

Imidazole Catalysis in Carbamate and Polyurethane Formation

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Synopsis

Polyurethanes have been prepared from the reactions of the diimidazole and ditiatriazole adducts of 2,4-toluene diisocyanate and ethylene glycol or polyols. Suitable formulations have been developed from these components which are useful in preparing polyurethane coatings and foams. Imidazole was established as an effective catalyst for the reactions of the diphenol adduct of 2,4-toluene diisocyanate with polyols. Imidazole-catalyzed polyurethane formation from the phenol-blocked diisocyanate occurs readily between 100° and 140°C. A mechanism for the catalytic activity of imidazole in these reactions is proposed.

INTRODUCTION

Although azoles form solid derivatives (azolides) with isocyanates¹ and their use to "mask" or mediate the reactivity of this functional group has been documented,² their use with diisocyanates for polymer preparation has not been reported. In addition, while azoles have been employed as catalysts in carbamate³ and polyurethane⁴ formation from aromatic isocyanates and alcohols or polyols, little is known concerning the catalytic effect of azoles on these reactions using "blocked" aryl isocyanates (i.e., phenyl N-arylcarbamates). We now describe the results of our investigation of polyurethane formation from the reactions of azole adducts of 2,4-toluene diisocyanate with polyols as well as azole catalysis in the reactions of polyols with the diphenol adduct of 2,4-toluene diisocyanate.

EXPERIMENTAL

Melting points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 337 Infracord. Mass spectra were recorded on a CEC Model 21-104.

Preparation of Intermediates

Diimidazole Adduct of 2,4-Toluene Diisocyanate. Imidazole (6.80 g, 0.1 mole) was dissolved in 550 ml of refluxing benzene in a 1-liter flask.

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About 50 ml of benzene was distilled out to remove water and a dry condenser was set for reflux. Toluene 2,4-diisocyanate (8.70 g, 0.05 mole) was added dropwise over 30 min at which time a white precipitate was present. After an additional 15 min of heating, the mixture was filtered while hot and the filter cake washed with hot benzene. The product was dried under a 20-mm vacuum for 48 hr to give 14.60 g, 94%, of title compound, mp 155–157°C, infrared (KBr) 1740 cm^{-1} . The mass spectrogram did not exhibit a molecular ion but rather the ions of the individual reactants, m/e 174 and 68.

ANAL. Calcd. for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_2$: C, 58.06%; H, 4.55%; N, 27.09%. Found C, 58.2%, H, 4.65%; N, 27.5%.

The same reaction was run using commercial toluene diisocyanate in 10% excess (80:20 mixture of the 2,4- and the 2,6-isomers) to give essentially a quantitative yield of a tan solid, mp 76–94°C with foaming.

Ditriazole Adduct of 2,4-Toluene Diisocyanate. This was prepared on the same scale as for the diimidazole adduct. The product was obtained in 95% yield and had mp 207–208°C. The mass spectrogram exhibited only the ions of the reactants, m/e 174 and 69.

ANAL: Calcd for $\text{C}_{13}\text{H}_{12}\text{N}_6\text{O}_2$: C, 49.67%; H, 3.87%; N, 35.88%. Found: C, 49.7%; H, 3.87%; N, 37.5%.

Diphenol Adduct of Toluene 2,4-Diisocyanate.⁵ A solution made from toluene 2,4-diisocyanate (17.4 g, 0.1 mole), six drops of pyridine, and 80 ml of benzene was placed in a flask, and to it was added rapidly a solution of phenol (18.8 g, 0.2 mole) in 20 ml of benzene. The reaction was heated at 65°C overnight, cooled, and the crystals that deposited were collected and dried to give the title compound, 22 g (60%).

Reactions of Azolides

Ethyl 2,4-N-Tolyldicarbamate. A solution of the diimidazole adduct of toluene 2,4-diisocyanate (3.10 g, 0.01 mole) in 50 ml of ethyl alcohol was heated at reflux for 12 hr. The solvent was removed under vacuum and the solid residue was recrystallized from ethyl alcohol–water to give the title compound as fine white needles, 2.01 g, 75%, mp 133–135°C, lit.⁶ mp 136°C.

The same reaction was run using 0.01 mole of the ditriazole adduct of toluene 2,4-diisocyanate in 50 ml of refluxing ethyl alcohol for 16 hr to give an 82% yield of title compound, mp 133–136°C.

Polyurethane Formation with Ethylene Glycol. The diimidazole adduct of toluene 2,4-diisocyanate (3.1 g, 0.01 mole) was blended with ethylene glycol (0.62 g, 0.01 mole). The free-flowing solid was heated to 100°C where a volume reduction occurred. The mixture was heated at 125°C for 2 hr, and the resultant clear oil was cooled, dissolved in dimethyl sulfide, and the polymer precipitated by addition to water. The white granular polyurethane isolated weighed 2.1 g.

Polyurethane Coating with a Polyol. The diimidazole adduct of toluene 2,4-diisocyanate (3.10 g, 0.02 NCO equivalent) was added to a benzene

solution of a polyol (2.36 g, 0.02 hydroxy equivalent). The adduct was not soluble in the benzene at ambient temperature. The benzene was removed on a rotary evaporator to give a thick white slurry. Some of this was spread on a glass plate and heated on a hot plate for a brief period. A white, hard, polymeric coating resulted. The remainder of the slurry retained its consistency for at least several weeks at ambient temperature and did not gel.

Polyurethane Foam Formation. The diimidazole adduct of commercial toluene 2,4-diisocyanate (1.78 g) and a commercial polyol-Freon mixture (1.0 g) was blended together to give a thick paste. (The manufacturer of this mixture recommends 1:1 by weight of toluene diisocyanate:polyol-Freon. The ratio of the diimidazole adduct of toluene diisocyanate to toluene diisocyanate is 1.78.) A portion of this was placed in the bottom of a test tube and heated with hot air to give a spongy foam. The tube was heated at 105°C overnight in forced-air oven. On cooling, a fairly rigid foam remained.

Imidazole Catalysis

Ethyl N-Phenylcarbamate. A solution of phenyl N-phenylcarbamate (0.39 g, 1.4 mmole) and imidazole (0.039 g, 0.6 mmole) in 2 ml of absolute alcohol was heated under reflux for 5 hr. Analysis of the reaction mixture by thin-layer chromatography and gas-liquid chromatography indicated an 80% yield. The major product was trapped from the GLC and identified as the title compound by comparison of its infrared spectrum with a published one.⁷

A solution of phenyl N-phenylcarbamate (0.4 g, 1.4 mmole) in 4 ml of ethyl alcohol was heated under reflux for 17 hr. TLC of the solution indicated that ca. 50% of title compound had been formed.

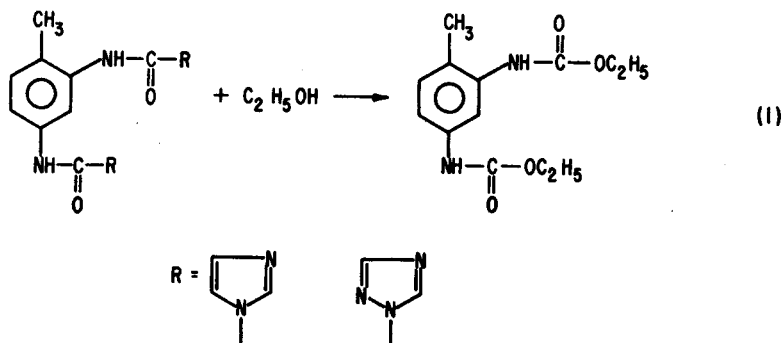
Polyurethane Film Formation. A mixture was made from the diphenol adduct of toluene 2,4-diisocyanate (3.62 g, 0.02 equivalent), a polyol (2.8 g, 0.02 equivalent), and 10 g of cresylic acid as a solvent. A portion of this mixture was treated with 5% imidazole (based on the diisocyanate adduct). Both the imidazole portion and the original formulation were placed in aluminum boats and heated at 115°C at 25 mm for 2 hr. The resultant films were submerged in 2 ml of a 7:3 mixture of ethyl alcohol:toluene for 10 min at ambient temperature. The film from the control completely dissolved, whereas the film from the imidazole portion did not dissolve but became tacky.

Polyol-Isocyanate Gel Times With and Without Imidazole. A commercial prepolymer (made from a polyol and the diphenol adduct of toluene 2,4-diisocyanate so that not all the blocked isocyanate groups reacted; 100 g, NCO content 5.5% by weight) was mixed with a polyol (15.5 g, 118 eq wt/OH unit). Portions were tested for gel time by placing 0.5 g in a 4-in. test tube and immersing in an oil bath at 100° and 145°C. The gel point was taken as that point where the mass did not move when the tube was taken from the bath and quickly inverted. A 0.5-g sample of the mixture gelled in 22.25 hr at 100°C and in 90 min at 145°C, while a

0.5-g sample of the mixture containing 4 mg of imidazole gelled in 6 hr at 100°C and in 25 min at 145°C.

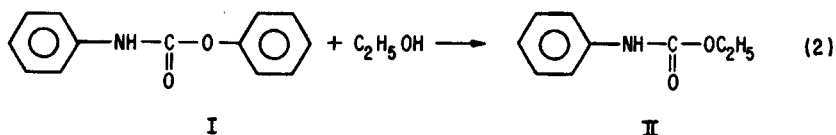
RESULTS AND DISCUSSION

The diimidazole and ditriazole adducts of 2,4-toluene diisocyanate were prepared and heated with ethyl alcohol as a model for the polyurethane reaction. Both adducts were found to convert easily to ethyl 2,4-toluene dicarbamate, eq. (1):



The reaction of the diimidazole adduct with ethylene glycol or with a polyol gave polymer. A slurry of the imidazole adduct and a polyol was stable for several weeks at ambient temperature and would give polymer by simply heating. A mixture of the diimidazole adduct of commercial toluene diisocyanate, a polyol, and Freon gave a foam on heating. However, the heterogeneity of these mixtures made them inconvenient to work with, and, in addition, any polymer made from them contained a stoichiometric amount of entrapped imidazole.

As an alternative approach, we turned our attention to a study of the catalytic effect of imidazole on the unblocking reaction of phenol-blocked isocyanates. The isocyanate can be regenerated by heating the phenol adduct above 140°C, and this can be utilized to prepare a one-component urethane system stable at ambient temperature which will produce polymer on heating.⁸ We have found that phenyl N-phenylcarbamate (I) can be converted to ethyl N-phenylcarbamate (II) in refluxing ethyl alcohol:



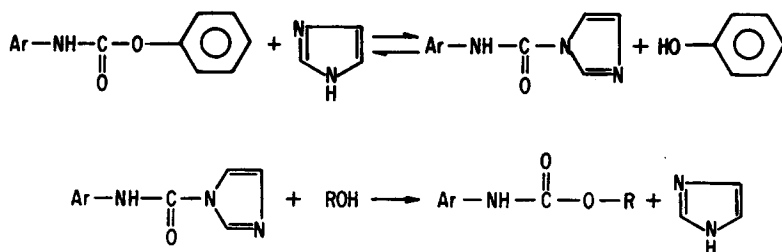
With imidazole present, the reaction proceeded faster and in better yield than without imidazole. The diphenol adduct of toluene diisocyanate reacted with a polyol at 115°C in the presence of 5% imidazole to give a polymeric film not soluble in ethyl alcohol-toluene, whereas the same reaction without imidazole gave a completely soluble film. The gel time of a

commercial prepolymer containing 5.5% of NCO content as the phenol adduct when reacted with a polyol occurred 3.8 times as fast at 100°C and 3.6 times as fast at 145°C with 10% imidazole present (relative to the NCO content) than without imidazole.

Thus, imidazole will catalyze the reaction of a phenol-blocked isocyanate with an alcohol and allow for faster cure times and lower curing temperatures with the appropriate polymeric systems.

A possible mechanism for the effect of imidazole is outlined in scheme I:

SCHEME I



R = ALKYL

A similar mechanism involving imidazole has been proposed for acyl transfer, and an explanation for the unique role of imidazole was given.⁹ We were unable to demonstrate the reversibility of the last (product-forming) step when the reaction of ethyl N-phenylcarbamate (II) in refluxing isobutyl alcohol containing a trace of imidazole failed to exchange the ethyl group.

Previous difficulty in the exchange reaction of isobutyl alcohol with ethyl N-phenylcarbamate under acid conditions has been reported by Gaylord and Sroog.¹⁰

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