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

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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. This reactivity difference has been the subject of investigation in the past. 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.

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.

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.

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).

The reaction of IPDI with alcohols may be completely described with four rate constants (K1-K4), 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 1—Isophorone diisocyanate (IPDI).](image1)

![Figure 2—Cis/trans-isomers of IPDI.](image2)
Assume that: (a) the urethane functionality of a monourethane monosoyanate exhibits neither a catalytic nor 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 Peabies, 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 disocyanate and the quotient $\Gamma$ 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 catalysts 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)acetylactonate (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 $\Gamma$ 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.