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### The qualitative and quantitative determination of toluenesulphonic acid isomers

KENNETH M. BAKER and GEORGE E. BOYCE

*Monsanto European Technical Centre, Rue Laid Burniat, 1348 Louvain-la-Neuve (Belgium)*

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In the determination of toluenesulphonic acids, the acid must usually be converted into a more volatile form before it can be investigated by a technique such as gas chromatography (GC). In the past, this has been achieved by preparation of the acid chlorides, which were then investigated directly by GC<sup>1-3</sup>, or the sulphonyl chlorides could be treated with an alcohol to form the volatile esters, which are suitable for GC examination. These methods suffer from the disadvantages that trace amounts of water disturb the course of the sulphonyl chloride formation, and water in the alcohol can lead to decomposition of the esters formed. Similarly, it is difficult to prepare anhydrous aromatic sulphonic acids for the preparation of the sulphonyl chloride and consequently inorganic salts are often used as precursors.

We report here a rapid single-step method for the quantitative preparation of aromatic sulphonic acid ethyl esters and the direct use of the reaction product in determining the isomeric composition and disulphonic acid content of sulphonic acid mixtures. The structures of the products were confirmed by mass spectrometry (MS).

#### EXPERIMENTAL

Gas chromatography was carried out on a Hewlett-Packard Model 5830A gas chromatograph equipped with flame ionization detector (FID). Columns were made of glass or stainless steel, of dimensions 1 m × 1/8 in. I.D., containing 3% OV-101 on Chromosorb W HP (Johns-Manville, Manville, N.J., U.S.A.).

Mass spectra were determined on an AEI MS12 mass spectrometer equipped with an AEI DS30 data system. This was connected to a Varian 2100 gas chromatograph via a Biemann separator. Operating conditions for the mass spectrometer were: accelerating voltage, 8 kV; ionizing voltage, 70 eV; trap current, 60  $\mu$ A. Ethyl *p*-toluenesulphonate was obtained from Aldrich (Beerse, Belgium) and *p*-toluenesulphonic acid from BDH (Poole, Great Britain).

Samples were prepared for analysis as follows. A weighed amount of the sulphonic acid (*ca.* 0.1 g) was added to a known volume of toluene (12 ml) and the excess of water removed azeotropically by distillation of approximately 5 ml of the toluene. The internal standard (*o*-terphenyl, as a solution of 0.05 g in 2.0 ml of toluene) was added, followed by 20-fold excess of triethyl orthoformate, and the

mixture was heated under reflux for 15 min. Reaction was complete after this time and a sample of the reaction mixture could be injected directly into the gas chromatograph. The ratios of the ester peaks to the *o*-terphenyl peak were determined and compared with a calibration graph. The graph had previously been prepared by plotting the ratios of the peak areas of different weights of ethyl *p*-toluenesulphonate versus the same amount of internal standard. The various esters showed the following mass spectra. Ethyl *o*-toluenesulphonate, *m/e* (%): 91 (100), 65 (38), 172 (26), 137 (18), 200 (16). Ethyl *p*-toluenesulphonate, *m/e* (%): 91 (100), 92 (41), 65 (36), 155 (19), 200 (7). Diethyl 2,4-toluenedisulphonate, *m/e* (%): 64 (100), 91 (20), 92 (12).

## RESULTS AND DISCUSSION

The ethyl esters of the sulphonic acids were formed directly by reaction of the acid with triethyl orthoformate in toluene, the side-products being ethanol and ethyl formate. The method has the unusual advantage that the whole of the reaction mixture can be injected on to the gas chromatograph without interference from solvents or reactants. Toluene is used as a solvent and also as the agent to remove azeotropically excess of water that the acids may have picked up due to their hygroscopicity.

The formation of the ester was shown to be quantitative by comparison of the GC response obtained from a sample of toluenesulphonic acid treated with the triethyl orthoformate-toluene mixture with the response from a commercially obtained sample of ethyl toluenesulphonate. The sulphonic acid had previously been shown to be essentially isomerically pure and to contain no disulphonic acid and, by titration, to contain 90% (w/w) of *p*-toluenesulphonic acid.

Fig. 1 shows the separation of the ethyl esters of *o*-, *m*- and *p*-toluenesulphonic

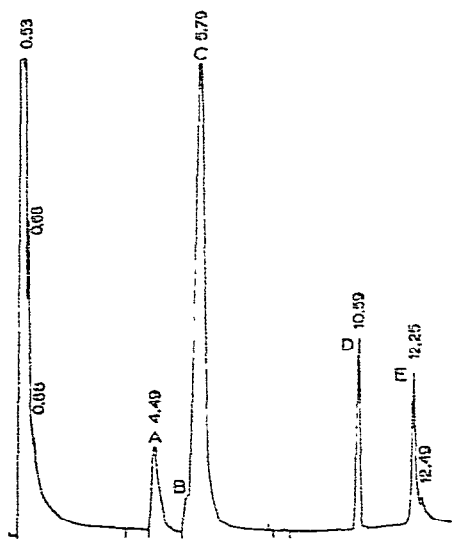


Fig. 1. Gas chromatographic trace of ethyl toluenesulphonates, obtained using a 2-m glass column with 3% OV-101 on Chromosorb W HP, programmed from 110 to 220° at 10°/min, with an FID. A = ethyl *o*-toluenesulphonate; B = ethyl *m*-toluenesulphonate; C = ethyl *p*-toluenesulphonate; D = *o*-terphenyl (internal standard); E = diethyl 2,4-toluenedisulphonate.

acids, the internal standard *o*-terphenyl, and the diethyl ester of 2,4-toluenedisulphonic acid. This mixture was obtained by the esterification of a crude laboratory-synthesized sulphonation product of toluene. All of the structures were verified by using GC-MS and the mass spectra showed fragmentation patterns consistent with the assigned structures.

The method described is useful because it provides a rapid single-step method of concurrently identifying and quantifying all of the acids present in a toluenesulphonic acid mixture. Although it has not been attempted, the method could probably be applied to any mixture of aromatic sulphonic acids either to determine isomeric purity or for quantification purposes.

#### REFERENCES

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