

Catalytic Effects of 1,1,3,3-Tetramethylguanidine for Isocyanate Reactions

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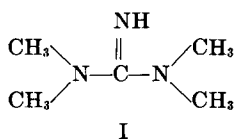
Synopsis

1,1,3,3-Tetramethylguanidine was found to be a more effective catalyst than triethylamine or 1,1,3,3-tetramethyl-1,4-butanediamine and poorer than diazobicyclooctane for the reaction of phenyl isocyanate with 2-ethylhexanol. Similar catalysis was found for the phenyl isocyanate-water reaction. It is postulated that the actual catalyst is the reaction product between 1,1,3,3-tetramethylguanidine and phenyl isocyanate, 1-phenyl-3-[bis(*N,N*-dimethylamino)methylene]urea.

INTRODUCTION

The kinetics of the reaction between an isocyanate group and a hydroxyl group in the presence of a variety of nitrogenous catalysts has been studied by several authors.¹⁻⁸ In most cases these catalysts have been tertiary amines. The role of isobiguanide catalysts has been reported previously by these laboratories.⁹ This paper reports the effectiveness of one member of another class of nitrogenous compounds, guanidines, in catalyzing the isocyanate reaction with 2-ethylhexanol and water.

1,1,3,3-Tetramethylguanidine (TMG) (I)



was chosen for study because of its commercial availability (American Cyanamid Company, Wayne, New Jersey) and also because it was of interest to investigate what effect that reactive hydrogen might have on the course of the catalysis reaction.

EXPERIMENTAL

Materials

Tetramethylguanidine (American Cyanamid Company), 1,4-diazo[2,2,2]bicyclooctane (Houdry Process Corp.), phenyl isocyanate (Eastman Kodak Co.) and *N,N,N',N'*-tetramethyl-1,4,-butanediamine (Ames

Laboratory, Inc.) were used as received. Triethylamine (Union Carbide and Carbon Corp.) was stored over potassium hydroxide and freshly distilled prior to use. 1,4-Dioxane (Union Carbide and Carbon Corp.) was refluxed overnight in the presence of sodium and distilled from sodium prior to use. Benzene (J. T. Baker Chemical Co., Reagent Grade) was distilled from calcium hydride. 2-Ethylhexanol (Union Carbide and Carbon Corp.) was distilled from sodium.

Procedure

Reaction mixtures were prepared in volumetric flasks by adding a small amount of the solvent, phenyl isocyanate solution, alcohol or water solution, catalyst solution and making up to the mark with additional solvent. Dioxane was used as the solvent for the water reaction and benzene for the 2-ethylhexanol reaction.

The reaction flasks were stoppered with rubber caps, thermostated at 26.0°C., and samples withdrawn periodically with a hypodermic syringe.

The reaction was followed by measuring the rate of decrease of the isocyanate peak in the 4.5 μ region⁵ of the infrared. A Beckman Model IR-4 infrared spectrophotometer was used to measure the optical density of the isocyanate peak.

Synthesis of 1-Phenyl-3-[bis-(*N,N*-dimethylamino)methylene]urea

To a solution of 1,1,3,3-tetramethylguanidine (12.0 g., 0.104 mole) in 50 ml. of hexane was added phenyl isocyanate (11.9 g., 0.10 mole) in 25 ml. of hexane. The exothermic reaction was cooled occasionally, and after 30 min. the hexane was decanted from the solid reaction product. Recrystallization once from methanol gave m.p. 105–106°C.; yield 5.0 g.

ANAL. Calcd. for $C_{13}H_{18}ON_4$: N, 23.91%. Found: N, 23.50%.

RESULTS

The reactions of phenyl isocyanate with 2-ethylhexanol and water were found to obey second-order kinetics in accordance with the theory of Baker and co-workers.^{1,2} Figures 1 and 2 show the various rate curves

TABLE I
Reaction of Phenyl Isocyanate (0.073 mole/l.) with 2-Ethylhexanol (0.073 mole/l.) in Benzene at 26°C.

Catalyst	Catalyst concn., mole/l.	k_2 , l./mole-hr.
Diazobicyclooctane	0.0014	7.95
Tetramethylguanidine	0.0014	3.75
	0.0028	7.80
Tetramethyl-1,4-butanediamine	0.0014	2.35
Triethylamine	0.0014	0.95
1-Phenyl-3-[bis(<i>N,N</i> -dimethylamino)methylene]urea	0.0014	3.75

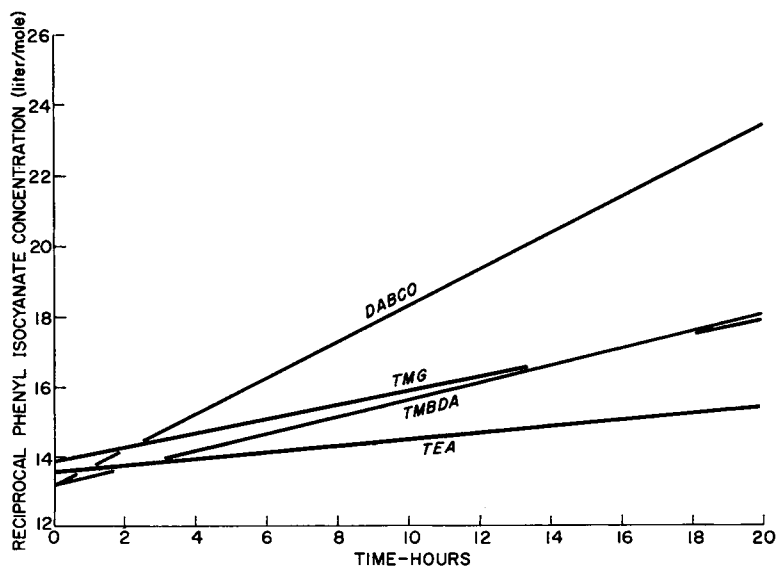


Fig. 1. Reaction of phenyl isocyanate (0.073 mole/l.) with 2-ethylhexanol (0.073 mole/l.) in benzene at 26°C. Catalyst concentration 0.0014 mole/l.

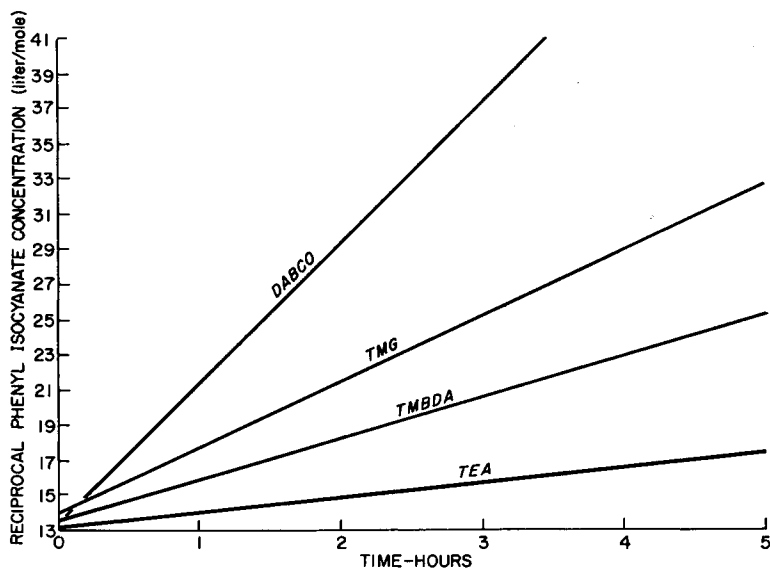


Fig. 2. Reaction of phenyl isocyanate (0.073 mole/l.) with water (0.036 mole/l.) in dioxane at 26°C. Catalyst concentration 0.0014 mole/l.

obtained. For comparison, several tertiary amines were also run: diazobicyclooctane (DABCO),¹ triethylamine (TEA),⁸ and 1,1,3,3-tetramethyl-1,4-butanediamine (TMBDA). The latter had not been reported previously. The rate constants k_2 calculated for the various catalysts are summarized in Tables I and II.

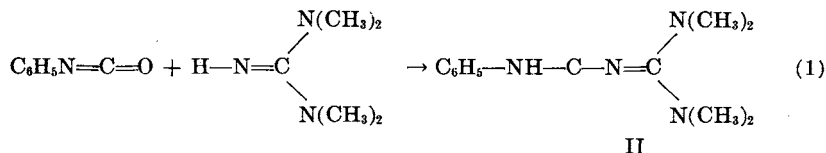
TABLE II
Reaction of Phenyl Isocyanate (0.073 mole/l.) with Water (0.036 mole/l.) in Dioxane at 26°C.

Catalyst	Catalyst concn., mole/l.	k_2 , l./mole-hr.
Diazobicyclooctane	0.0014	0.51
Tetramethylguanidine	0.0014	0.20
	0.0028	0.39
Tetramethyl-1,4-butanediamine	0.0014	0.23
Triethylamine	0.0014	0.09

DISCUSSION

At equivalent concentrations, tetramethylguanidine is seen to be a relatively more active catalyst for the isocyanate reaction than triethylamine or tetramethyl-1,4-butanediamine and poorer than diazobicyclooctane. This is especially true for the 2-ethylhexanol reaction. Tetramethylguanidine and tetramethyl-1,4-butanediamine are about equal in activity in catalyzing the water reaction.

Of particular interest is the reactivity of the substituted urea (II) prepared from TMG and phenyl isocyanate:



It has the same reactivity as TMG ($k_2 = 3.75$ l./mole-hr.), which leads one to believe that the urea (II) is the actual catalyst, since reaction (1) is very fast.

In the preparation of polyurethanes, therefore, the TMG has a dual functionality. Besides acting as a catalyst for the isocyanate reaction—as the guanidine or as a urea—the TMG becomes bound into the polyurethane, forming a homogeneous product. Since tertiary amine catalysts such as triethylamine do not possess this dual functionality, they remain unchanged in the final polyurethane, contributing an objectional ammoniacal odor. TMG should not contribute to this objectional odor, and indeed this has been found to be the case.¹⁰

The authors are indebted to Mr. S. E. Polchlopek and Mr. M. J. Robertson of these laboratories for the infrared measurements.

References

1. Baker, J. W., and J. Gaunt, *J. Chem. Soc.*, **1949**, 9, 19, 27.
2. Baker, J. W., and J. B. Holdsworth, *J. Chem. Soc.*, **1947**, 713.
3. Burkus, J., and C. F. Eckert, *J. Am. Chem. Soc.*, **80**, 5948 (1958).
4. Baker, J. W., M. M. Davies, and J. Gaunt, *J. Chem. Soc.*, **1949**, 24.
5. Bailey, M. E., V. Kirss, and R. G. Spaunburgh, *Ind. Eng. Chem.*, **48**, 794 (1956).

6. Dyer, E., H. A. Taylor, S. J. Mason, and J. Samson, *J. Am. Chem. Soc.*, **71**, 4106 (1949).
7. Ephraim, S., A. E. Woodward, and R. B. Mesrobian, *J. Am. Chem. Soc.*, **80**, 1326 (1958).
8. Farkas, A., and K. G. Flynn, *J. Am. Chem. Soc.*, **82**, 642 (1960).
9. Flynn, K. G., and D. R. Nenortas, *J. Org. Chem.*, **28**, 3527 (1963).
10. American Cyanamid Company, New Product Data Sheet: "Tetramethylguanidine as Catalyst for Urethane Foams," Wayne, N. J., July, 1960.

Résumé

On a trouvé que, pour la réaction de l'isocyanate de phényle avec le 2-éthylhexanol, la 1,1,3,3-tétraméthylguanidine est un catalyseur plus efficace que la triéthylamine ou la 1,1,3,3-tétraméthyl-1,4-butanediamine et moins efficace que le diazobicyclooctane. Pour la réaction de l'isocyanate de phényle avec l'eau, on a trouvé une catalyse semblable. On postule que le catalyseur est le produit de la réaction entre la 1,1,3,3-tétraméthylguanidine et l'isocyanate de phényle, la 1 phényle-3-[bis(*N,N*-diméthylamino)-méthylène]-urée.

Zusammenfassung

1,1,3,3-Tetramethylguanidin erwies sich für die Reaktion von Phenylisocyanat mit 2-Äthylhexanol als wirksamerer Katalysator als Triäthylamin oder 1,1,3,3-Tetramethyl-1,4-butandiamin und als weniger wirksam als Diazobicyclooctan. Eine ähnliche Katalyse wurde für die Phenylisocyanat-Wasserreaktion gefunden. Es wird angenommen, dass der tatsächliche Katalysator das Reaktionsprodukt zwischen 1,1,3,3-Tetramethylguanidin und Phenylisocyanat, 1-Phenyl-3-[bis(*N,N*-dimethylamino)methylen]harnstoff, ist.

Received May 4, 1964