Selectivity of Isophorone Diisocyanate in the Urethane Reaction Influence of Temperature, Catalysis, and Reaction Partners

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In a model study of the selectivity of isophorone diisocyanate (IPDI) in the urethane reaction, the influence of the type of catalyst, temperature, and type of OH-group was demonstrated using primary and secondary butanol as reaction partners.

In particular, the choice of catalyst has a dramatic effect on the composition of the final product mixture. The most important conclusions of the model study were confirmed in NCO-prepolymer synthesis.

INTRODUCTION

Isophorone diisocyanate (IPDI) (*Figure* 1) is the leading cycloaliphatic diisocyanate worldwide for the preparation of light-stable, urethane-modified coating resins such as PU dispersions, urethane alkyds, radiation-curable urethane acrylates, and moisture-cure isocyanate prepolymers. One of the main reasons for the expanding use of this product in numerous applications, besides the very broad compatibility with co-reactants and solvents, is the unequal reactivity of the primary aliphatic and the secondary cycloaliphatic isocyanate groups of IPDI, which leads to low viscosity products with a narrow molecular weight distribution and a low free monomeric diisocyanate content.[1] This reactivity difference has been the subject of investigation in the past.[2-8] As a result of various assumptions, stoichiometry, reaction partners, experimental methods and interpretations, the reactivity difference between the NCO groups has been reported to be in the range of 0.2:1 to 12:1.

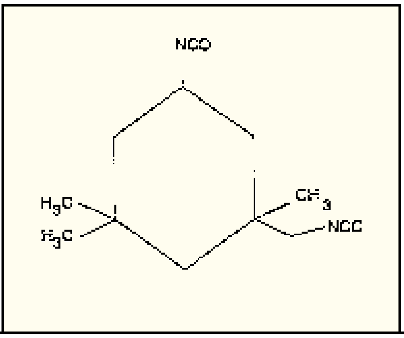

Figure 1—Isophorone diisocyanate (IPDI).

In this study the influence of various catalysts for the urethane reaction, temperature (in all previous publications a constant), steric hindrance, and/or the reactivity of alcohols on the selectivity in model reactions as well as the applicability to commercially viable systems were investigated.

Corresponding to the possible orientations of the substituents of the cyclohexane ring, IPDI is differentiated between *cis*- (Z) and *trans*- (E) isomers. Commercially available IPDI represents an isomer mixture of approximately 75:25 in favor of the cis- (Z) isomer (*Figure* 2).[9]

The reaction of IPDI with alcohols may be completely described with four rate constants (K_1-K_4), corresponding to the two unequal NCO groups (prim/sec) for each of the two IPDI isomers. In total, eight rate constants and eight products have to be considered (*Figure* 3). This very complex system can be treated with some clearly evident simplifications with regard to the reaction rates:

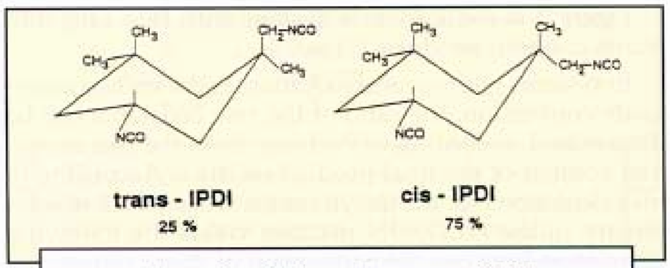

Figure 2—Cis/trans-Isomers of IPDI.

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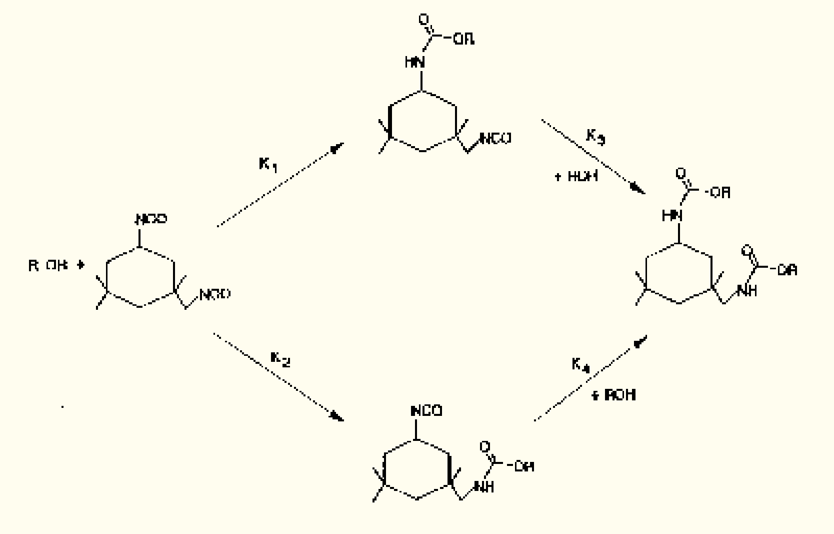

Figure 3—Rate constants for the reaction of IPDI with alcohols.

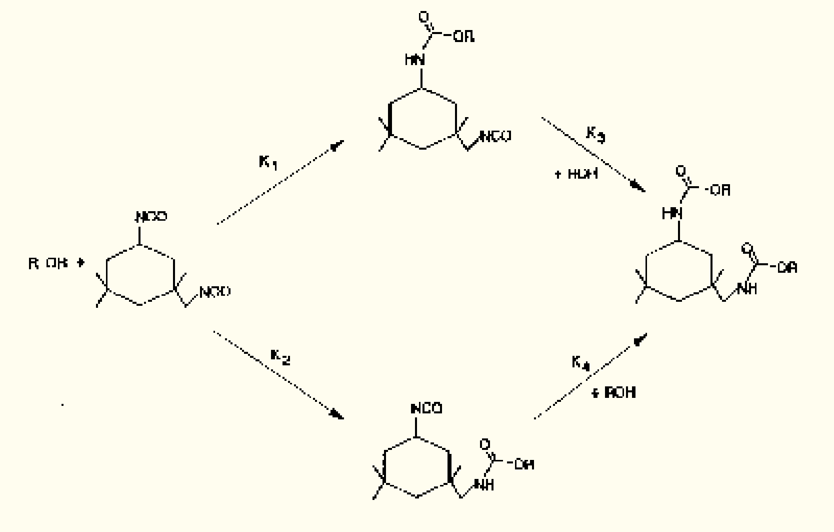

Figure 4—Simplified kinetic model for urethane reaction of IPDI (K(cis) = K(trans)).

Assume that: (a) the urethane functionality of a monourethane monisocyanate exhibits neither a catalytic or inhibitive influence on the reactivity of the remaining isocyanate group; and (b) a comparable reactivity of *cis*- and *trans*-IPDI.

Figure 3 is reduced to a system with two rate constants and four products (*Figure* 4).

In systems with excess isocyanate and a known isocyanate conversion, the ratio of the rate constants can be determined, according to Peebles,[1] from the free monomer content of the final product mixture. According to his calculations for the unsymmetrical case, a 2:1 stoichiometry of the NCO/OH reaction yields the following correlation between the conversion of diisocyanate and the quotient Γ of the rate constants K_1 and K_2 (*Figure* 5).

EXPERIMENTAL

Model reactions were carried out without solvent in a stirring apparatus under nitrogen at a constant temperature. Vestanat® IPDI (Hüls AG) and catalyst were charged and alcohol added dropwise over a five-hour period. Stoichiometry was NCO:OH=2:1. Reactions were run until the conversion was complete. Determination of the monomer content was performed by GC using tetradecane as the standard. In the case of reactions with 1-butanol, these GC-techniques permitted the resolution of the four monourethanes of IPDI and 1-butanol. Both 1-butanol and 2-butanol contained < 0.2% water, polyols <0.5% water as determined by Karl Fischer methods. Tertiary amine catalysts were supplied by Aldrich; DBTL (dibutyltindilaurate) by Elf-Atochem; zinc octoate (bis (2-ethylhexoyl) zinc) dissolved in mineral spirits: aromatics at 80:20 at a zinc level of 8% by Borchers; Iron(III)acetylacetonate(FeAcAc) by Hüls AG; and a bismuth catalyst (16% Bi) Coscat 83 by Caschem.

RESULTS AND DISCUSSION

Selectivity of IPDI by Application of Various Urethane Catalysts

Metal catalysts (Lewis acids) as well as tertiary amine types (Lewis bases) are well known in urethane chemistry. *Table* 1 shows the results of the IPDI/1-butanol reaction at an NCO:OH stoichiometry of 2:1 and a temperature of 20°C. Sn, Zn, Fe, and Bi catalysts were used at constant metal atom/ion concentration as well as four tertiary amine catalysts (Diazabicyclo[2.2.2]octane (DABCO), 1.8-Diazabicyclo-[5.4.0]-undec–7-ene (DBU), N,N-Dimethylcyclohexylamine (DMCA) and 1,5-Diazabi-cyclo[2.3.0]non-5-ene (DBN) at typical concentrations for IPDI systems (0.4%, except DBU: 0.2%). The uncatalyzed system is shown for reference (*Table* 1).

Besides the generally clear effect of catalysis, a differentiation in the effectiveness of the catalysts was recognized. With the exception of the Zn catalyzed systems, metal catalysis was found to be essentially more effective than that of the tertiary amines. Surprising, however, was the selectivity with the catalyst types utilized. DBTL is the most selective catalyst in this study, increasing Γ to 11.5 compared to 5.5 for the uncatalyzed system. In the case of the tertiary amines, DABCO led to an inversion of the selectivity, while all other tertiary amines showed no significant influence.

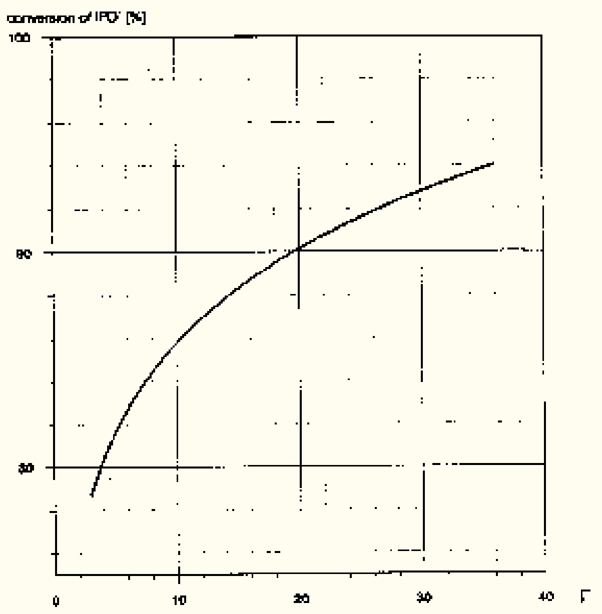

Figure 5—Relation between ratio of rate constants (Γ) and conversion of IPDI monomer (NCO:OH = 2:1).

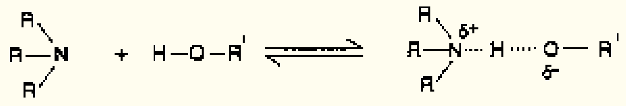

Figure 8—Lewis-base catalyst in urethane reaction.

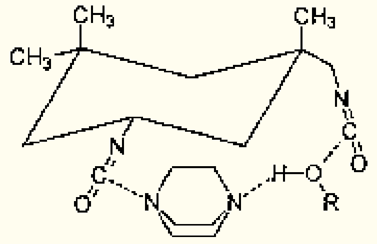

Figure 9—Possible mechanism for DABCO catalysis.

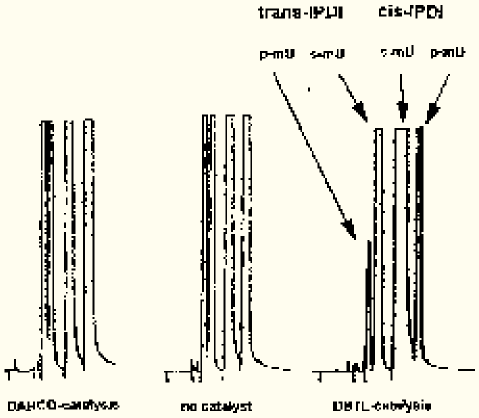

Figure 6—GC-chromatographs of the IPDI-1-butanol reaction: section of the mono-urethanes. (S-M-U = sec. NCO reacted, p - mu = prim. NCO reacted).

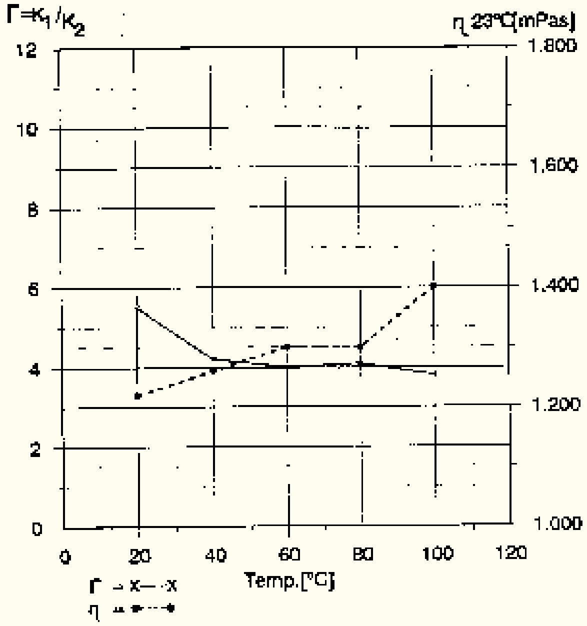

Figure 10—Urethane reaction of IPDI and 1-butanol, uncatalyzed (NCO:OH - 2:1). Selectivity of IPDI and viscosity of final products.

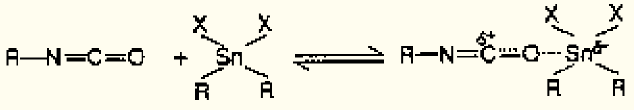

Figure 7—Lewis-acid catalyst (DBTL) in urethane reaction.

Table 1—Influence of Catalysts on Urethane Reaction of IPDI with 1-butanol

Catalyst	$T = K_1/K_2$	Time of Complete Conversion
none	5.5	8 d
DBTL (0.075%)	11.5	6 h
Zn-Octoate (0.42%)	7	1 d X_1
Bi-Cat. (0.135%)	2.5	6 h
Fe III AcAc (0.042%)	5.5	6 h
DABCO (0.4%)	0.18	1 d X_1
DBU (0.2%)	5.5	1 d X_1
DMCA (0.4%)	4.4	1 d X_1
DBN (0.4%)	6.2	3 d

X_1: > 6h, < 24h
Conditions: NCO:OH - 2:1; 20°C (68°F).

The clear increase of the selectivity by DBTL catalysis was also described by Hatada and Pappas.[3] They determined with ^1H and ^{13}C NMR techniques, that with DBTL catalysis, the secondary cycloaliphatic isocyanate group is without a doubt the more reactive. Apparently the primary isocyanatomethyl group is effectively shielded by the β-situated methyl substituents, the cyclohexane ring, and its neighboring methyl group.

Furthermore, Hatada and Pappas described the inversion of the selectivity by DABCO. *Figure* 6 shows the section of the gas chromatograph in the important area of monourethane for the uncatalyzed, DBTL, and DABCO catalyzed reactions. This clearly illustrates the increases as well as the inversion of the selectivity of IPDI, and confirms the results of Hatada and Pappas.

The reason for the increase in selectivity by metal catalysis can be approached by examining the mechanism of these catalysts: metals work as Lewis acids and activate the isocyanate group by a coordination of the carboxyl group.[10-13] The additional space demand of the activated transition state may be responsible for the preferential catalysis of the already more reactive and sterically less hindered cycloaliphatic NCO group (*Figure* 7).

Table 2—IPDI-Prepolymers Based on Various Polyols

	Prepolymer			
	A	B	C	D
Basis	Polyester	p-THF	PPG	Polycaprolactone
MW of polyol	1000	1000	1000	540
Functionality	2	2	2	3
Solids content (%)	100	100	100	75 (Mop-acetate)

Tertiary amines catalyze the urethane reaction mainly through activation of the OH-group of the alcohol,[11,13] but also an activation of the NCO groups has been discussed. By the activation of the OH-groups, the activated transition state requires less space than is the case with metal catalysts. This could be the reason for the absence of additional selectivity of amine catalysts. With the exception of DABCO, the tertiary amines showed no significant effect on the selectivity of IPDI. Interestingly, DABCO resulted in an inversion of selectivity causing the primary isocyanate group to become the more active (*Figure* 8). One explanation could be that the remaining free tertiary amine function of the DABCO-1-butanol complex is precoordinated by the secondary, more reactive isocyanate group. Via arrangement to an intramolecular macrocyclus (14-membered), the activated hydroxyl group could be directed to the primary NCO-group. *Figure* 9 illustrates a possible mechanism for DABCO catalysis.

Influence of Temperature on the Selectivity of IPDI

Studies of the selectivity of IPDI which have been published deal with temperature as a constant. To serve as examples of the effects of temperature, the uncatalyzed and, on the basis of its unusual effectively, DBTL catalysis were studied to determine the dependence of selectivity in the range of 20-100°C. The viscosity of the products was regarded as a further system parameter.

Figure 10 shows the course of Γ and the viscosity of the uncatalyzed urethane reaction of IPDI and n-butanol in the temperature range of 20-100°C (NCO:OH = 2:1). As expected, the selectivity varied inversely with increasing temperature going from 5.5 (20°C) to 3.9 (100°C). The lower selectivity led to an increasing proportion of bisurethanes and a corresponding increase in viscosity. In the case of uncatalyzed resin synthesis, the temperature range of 60-80°C appears to be optimal for viscosity and economic considerations (approximately eight days at 20°C versus six hours at 80°C for complete conversion).

Figure 11 clearly shows that DBTL catalyzed reactions have higher selectivity and exhibit a greater dependence on temperature compared to uncatalyzed reactions. Nevertheless, the selectivity at 100°C is greater than that of the uncatalyzed reaction at 20°C. Interestingly, the viscosity of

Table 3—Results of Prepolymer Synthesis at Different Temperatures (NCO:OH = 2:1, DBTL - Catalyst - 0.075%)

	Prepolymer							
	A		B		C		D	
T (°C)	η 23°C (Pas)	monom. IPDI (%)	η 23°C (Pas)	monom. IPDI (%)	η 23°C (Pas)	monom. IPDI (%)	η 23°C (Pas)	monom. IPDI (%)
20	206	3.9	16.7	4.3	12.2	3.2	3.4	4.8
40	216	4.0	18.7	4.4	12.5	3.3	4.2	5.0
60	219	4.1	19.1	4.4	13.0	3.6	4.2	5.2
100	264	4.3	22.8	4.5	16.0	3.7	4.3	6.5
80, no catalyst	284	6.3	27.2	6.0	15.0	5.7	5.6	8.8

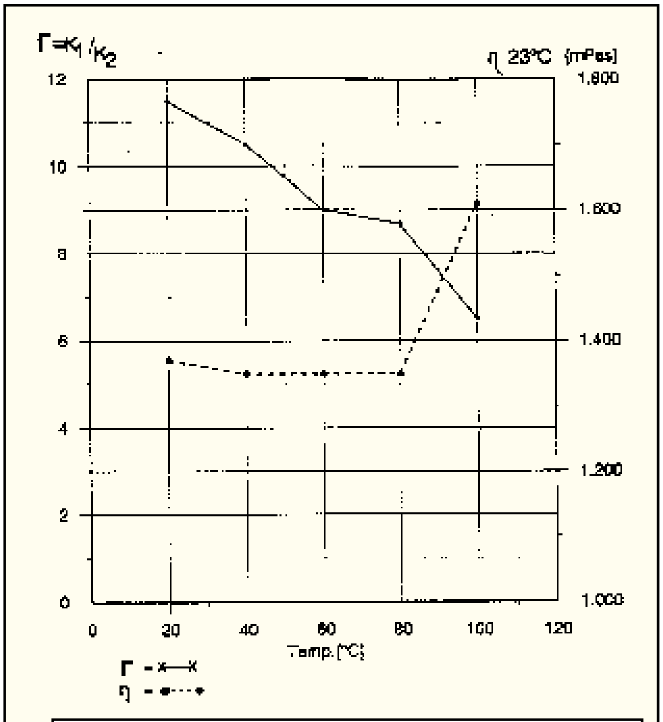

Figure 11—Urethane reaction of IPDI and 1-butanol using DBTL catalyst (0.075%) (NCO:OH = 2:1). Selectivity of IPDI and viscosity of final products.

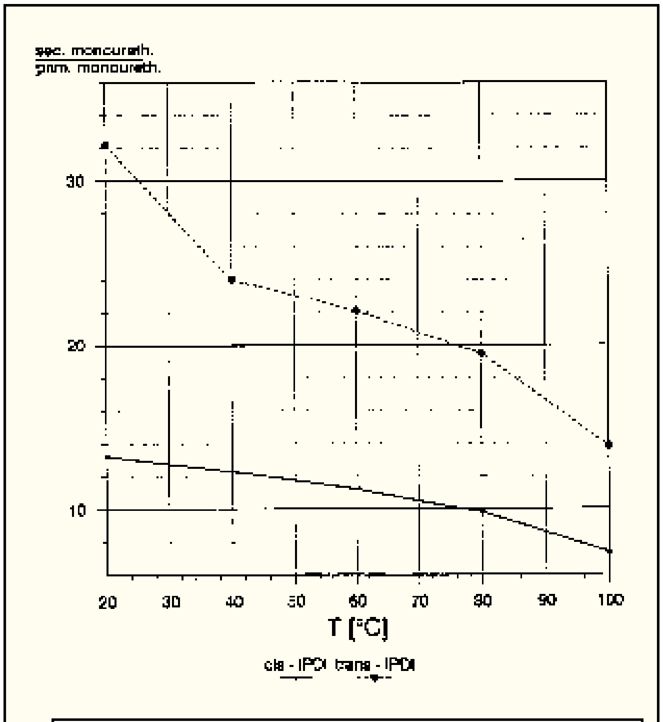

Figure 13—Ratio of sec. and prim. monourethanes of *cis*- and *trans*-IPDI in urethane reaction with 1-butanol (0.075% DBTL catalyst).

the product mixture remains nearly constant up to 80°C. As in the uncatalyzed case, we would expect the viscosity to increase with decreasing selectivity due to the higher concentration of bisurethane. Obviously, in this range of product composition of monomer, monourethane, and bisurethane, the viscosity-increasing effect of higher amounts of bisurethane is compensated by the viscosity-decreasing effect of a higher IPDI monomer concentration. Surprising is the dramatic viscosity increase observed between 80°C and 100°C. SFC methods confirm two percent of a high molecular weight component in the 100°C reaction mixture, which can either be interpreted as allophonate from bisurethane or monourethane of IPDI (*Figure* 12).

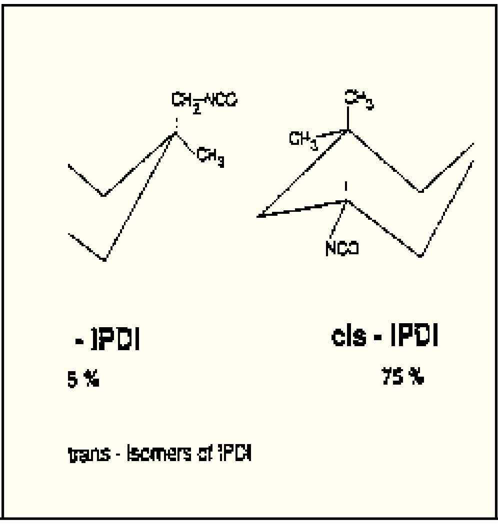

Figure 12—SFC chromatograph of DBTL catalysis at 100°C.

On the basis of by-products as well as the very specific selectivity apparent of DBTL catalysis in the range of 40-60°C, technical IPDI urethane reactions in this temperature range are most practical and are preferred over uncatalyzed versions.

By using GC techniques to separate the four monourethanes, it is possible to demonstrate the selectivity of *cis*- and *trans*-IPDI as a function of the temperature of the DBTL catalyzed reaction of IPDI and 1-butanol. *Figure* 12 shows the selectivity of *cis*- and *trans*-IPDI expressed as the ratio of secondary and primary monourethanes. In accord with expectations, both isomers display declining selectivity with increasing temperature. The *trans*-isomer exhibits a clearly higher selectivity (factor approx. 2 at 40-100°C) and shows a stronger temperature dependence. The more pronounced reactivity difference of the NCO groups of the *trans*-isomer could be explained by a more efficient shielding of the primary NCO function by the cyclohexane ring and its substituents. According to Wendisch et al,[14] the cycloaliphatic group is found to prefer an equatorial position. Resulting from that, the isocyanatomethyl group of the *trans*-isomer is in an axial position and, therefore, sterically more efficiently shielded than the equatorial pendant group of *cis*–IPDI (see *Figure* 2).

An effect which also has to be attributed to the more shielded and less reactive primary group of the *trans*-

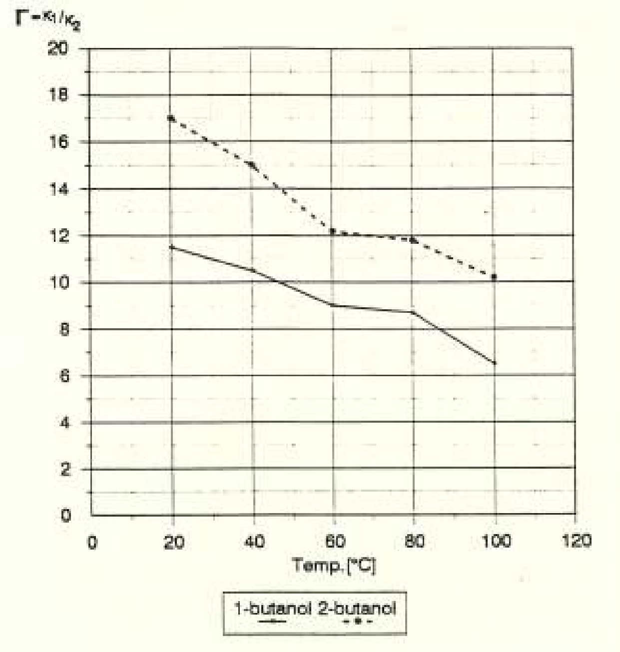

Figure 14—Selectivity of IPDI in urethane reactions with (a) 1-butanol, (b) 2-butanol. (NCO:OH = 2:1, DBTL - catalyst = 0.075%).

isomers of isophorone derivatives has recently been reported in the field of epoxy-systems: more trans-IPD (isophorone diamine) led to a longer pot life in two-pack epoxy formulations.[15]

Additional Steric Hindrance: 2-butanol

Isocyanate prepolymers for the elastomer market are often based on polypropylene glycols, having predominantly secondary OH groups. Therefore, it was of interest to further expand the study of selectivity to the more sterically hindered and less reactive 2-butanol. In *Figure* 14, the temperature dependence of the reaction of IPDI with 1- and 2-butanol under DBTL catalysis are compared.

Presumably as a result of the additional space demand by the use of 2-butanol, the selectivity of IPDI is further increased. The ratio of the rate constants at 20°C is 17, compared to the reaction with 1-butanol, which ranges from 11.5 (DBTL) to 5.5 (uncatalyzed). The conversion at 80°C with 2-butanol is even more selective than that with 1-butanol at 20°C. Both curves are seen to run in parallel, meaning that the dependence of selectivity on temperature is similar.

The selected gas chromatographic conditions used in this study did not allow separation of the monourethanes of *trans*-IPDI and 2-butanol. By reaction with 2-butanol, the selectivity of the *cis*-isomer is increased to the level of the *trans*-isomer when reacted with 1-butanol (secondary monourethane/primary monourethane = 30.1/1 at 20°C).

Back to the Practical: NCO Prepolymers

IPDI prepolymers for moisture curing coating systems are normally produced from 2-3 functional, hydroxyl-bearing polymers with molecular weights in the range of 500 to about 3000, using a stoichiometry of NCO:OH of 1.8:1 to 2.0:1. In order to demonstrate the applicability of the model system results using 1- and 2-butanol, IPDI was reacted with four different polyols in a stoichiometric ratio of NCO:OH of 2:1. The polyols chosen were linear NPG (neopentyl glycol), adipate, poly(tetramethylene glycol)ether, poly(propylene glycol)ether of molecular weight approximately and a trifunctional polycaprolactone, MW 540, the last of which was used as a 75% solution in 1-methoxypropyl-2-acetate (MOP acetate) (*Table* 2).

Table 3 summarizes the results of the prepolymer synthesis, both DBTL catalyzed at various temperatures, as well as uncatalyzed at 80°C. The results of the model studies were closely approximated: using DBTL, viscosity and monomer content increased only slightly with increasing temperature (20-60°C), while the uncatalyzed reaction carried out at 80°C led to the highest viscosity and monomer content. The somewhat surprising low viscosity of the PPG-based system produced at 80°C with no catalyst (15 Pa·s) could be traced back to the thermal degradation of the comparably weak backbone polyol. This significant viscosity increase of the catalyzed variants observed at 100°C compared to that at 60°C also paralleled the model studies and could be attributable to the formulation of allophonates.

A significant deviation from the model study was observed for the catalyzed variants at 100°C. There was only a slight increase in the monomer content (prepolymers A-C) compared to 60°C. This result is illustrated in *Table* 4 through the contrast of Γ of the model and prepolymer systems indicating that IPDI is more selective in prepolymer synthesis. Due to the higher viscosities of the prepolymers compared to the model systems, the diffusion of IPDI monomer could be

Table 4—Ratio of Rate Constants (Γ) Derived from Prepolymer Synthesis (A-D) and Model Reactions (1-butanol, 2-butanol)

	Γ					
T (°C)	**1-butanol**	**A**	**B**	**D**	**2-butanol**	**C**
20, DBTL	11.5	11.5	10.2	14.5	17.0	16.5
40, DBTL	10.5	10.9	9.5	12.9	15.0	15.7
60, DBTL	9.0	10.5	9.5	12.0	12.2	12.6
100, DBTL	6.5	9.3	9.3	7.2	10.1	12.0
80, no catalyst	4.1	3.6	4.3	3.2	3.3	4.3

more hindered, meaning that significant allophonate formation as a competing reaction must be considered. This fact lead to a lower monomer content of the final product and could be misinterpreted as a higher selectivity. This interpretation is confirmed by the result of the low viscosity 75% prepolymer solution (System D), in which a jump in monomer content was observed at 100°C.

In principle, the comparison of Γ in prepolymer syntheses with model reactions (*Table* 4) demonstrates a very good correlation: not only for the absolute values of Γ for both the primary OH/IPDI reaction (1-butanol and systems, A, B, D) and the secondary OH/IPDI reaction (2-butanol and system C), but also the temperature dependence up to 60°C and the influence of DBTL catalyst on viscosity and monomer content.

In general, these studies confirm the proven practice of carrying out IPDI prepolymer syntheses in the temperature range of 40-60°C with the use of DBTL catalysis, from viscosity and monomer content as well as economical considerations.

SUMMARY

The selectivity of isophorone diisocyanate (IPDI) in the urethane reaction demonstrates a strong dependence on temperature, catalyst type, and degree of substitution of the reaction partner.

The model study of IPDI selectivity was carried out using primary and secondary butanol as reaction partners. The influence of a series of metal catalysts (Sn, Zn, Bi, and Fe) and tertiary amines was investigated. All catalysts accelerated the urethane reaction compared to the uncatalyzed version. In principle, the use of metal catalysts resulted in an improvement of selectivity of IPDI, with DBTL as the most selective catalyst. In a series of tertiary amine catalysts, only DABCO led to an inversion of selectivity. Other tertiary amines had no significant influence.

The phenomenon of decreasing selectivity with increasing temperature was generally confirmed. Surprising, however, catalysis of IPDI with DBTL promoted a higher degree of selectivity, even at elevated temperatures, than could be achieved without catalyst at low temperatures.

Two additional factors influencing selectivity were identified. Secondary butanol yielded a higher selectivity than primary butanol, demonstrating the effect of the degree of substitution of the reaction partner. In addition, *trans*-IPDI was found to be more selective than *cis*-IPDI.

A very good correlation between prepolymer synthesis and the model reaction was observed. Recommended optimal conditions for prepolymer synthesis based on IPDI are temperatures between 40 and 60°C using DBTL catalysis.

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