Journal of Chromatography, 644 (1993) 383–387
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 236

Determination of furan-based amines in reaction mixtures by gas chromatography

Michael S. Holfinger*

Department of Chemical Engineering, University of Wisconsin–Madison, 1415 Johnson Drive, Madison, WI 53706 (USA)

Anthony H. Conner

US Department of Agriculture–Forest Service, Forest Products Laboratory, 1 Gifford Pinchot Drive, Madison, WI 53705-2398 (USA)

Charles G. Hill, Jr.*

Department of Chemical Engineering, University of Wisconsin–Madison, 1415 Johnson Drive, Madison, WI 53706 (USA)

(Received March 4th, 1993)

ABSTRACT

A protocol which employs a methyl silicone gum capillary column for gas chromatographic analysis of the products of the acid-catalyzed reaction of furfurylamine with aldehydes is presented, and its efficacy is demonstrated.

INTRODUCTION

The synthesis of difurfuryl diamines (Fig. 1) via amido derivatives of furfurylamine has recently been reported [1]. Difurfuryl diamines are excellent curing agents for epoxy resins [2]. In addition, they are readily converted to the corresponding diisocyanates, which can be utilized in the preparation of polyurethanes [3,4] and adhesive resins [5]. These compounds are of particular interest to the composite wood products industry because they can be derived from renewable resources (biomass), rather than petroleum.

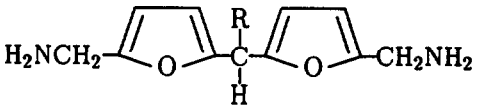

Fig. 1. Difurfuryl diamines.

The condensation reaction of furfurylamine with an aldehyde in the presence of hydrochloric acid offers a simpler route to difurfuryl diamines [6] than that previously reported [1]. Design and optimization of reactors for carrying out this reaction on a commercial scale necessitate the development of mathematical models which describe how reaction rates depend on temperature and on reactant and catalyst concentrations. To obtain the data on which such models are based, one requires a method for measuring the concentrations of amino species in sample aliquots from a reaction mixture. Although products of the

* Corresponding author.
* Present address: The Upjohn Company, 7000 Portage Road, Kalamazoo, MI 49001, USA.

0021-9673/93/$06.00

industrially important aniline–formaldehyde condensation reaction have been analyzed by TLC, HPLC, GC and gel permeation chromatography [7–9], chromatographic methods suitable for the analysis of the analagous reaction products of furfurylamine have not been previously reported in the literature. The purpose of this investigation was to develop a simple, reliable method for the analysis of mixtures of furfurylamino compounds by capillary column GC. The utility of the method that was developed is illustrated for the reaction of furfurylamine with formaldehyde to give 5,5′-methylene difurfurylamine via the intermediate 5-hydroxymethyl furfurylamine.

EXPERIMENTAL

Synthesis of standards

A pure sample of 5,5′-methylene difurfurylamine (Fig. 1; R = H) was prepared from furfurylamine (QO Chemicals; Memphis, TN, USA) by the method described in the literature [1]. 5-Hydroxymethyl furfurylamine was prepared by the reaction at 30°C in 6 *M* hydrochloric acid (Baker, Phillipsburg, NJ, USA) of 8.0 g of furfurylamine with 7.1 g of 35% (w/w) formaldehyde solution (Fisher, Fairlawn, NJ, USA). After 15 min, the reaction mixture was quenched with 104 ml of 6 *M* sodium hydroxide and 14.3 g of hydroxylamine hydrochloride. The mixture was then extracted with three 150-ml portions of chloroform. Crude 5-hydroxymethyl furfurylamine (2 g) was recovered from the second and third extracts. The crude compound was purified by vacuum distillation. A pure sample of furfurylamine (Aldrich, Milwaukee, WI, USA) was prepared by vacuum distillation. The identity and purity of all standards were verified by HPLC, by ^{1}H NMR, ^{13}C NMR and IR spectroscopies, and by GC–mass spectrometry.

Preparation of standard solutions

A series of 10 standard solutions was employed for the determination of relative response factors for furfurylamine, 5,5′-methylene difurfurylamine and 5-hydroxymethyl furfurylamine. The standard solutions were prepared by careful dilution of a chloroform stock solution of the compounds of interest in volumetric flasks containing pre-weighed quantities of the internal standard (methyl stearate). Solute concentrations ranged from 0.20–20 mg/ml. The approximate concentration of the internal standard in all standard solutions was 2 mg/ml. If stored in a freezer, the standard solutions were stable for several months.

Instrumentation

Instrumentation consisted of a Hewlett-Packard Model 5890A gas chromatograph equipped with flame ionization detection (FID) and a Model 7670 automatic sample injector. Peak areas were measured with a Hewlett-Packard Model 3387 electronic integrator.

Column and conditions

An HP-1 (Hewlett-Packard) wide-bore capillary column (5 m × 0.53 mm I.D., 2.65 μm film thickness) was employed for separations. The flow-rate of carrier gas (helium) was 17 ml/min, and the split ratio was approximately 9:1. No make-up gas was used. The initial column temperature was 40°C. After 1.5 min, the column temperature was increased to 200°C at a programmed rate of 30°C/min. A column temperature of 200°C was maintained for the remainder of the analysis. An injection volume of 1 μl was employed in all experiments. Samples were analyzed in triplicate.

Sample preparation and analysis

A 1-ml sample from the reaction mixture of furfurylamine and formaldehyde in hydrochloric acid was pipetted directly into a quench solution containing a slight stoichiometric excess of 6 *M* sodium hydroxide and 0.20 g of hydroxylamine hydrochloride. Then, the resultant mixture was extracted with chloroform (4 × 3 ml). The extracts were combined with a known amount of internal standard. A sample of the resultant solution was injected into the gas chromatograph.

Recovery studies

The recovery of the chloroform extraction procedure was examined for the reaction of furfurylamine with formaldehyde. A 1-ml aliquot from a reaction of furfurylamine and formal-

dehyde in 6 *M* HCl at 30°C was withdrawn after 30 min. The sample was neutralized with 6 *M* NaOH and quenched with hydroxylamine hydrochloride. Then, the sample was extracted with chloroform (3 × 4 ml) by the standard procedure, but without combination of these extracts. A known amount of internal standard was added to each extract, and each was analyzed by gas chromatography.

Accuracy studies

To examine the accuracy of the method, six representative samples were prepared by mixing various amounts of the furfurylamine, 5-hydroxymethyl furfurylamine, and 5,5′-methylene difurfurylamine standards. The concentrations of furfurylamine (reactant) and 5,5′-methylene difurfurylamine (product) increased in reverse order in this set of samples, as would be expected for samples from an actual kinetics experiment. Each sample was diluted with 2.85 ml of a "reaction matrix" consisting of 6 *M* hydrochloric acid (8 ml), 6 *M* NaOH (12.4 ml), 34.7% (w/w) formaldehyde (0.47 ml), and hydroxylamine hydrochloride (1.52 g). Samples were worked up and analyzed by the standard procedure.

RESULTS AND DISCUSSION

The results obtained indicate that the products from the reaction of furfurylamine with aldehydes can be determined by a GC–FID method. A gas chromatogram obtained by the procedure utilized is depicted in Fig. 2. The chromatogram in Fig. 2 corresponds to a sample from the acid-catalyzed reaction of furfurylamine with formaldehyde. Chromatographic peaks for furfurylamine (reactant), 5-hydroxymethyl furfurylamine (intermediate) and 5,5′-methylene difurfurylamine (product) are well separated from one another and from peaks associated with the solvent and internal standard.

Data from the recovery studies are summarized in Table I. These data indicate that both furfurylamine and 5,5′-methylene difurfurylamine are quantitatively recovered from the aqueous reaction mixture by the standard extraction procedure. By contrast, the recovery of

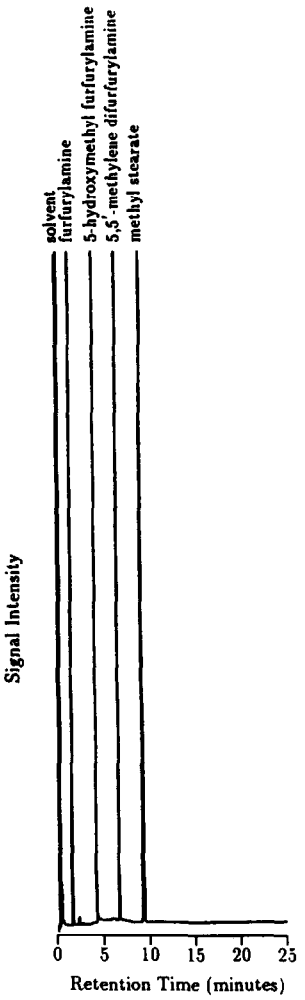

Fig. 2. Typical chromatogram for mixtures of furfurylamine, 5-hydroxymethyl furfurylamine, 5,5′-methylene difurfurylamine and the internal standard (methyl stearate).

5-hydroxymethyl furfurylamine was much less than 100%. Favorable interactions of the primary hydroxyl of 5-hydroxymethyl furfurylamine with the aqueous reaction matrix are believed to be primarily responsible for its preferential distribution into the aqueous phase.

Plots of measured *vs.* actual amounts of compounds based on data from the accuracy studies are depicted in Fig. 3. For both furfurylamine and 5,5′-methylene difurfurylamine, there is excellent agreement between measured and actual values, as indicated by the proximity of the data points to the line $y = x$ (see Fig. 3). The

TABLE I

ANALYSIS VIA GAS CHROMATOGRAPHY OF SUCCESSIVE CHLOROFORM EXTRACTS (3 ml) FROM A REACTION MIXTURE (1 ml) OF FURFURYLAMINE AND FORMALDEHYDE

Extract No.	Chromatographic peak area			
	Furfurylamine	5-Hydroxymethyl furfurylamine	5,5'-Methylene difurfurylamine	Internal standard
1	3 484 714	453 783	1 493 609	517 749
2	245 836	265 413	88 303	519 497
3	–	200 655	–	507 600
4	–	137 109	–	506 137

agreement between actual and measured amounts establishes the accuracy of the method for the analysis of these compounds. Due to incomplete recovery of 5-hydroxymethyl furfurylamine by the chloroform extraction procedure, the data for this compound fall close to the line $y = 0.68x$ (see Fig. 3). The slope of this line represents the overall recovery (68%) of 5-hydroxymethyl furfurylamine by the extraction procedure. In kinetics experiments, this value was employed for correction of the concentration data for this compound.

For analysis of amino compounds, derivatization is often employed to minimize the strong interactions of this functionality with surface sites in the GC column [10]. In initial work, both Schiff base (acetone) [11] and silyl ether [bis-(trimethylsilyl)acetamide (BSA), Pierce, Rockford, IL, USA] [12] derivatives were evaluated. The Schiff base derivatives could not be formed quantitatively, whereas chromatographic peaks arising from the BSA derivatizing agent interfered with the determination of furfurylamine. Consequently, derivatization of the amino group is not employed in the present method.

The chromatographic method described above was used to determine concentration *vs.* time profiles for the reaction conditions of interest (see Fig. 4). These representative data are for reaction of furfurylamine and formaldehyde in 4.5 *M* hydrochloric acid at 50°C. The lack of appreciable scatter in the data, especially at long reaction times where the concentrations of the various species are approaching their asymptotic

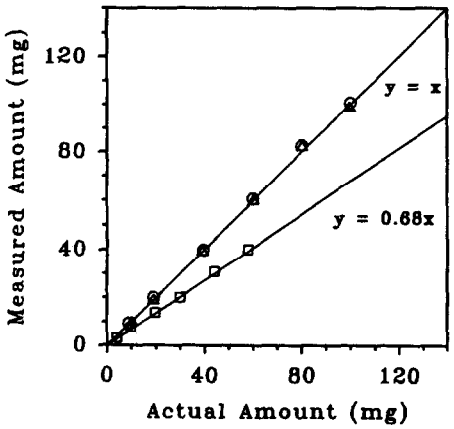

Fig. 3. Plots of measured *vs.* actual amounts of (○) furfurylamine, (△) 5,5'-methylene difurfurylamine and (□) 5-hydroxymethyl furfurylamine.

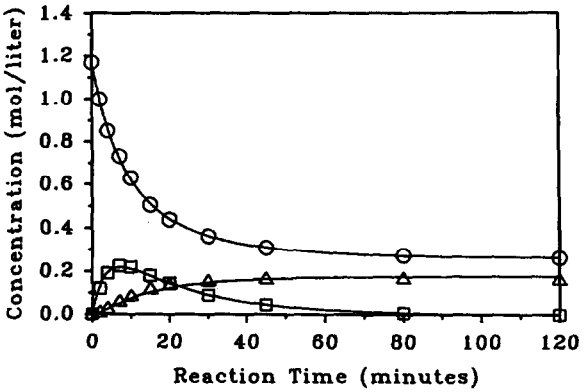

Fig. 4. Concentration profiles determined by gas chromatography for the reaction of furfurylamine and formaldehyde in 4.5 *M* HCl at 50°C. ○ = Furfurylamine; △ = 5,5'-methylene difurfurylamine; □ = 5-hydroxymethyl furfurylamine.

values is indicative of the good precision of the method.

CONCLUSIONS

A GC–FID method for the determination of products of the acid-catalyzed reaction of furfurylamine with aldehydes has been developed and demonstrated. The method involves the chloroform extraction of the compounds of interest from reaction mixtures followed by analysis on a methyl silicone gum (HP-1) capillary column. The method uses an internal standard (methyl stearate) for quantitation.

ACKNOWLEDGEMENTS

This article is based upon work supported under a National Science Foundation Graduate Fellowship. Additional financial support was provided by QO Chemicals Inc., Eureka Trading Ltd., and the USDA Forest Service Cost Share Program.

REFERENCES

1 J.L. Cawse, J.L. Stanford and R.H. Still, *Makromol. Chem.*, 185 (1984) 697.
2 X. He, A.H. Conner and J.A. Koutsky, *J. Polym. Sci., Polym. Chem. Ed.*, 30 (1992) 533.
3 J.L. Cawse, J.L. Stanford and R.H. Still, *Makromol. Chem.*, 185 (1984) 709.
4 J.L. Stanford, R.H. Still, J.L. Cawse and M.J. Donnelly, in R.W. Hemingway and A.H. Conner (Editors), *Adhesives from Renewable Resources*, American Chemical Society, Washington, DC, 1989, Ch. 30, p. 424.
5 M.S. Holfinger, A.H. Conner, L.F. Lorenz and C.G. Hill, Jr., in A.H. Conner, A.W. Christiansen, G.E. Myers, B.H. River, C.B. Vick and H.N. Spelter (Editors), *Wood Adhesives 1990*, Forest Products Research Society, Madison, WI, 1991, p. 61.
6 M.S. Holfinger, A.H. Conner and C.G. Hill, Jr., in preparation.
7 D.J. Francis, T.K. Radhakrishnan and M.R.G. Nayar, *J. Chromatogr.*, 103 (1975) 372.
8 M.R.G. Nayar and J.D. Francis, *Makromol. Chem.*, 179 (1978) 1783.
9 P. Falke, R. Tenner and H. Knopp, *J. Prakt. Chem.*, 328 (1986) 142.
10 M.W. Scoggins, L. Skurcenski and D.S. Weinberg, *J. Chromatogr. Sci.*, 10 (1972) 678.
11 W.J.A. Vanden Heuvel, W.L. Gardiner and E.C. Horning, *Anal. Chem.*, 36 (1964) 1550.
12 J.F. Klebe, H. Finkbeiner and D.M. White, *J. Am. Chem. Soc.*, 88 (1966) 3390.