

Determination of Hydroxyl Number of Polyoxyalkylene Ethers by Reaction with Toluene Diisocyanate

F. H. OTEY, BONNIE L. ZAGOREN, and C. L. MEHLTRETTER,
*Northern Regional Research Laboratory, Northern Utilization Research and
Development Division, Agricultural Research Service, U. S. Department of
Agriculture, Peoria, Illinois*

Synopsis

A new method for hydroxyl analysis is described in which excess toluene diisocyanate is reacted with a hydroxy compound, preferably in the presence of a catalyst, and the unreacted isocyanate is determined with dibutylamine reagent. The method is particularly applicable to polyethers intended for urethane foam preparation. It is rapid, is accurate, and has the added advantage of including such impurities as would be expected to consume isocyanate during a foam preparation.

INTRODUCTION

Generally, urethane foams are made by one of two methods. By the quasi-prepolymer method,¹ a polyisocyanate such as toluene diisocyanate (TDI) is mixed with a polyether to give an NCO/OH equivalent ratio of about 4-5/1.0 and then reacted at 70-100°C. for 0.5-1.0 hr. Foams are prepared by introducing additional polyether to the prepolymer to react with excess TDI. By the one-shot method,² all the required TDI and polyether are reacted at one time in the presence of an active catalyst, such as triethylenediamine.

For each method the quantity of TDI that will react with a given amount of polyether must be determined. The quantity is calculated from the hydroxyl number of the polyether and the equivalent weight of TDI. Usually hydroxyl number is determined by the acetic anhydride-pyridine method, which reportedly has several disadvantages, including slowness of acetylation³ (particularly with secondary alcohols), interference from low molecular weight aldehydes,⁴ and lack of reliability under routine conditions.⁵ Phthalic anhydride is also used to determine hydroxyl groups; Elving and Warshowsky⁴ report that water, acids, aldehydes, and phenols do not interfere. Improved methods that utilize anhydrides have recently been reported.⁵⁻⁷

The quantitative reaction of TDI with alcohols provides a new method for determining hydroxyl numbers that is particularly suitable for polyethers

intended for urethane foam preparations. Isocyanates are very reactive, not only toward hydroxylic polyethers, but also toward acids, amines, amides, phenols, and water. Polyoxyalkylene ethers used in foam preparations are generally mixtures of polyethers with primary and secondary hydroxyls and contain small amounts of impurities depending upon their method of preparation. These impurities can react with isocyanates and thus change the quantity of isocyanate available for reaction with polyethers. To overcome this difficulty, a hydroxyl determination based on the reaction of isocyanates with crude polyether, under conditions similar to those used in foam preparations, has been developed and is described in this paper. The procedure utilizes an excess of TDI, which is heated with a polyether in the presence or absence of a catalyst. The use of a catalyst shortens heating time and requires less excess TDI for completion of the reaction. After all the polyether is reacted, any excess TDI is combined with dibutylamine to form a urea, and the excess amine is determined by back-titration with standard hydrochloric acid solution. Crude or modified isocyanates may be used as a reagent in this analysis; however with less reactive isocyanates, the reaction time and percentage of catalyst must be increased.

EXPERIMENTAL

Reagents and Solutions

Toluene Diisocyanate (TDI). Into a 100-ml. volumetric flask was placed 50 ml. of toluene diisocyanate (Eastman Organic Chemicals, P-6590, toluene-2,4-diisocyanate) and dry toluene was added to the mark.

2*N* Dibutylamine. Into a 1-liter volumetric flask was weighed 258.5 g. of dibutylamine (Eastman, 1260) and dry toluene was added to the mark. The solution was used without standardization.

1*N* Hydrochloric Acid. Standardized 1*N* hydrochloric acid was used.

Catalyst. Approximately 0.5 g. of triethylenediamine (Houdry Process and Chemical Company, Dabco) was weighed into a 25-ml. volumetric flask and dry toluene was added to the mark.

Indicator. About 0.1 g. of bromphenol blue was dissolved in 100 ml. of 20% aqueous ethanol.

Procedure

Approximately 0.012 equiv. of polyether was accurately weighed into the bottom of a test tube (25 × 150 mm.) so that none of the sample touched the sides. A 1-ml. portion of the catalyst solution was immediately pipetted into the sample and a loosely fitting glass cover was placed over the mouth of the test tube. After all the samples were weighed, the test tubes were placed in an oil bath at 70°C. until solution occurred. After cooling slightly, 5 ml. TDI reagent (0.035 equivalent of TDI) was pipetted into each test tube and mixed in by shaking. The samples were again heated at

70°C. for 30 min. To each sample was then added 25 ml. of dibutylamine reagent with stirring, after which the heating at 70°C. was continued for an additional 10 min. Each sample was then transferred to a 250-ml. Erlenmeyer flask with 100 ml. of isopropyl alcohol and titrated with standard 1*N* hydrochloric acid solution in the presence of a few drops of indicator.

In an alternative procedure, no catalyst was used, the amount of TDI was increased to about 0.05 equiv., and heating time was extended to 1 hr.

In still another method, about 0.012 equiv. of polyether was dissolved in 1 ml. of catalyst reagent (1.5 g. Dabco in 25 ml. of toluene) and then mixed with 10 ml. of modified TDI reagent (36 ml. of National Aniline's Nacconate 4040 in 64 ml. of toluene). Samples were heated at 70°C. for 1 hr. and then treated with 25 ml. of 2*N* dibutylamine. After heating for an additional 10 min. at 70°C., the samples were allowed to cool at room temperature for 30–60 min. and then were transferred to a 250-ml. beaker with 100 ml. of isopropyl alcohol. The dark solutions were titrated with 1*N* hydrochloric acid to a pH range of 4.2–4.5, determined by using a pH meter.

A blank determination was made for each procedure, omitting only the polyether.

The hydroxyl number in all procedures is calculated from eq. (1):

$$\text{Hydroxyl number} = 56.1 N(A - B)/W \quad (1)$$

where *A* is the number of milliliters of standard HCl used in the sample determination, *B* is the number of milliliters of standard HCl used in the blank determination, *N* is the normality of HCl, and *W* is the weight of the sample in grams.

RESULTS AND DISCUSSION

Hydroxyl numbers obtained by the isocyanate procedure were comparable to those obtained by the acetic anhydride–pyridine method (Table I). Polyethers used for this comparison were deionized with Dowex 50, followed by Duolite A-4, and concentrated at 100°C. and 1 mm. Hg for 3 hr. to remove impurities.⁸ The TDI method gives rapid, consistent results and utilizes reagents normally used for prepolymer analysis. Since determinations are made in test tubes, several can conveniently be made simultaneously. Toluene was used as a reaction medium, but other non-reactive solvents are satisfactory. The catalyst procedure is preferred because the lower NCO/OH ratio gives a larger titration difference and because the method requires less time. Data reported in Table I were obtained by the catalytic procedure.

The same TDI suitable for a particular foam preparation is used for hydroxyl analysis since the nature of the reagent is not important. To illustrate the use of modified TDI, a procedure is included for National Aniline's Nacconate 4040. With less reactive isocyanates the reaction time and percentage of catalyst should be increased. The isocyanate method

TABLE I
Comparison of Isocyanate and Acetylation Procedures

Samples	Hydroxyl no. by isocyanate method			Hydroxyl no. by acetylation ^a	
	No. of detns.	Found	Std. dev.	No. of detns.	Found
Ethylene glycol glycosides ^b					
+ 6.8 Moles propylene oxide	3	416	0.7	2	415
+ 6.3 Moles propylene oxide	4	419	2.5	2	427
+ 5.9 Moles propylene oxide	2	446, 449	—	2	446
Glycerol glycosides ^b					
+ 10 Moles propylene oxide	7	384	2.2	2	381
+ 10 Moles propylene oxide	4	383 ^c	2.4	2	381
+ 8 Moles propylene oxide	4	447	2.1	2	449
Sorbitol					
+ 10 Moles propylene oxide	4	491	2.6	—	496 ^d
+ 10 Moles propylene oxide	4	494 ^c	2.2	—	496 ^d
Borneol	2	366, 367	—	—	364 ^e
1-Heptanol	5	487	2.3	—	483 ^e

^a ASTM D 1638-61T, 20-min. reaction at reflux.

^b Obtained by reacting starch with ethylene glycol or glycerol.⁸

^c With Nacconate 4040 as reagent.

^d Atlas G-2410, value reported by Atlas Chemical Industries, Inc.

^e Calculated.

is not limited to polypropylene oxide adducts, but it may be extended to include other soluble alcohols such as the fatty alcohols and borneol as shown in Table I.

Trade names are given as part of the exact experimental conditions and not as an endorsement by the U. S. Department of Agriculture of the products named over those of other manufacturers.

References

1. Wilson, J. E., H. M. Truax, and M. A. Dunn, *J. Appl. Polymer Sci.*, **3**, 343 (1960).
2. Erner, W. E., A. Farkas, and P. W. Hill, *Mod. Plastics*, **37**, 107 (1960).
3. Burns, E. A., and R. F. Muraca, *Anal. Chem.*, **31**, 397 (1959).
4. Elving, P. J., and B. Warshowsky, *Anal. Chem.*, **19**, 1006 (1947).
5. Sully, B. D., *Analyst*, **87**, 940 (1962).
6. Siggia, S., J. G. Hanna, and R. Culmo, *Anal. Chem.*, **33**, 900 (1961).
7. Stetzler, R. S., and C. F. Smullin, *Anal. Chem.*, **34**, 194 (1962).
8. Otey, F. H., B. L. Zagoren, and C. L. Mehlretter, *Ind. Eng. Chem., Prod. Res. Develop.*, **2**, 256 (1963).

Résumé

On décrit une nouvelle méthode pour l'analyse des fonctions hydroxyles dans laquelle un excès de diisocyanate de toluène réagit avec le composé hydroxylé de préférence en présence d'un catalyseur, et l'isocyanate restant est déterminé par la dibutylamine. La méthode s'applique particulièrement aux polyéthers destinés à la préparations de mousse d'uréthane. Elle est rapide, précise, et a en outre l'avantage d'inclure les impuretés qui peuvent consommer l'isocyanate lors de la préparation de la mousse.

Zusammenfassung

Eine neue Methode zur Hydroxylgruppenanalyse wird beschrieben, bei welcher überschüssiges Toluoldiisocyanat mit einer Hydroxylverbindung, am besten in Gegenwart eines Katalysators, zur Reaktion gebracht und das nichtumgesetzte Isocyanat mit Dibutylamin bestimmt wird. Die Methode ist für die zur Urethanschaumstoffbereitung verwendeten Polyäther besonders geeignet. Sie ist rasch und genau und hat den zusätzlichen Vorteil, solche Verunreinigungen mit zu erfassen, von denen man einen Isocyanatverbrauch während der Schaumstoffherstellung erwarten würde.

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