppa as well. TMP was converted with MDI at low temperatures (20–50°C). This was necessary to observe significant data for kinetics due to the high reactivity of MDI. The analysis of the obtained data proved to be complicated for the experiments with MDI because of its composition. In the representation of the logarithmic concentration as a function of time (pseudo-first-order; Fig.

5), the reaction with TMP and MDI at 20°C and 70 ppa slows after a conversion of approximately 60%. This reaction course can be observed in all experiments with MDI and may be explained by the composition of MDI. First, the approximately 60% diphenylmethane-4,4'-diisocyanate may react, and then the sterically more hindered polymeric MDIs may react. The consumption of MDI to 60% in the reactions with TMP is achieved after only 5–27 min.

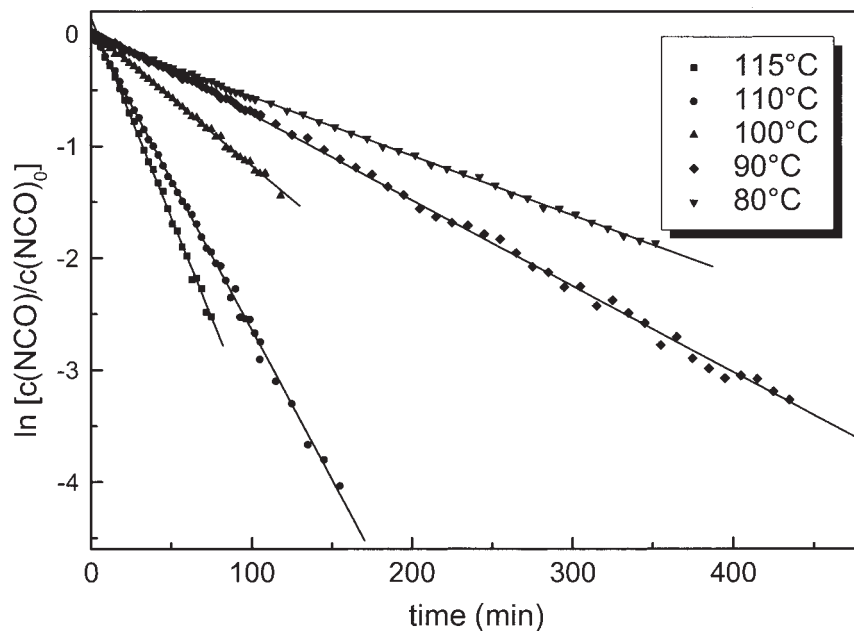


Figure 4 Logarithms of the TMXDI concentrations.

TABLE I
Kinetic Parameters for the Reactions of TMXDI and the Alcohols

Alcohol	ppa	Temperature (°C)	$k \times 10^5$ ($\text{kg mol}^{-1} \text{s}^{-1}$)	E_a (kJ/mol)	$\ln k_\infty$
TMP	70	115	4.11	63	9.46
		110	3.10		
		100	1.39		
		90	0.89		
		80	0.61		
msTMP	70	115	2.61	59	7.59
		115	2.29		
		110	2.11		
		110	1.66		
		105	1.45		
		105	1.32		
		100	1.22		

Because of the lesser solubility of msTMP, the reactions with MDI had to be carried out at considerably higher temperatures (105–115°C). The high temperatures resulted in a very high reaction rate, and so only a few data points were obtained for analysis. Consequently, the analysis of these measurements is weak. Table II shows the kinetic parameters for the experiments with MDI. Because of the insolubility of dsTMP in MIBK with 70 ppa, measurement was impossible.

In the case of 30 ppa, all three alcohols could be measured because of the raised solvent part. The reactions of TMP with MDI with 30 ppa ran only slightly slower than those with 70 ppa.

The reaction rate of msTMP with respect to MDI decreased a bit from 70 to 30 ppa. However, this decrease cannot be explained clearly by the increase in

the solvent because the reactions above 100°C at 70 ppa, as already mentioned, ran so fast that measurement inaccuracies occurred. Although the reactions of TMP with MDI were carried out in a temperature range different from that of the reactions of msTMP with MDI, it is recognized that TMP reacts faster than msTMP. Thus, the rate constant of the reaction of TMP with MDI at 30 ppa and 50°C is of the same order of magnitude as that of the reaction of msTMP and MDI at 30 ppa and 93°C.

dsTMP could be measured at higher temperatures (70–110°C) at 30 ppa. The conversions with MDI passed more slowly than those of msTMP with MDI. The rate constant of the reaction of dsTMP with MDI is clearly even smaller at 110°C than that of the reaction of msTMP with MDI at 85°C.

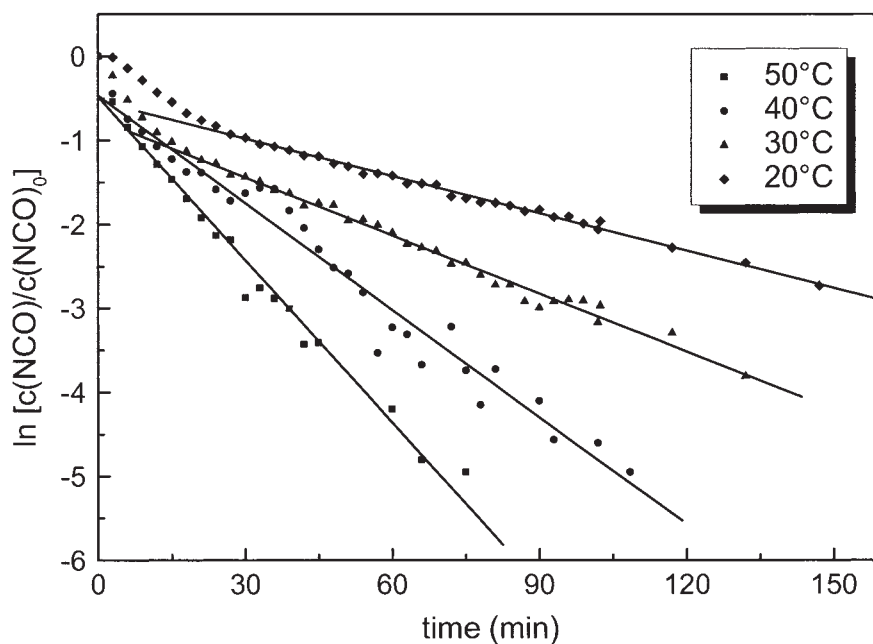


Figure 5 Logarithms of the MDI concentrations.

TABLE II
Kinetic Parameters for the Reactions of MDI and the Alcohols

Alcohol	ppa	Temperature (°C)	$k \times 10^5$ ($\text{kg mol}^{-1} \text{s}^{-1}$)	E_a (kJ/mol)	$\ln k_\infty$
TMP	70	50	28.8	44	8.17
		40	14.6		
		30	9.02		
		20	5.18		
msTMP	70	115	157	58	11.5
		110	120		
		110	124		
TMP	30	105	122	40	6.50
		50	23.2		
		40	14.3		
msTMP	30	100	33.2	38	4.43
		93	25.9		
		85	19.7		
dsTMP	30	110	18.8	44	5.27
		90	10.6		
		70	3.79		

The E_a values have been calculated from the evaluated rate constants according to eq. (5). Those calculations have also been performed for Tables I and II. The rate constants for temperature ranges that were not examined experimentally can be calculated from the evaluated rate constants. The pre-exponential factors that resulted from the linear regression of the logarithmic rate constants over the reciprocal of time are applied to temperatures of infinite values. There-

fore, the calculation of the rate constants is referred to 60°C. The rate constants have been estimated for the temperature range of 20–120°C according to the following formula:

$$k = k_{(60)} \times \exp\left[-\frac{E_a}{R}\left(\frac{1}{T} - \frac{1}{T_{(60)}}\right)\right] \quad (6)$$

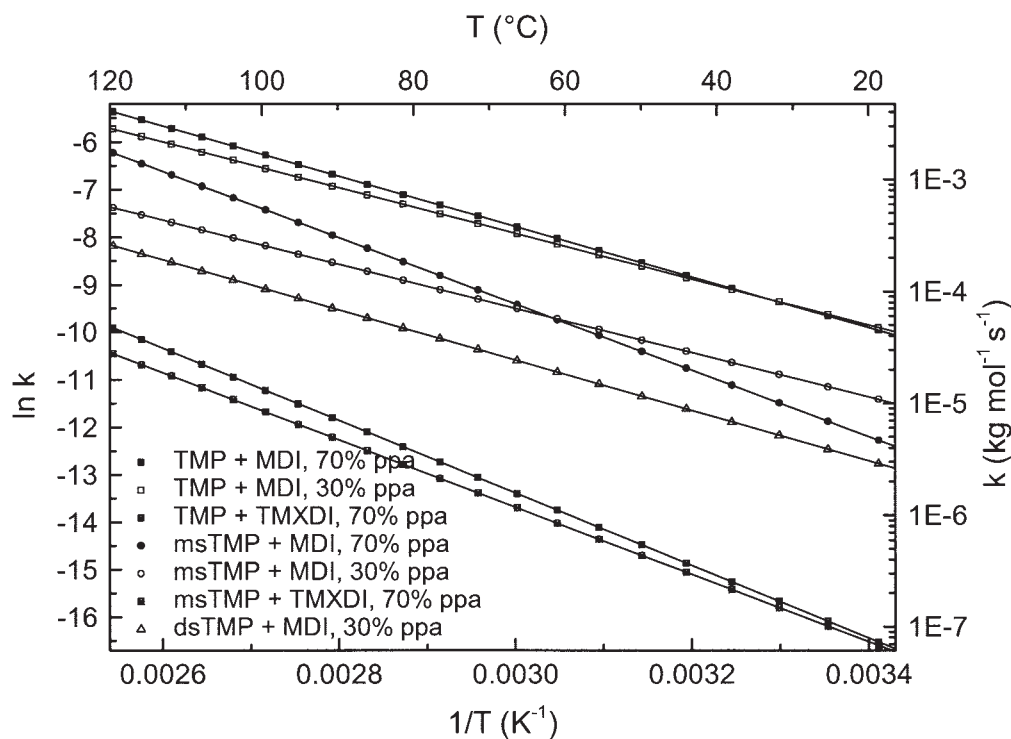


Figure 6 Calculated rate constants.

The calculated rate constants of the individual series of experiments are shown in Figure 6. The aliphatic diisocyanate TMXDI reacts considerably more slowly over the entire temperature range than aromatic MDI. The rate constant of TMP in reaction with TMXDI is, at 120°C, approximately 90 times smaller than that of TMP with MDI at the same temperature. At 20°C, the difference grows to 700 times.

For msTMP, the difference is not so striking. At both temperatures, 120 and 20°C, the reactions with TMXDI are about 70 times slower than the reactions with MDI (at 70 ppa).

Figure 6 supplies an answer to the initial question concerning the reactivity of the original equivalent hydroxyl groups modified by the addition of sterically more bulky substituents. In fact, it can be recognized that for the series of experiments at 30 ppa, the reactivity of the free hydroxyl groups decreases with the increasing addition of substituents. In this case, msTMP reacts more slowly than TMP, and dsTMP reacts again more slowly than msTMP. The two series of experiments with MDI at 70 ppa show a decrease in the reaction rate from TMP to msTMP as well.

CONCLUSIONS

An analysis of the reactivity of the primary alcohol groups of TMP in reaction with the diisocyanates MDI and TMXDI shows that substituents of the polyol influence the reactivity of its free primary hydroxyl groups. The greater the steric hindrance is for reac-

tions between free hydroxyl groups and isocyanate groups, the smaller the reaction rate is. This fact is of importance for the production of polyurethane materials because branching and crosslinking behavior can be influenced by the compositions of the monomers and functional groups. However, the influence of steric hindrance depends on the type of inserted diisocyanates. With aromatic diisocyanates, such as the very reactive MDI, steric hindrance plays a significant role, whereas reactions with aliphatic diisocyanates such as TMXDI generally run much too slowly for steric hindrance, and this greatly affects the reaction rates.

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