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Determination of sulphonic compounds as their thiotrifluoroacetate derivatives by gas chromatography with ion trap detection

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Abstract

A reductive method for the derivatization of sulphonates is described that is rapid (completed in a few minutes at room temperature) and uses mild conditions. Aromatic and aliphatic sulphonates were converted into the corresponding thiotrifluoroacetate derivatives using the reductive system sodium iodide–dimethylformamide–trifluoroacetic anhydride. 2-Amino-5-naphthol-7-sulphonic acid (J acid) was also derivatized successfully under the same conditions. All the derivatives were stable and could be separated easily by GC. The abundances of the molecular ion peaks were high on the ion trap detector and were convenient for identification.

1. Introduction

Sulphonic compounds are highly polar, non-volatile compounds that are applied extensively in the chemical and pharmaceutical industries. Methods such as IR, NMR and mass spectrometry and GC and HPLC are commonly used for the determination of sulphonates [1–3].

GC determinations are normally performed after converting sulphonates into volatile derivatives. The derivatization methods include sulphonyl esterification [4,5], trimethylsilylation [6], chlorination [7] or fluorination [8], desulphonation with acids [9,10] and alkali fusion [11]. However, the usefulness of these methods may be limited by the time-consuming derivatization process and the poor volatility of some derivatives.

Based on the high volatility of thiols, we attempted to establish a method of reducing sulphonates to their thiol derivatives. There were few reports on direct reduction methods for sulphonates before the 1980s owing to the inert chemical properties of the sulphonic group. The common method was to convert the sulphonates into sulphonyl chloride [12,13] and then to use reductive reagents such as Zn–HCl or $LiAlH_4$ [14] to form the thiol. In 1980, Numats *et al.* [15] reported a reductive system composed of $(CF_3CO)_2O$–Bu_4Ni–CH_2Cl_2 and the direct reduction of sulphonates to thiols. Direct reduction methods were subsequently extended with the use of triphenylphosphine [16,17], polyphosphoric acid [18] and boron halides [19].

After investigating many compounds and making various improvements, we have adopted a reductive system consisting of sodium iodide–dimethylformamide–trifluoroacetic anhydride

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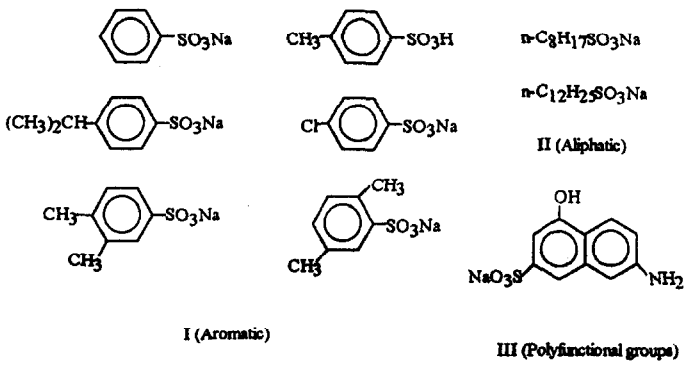


[NaI–DMF–$(CF_3CO)_2O$]. Many kinds of sulphonates have been reduced with the system and the derivatives have been characterized successfully by GC with ion trap detection (ITD).

2. Experimental

2.1. Reagents

p-Toluenesulphonic acid as the free acid and benzene-, 2,5-dimethylbenzene-, 3,4-dimethylbenzene-, dodecyl- and 2-amino-5-naphthol-7-sulphonate as sodium salts were purchased from Shanghai No. 1 Chemical Reagents Factory (Shanghai, China). Sodium octanesulphonate was purchased from Nacalai Tesque (Kyoto, Japan). *p*-Chlorobenzene and *p*-isopropylbenzene as sodium salts were synthesized in the laboratory [20] and confirmed by their IR spectra (Nicolet 5BX Fourier transform IR spectrometer). Sodium iodide and N,N-dimethylformamide were purchased from Shanghai No. 1 Chemical Reagents Factory. Trifluoroacetic anhydride was purchased from Merck.

2.2. Gas chromatography with ion trap detection

A Model 8810 gas chromatograph–Finnigan Mat Model 800 ion trap detector with a DB-5 capillary column (30 m × 0.25 mm I.D.) was employed under following conditions: carrier gas (helium) flow-rate, 25 ml/min; injection port temperature, 250°C; column temperature, 90°C isothermal for 3 min, then increased at 10°C/min to 250°C and maintained at 250°C for 10 min; transfer line temperature, 200°C; ion trap temperature, 200°C; amplifier voltage, 1350 V; mass range scanned, 45–650 u; 1.000 s per scan. Version 4.1 of the ITDS software (Finnigan Mat) was used with the instruments.

2.3. Derivatization procedure

A 10–30-mg amount (about 0.1 mmol) of sulphonate was dissolved in DMF (2 ml) containing 5–12 equiv. of $(CF_3CO)_2O$ and NaI. The solution was allowed to stand at room temperature for several minutes and the resulting solution became coloured dark red with free iodine. A 0.1-μl volume of the solution was injected in the GC–ITD system.

3. Results and discussion

3.1. Derivatization reaction

Sulphonates were converted into the corresponding thiols after reduction with NaI–DMF–$(CF_3CO)_2O$ and the excess of $(CF_3CO)_2O$ reacted with thiols to form thiotrifluoroacetates eventually:

$$RSO_3Na + (CF_3CO)_2O + NaI \xrightarrow[DMF]{\text{room temperature}} RSCOCF_3 + I_2 + CF_3CO_2Na$$

The reaction was rapid, being completed in a

few minutes at room temperature, and the thiotrifluoroacetate was the sole product. The optimum conditions were 8 equiv. of NaI and 10 equiv. of $(CF_3CO)_2$ with respect to the sulphonates. The yields ranged from 75% to 85% measured by the internal standard method (naphthalene as standard).

Many reports [16–18] have considered the mechanism of the reduction. The reaction rates were accelerated if the polar aprotic solvent DMF was used, which might be due to the following reasons [21,22]: the nucleophilicity of I^- was strengthened in DMF because of the creation of "naked anions", making I^- more reactive; and the charges on the sulphonate molecule and its intermediate were dispersed in DMF, the weakened solvation causing the molecule to be attacked more readily.

The advantage of this approach is that no by-products are present in the solution after derivatization and therefore interferences from by-products are avoided in the chromatographic separation. Further, the retentions of iodine, trifluoroacetic anhydride and the solvent DMF were very short on the capillary column and therefore they do not affect the separation and identification of the derivatives. The residual sulphonates and inorganic salts such as $NaCO_2CF_3$ and NaI are non-volatile and are incapable of generating chromatographic peaks, hence the reaction solution can be injected directly into the GC system without treatment.

3.2. Derivatives

The structures of all the derivatives were confirmed by GC–ITD. The experiments showed that not only do the thiotrifluoroacetates have good chromatographic properties but also the high abundance of the molecular ion in the ITD system made structure identification easy.

The mass spectrum of *p*-toluic thiotrifluoroacetate is shown in Fig. 1. The molecular ion peak (M^+) with the postulated m/z 220 and the prominent fragment ion peaks at m/z 151 ($M^+ - CF_3$), 123 ($M^+ - COCF_3$) and 91 ($M^+ - SCOCF_3$) were observed and were useful for structure elucidation.

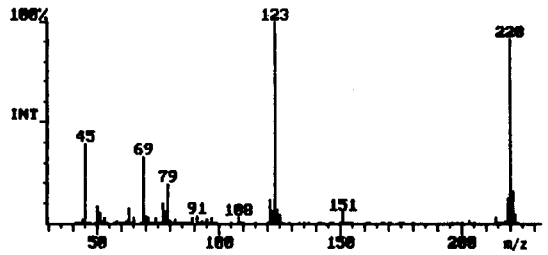


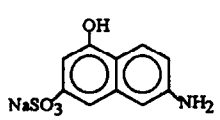
Fig. 1. Mass spectrum of *p*-toluic thiotrifluoroacetate.

In addition to the derivatization of aromatic sulphonates, the reductive system could also be employed as a derivatization reagent for aliphatic sulphonates.

A solution of dodecylsulphonate derivatized under the same procedure as above was prepared and 0.1 μl of the sample was injected into the GC system. The chromatographic peak of derivatives of aliphatic sulphonates were stable and underwent no thermal decomposition during GC–ITD. The mass spectrum of dodecyl thiotrifluoroacetate is shown in Fig. 2.

The formation of the $(M+1)^+$ ion is attributed to the self-chemical ionization and space charging in the ion trap [23]. The principal fragmentation pathway of dodecyl thiotrifluoroacetate is shown in Fig. 3.

2-Amino-5-naphthol-7-sulphonic acid (J acid):



is a dye synthetic intermediate with hydroxyl, amino and sulphonic groups in the molecule. Because of this variety of groups, J acid is

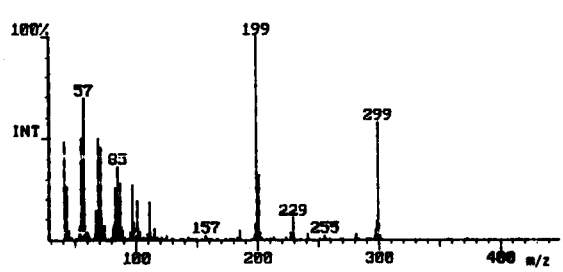


Fig. 2. Mass spectrum of dodecyl thiotrifluoroacetate.

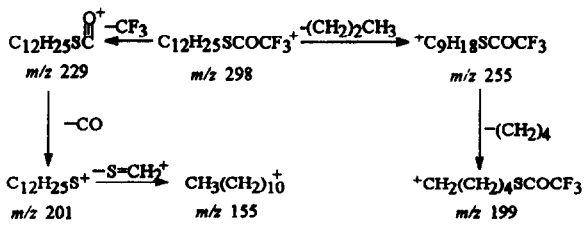
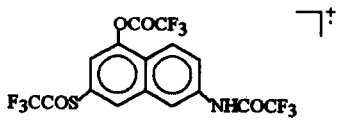


Fig. 3. Principal fragmentation pathway of dodecyl thiotrifluoroacetate.

difficult to separate and identify. The acylation of NH_2, OH and SH groups with trifluoroacetic anhydride is one of the most commonly used derivatization methods and proceeds under mild conditions [24]. The reduction products of J acid were acylated by the excess of trifluoroacetic anhydride in the reductive system. We considered that the OH and NH_2 groups could be acylated while the sulphonate was being reduced, which could improve the volatility of the compounds.

The results indicated that the sulphonic group of J acid was reduced to the thiol and the three polar functional groups (OH, NH_2 and SH) were trifluoroacetylated. The material representing the chromatographic peak of the J acid derivative was separated in a DB-5 capillary column at 250°C. Because of the conjugated bonds in the structure of the derivatives, the molecular ion peak was the base peak and few fragments were produced. The mass spectrum of the J acid derivative is shown in Fig. 4.

The molecular ion at m/z 479 has the structure



To examine a sulphonate mixture, eight sodium sulphonates were mixed and derivatized as described above, and 0.1 μl of the solution was injected into the GC–ITD system. Fig. 5 shows the total ion current chromatogram obtained. Each chromatographic peak represented different amounts of derivatives, ranging from 20 to 400 ng.

It could be concluded that all sulphonates were derivatized to thiotrifluoroacetates by the reductive system and were separated well by GC.

The derivatives of 2,5-dimethylbenzene sulphonate and 3,4-dimethylbenzene sulphonate were separated in the column, indicating that compounds with very similar structures could be separated by GC after derivatization. Different fragmentation pathways of the two isomers could be inferred from their mass spectra. For exam-

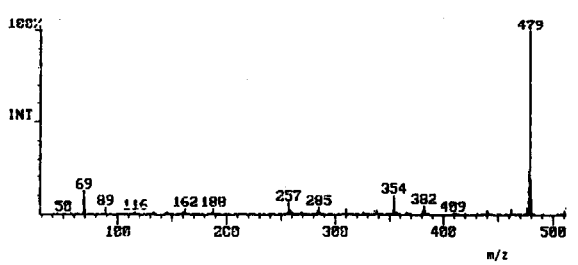


Fig. 4. Mass spectrum of J acid derivative.

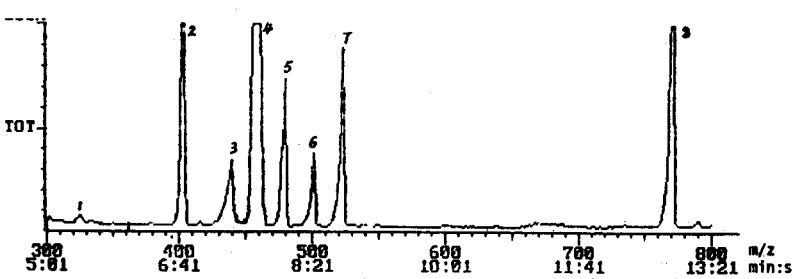


Fig. 5. Total ion current chromatogram of sulphonates as the thiotrifluoroacetate derivatives. Peaks: 1 = phenyl; 2 = toluic; 3 = *p*-chlorophenyl; 4 = *n*-octyl; 5 = 2,5-dimethylphenyl; 6 = 3,4-dimethylphenyl; 7 = *p*-isopropylphenyl; 8 = dodecyl thiotrifluoroacetate.

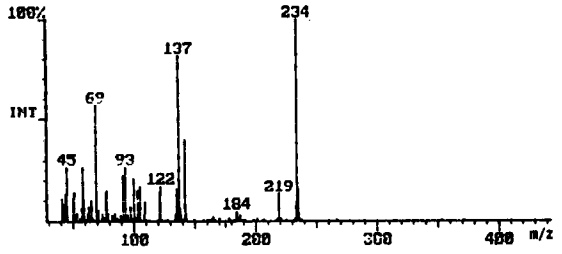


Fig. 6. Mass spectrum of 2,5-dimethyl thiotrifluoroacetate.

ple, the fragments ion at m/z 219 of the 2,5-dimethyl compound was deduced to be the fragment ($M^+ - CH_3$) and the steric exclusion between the *o*-methyl and trifluoroacetyl groups of the 2,5-dimethyl compound led to high abundances of the fragment ions at m/z 137 and 69 which differed from the abundances for the 3,4-dimethyl compound. Figs. 6 and 7 show the mass spectra of the two isomers.

4. Conclusions

Aromatic and aliphatic sulphonates and sulphonates with polyfunctional groups could be derivatized in a few minutes at the room temperature by a simple reduction method. The resolution of two isomeric derivatives of dimethylbenzene sulphonates revealed that the derivatives showed excellent GC behaviour and the derivatization of J acid showed that this method has potential application to the GC analysis of complicated sulphonates.

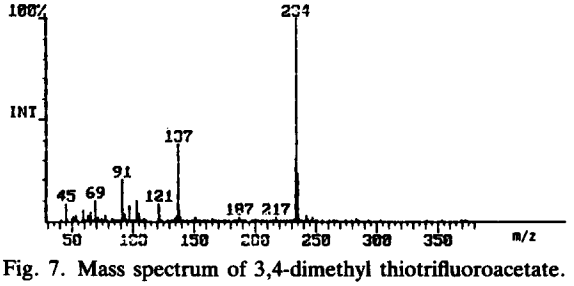


Fig. 7. Mass spectrum of 3,4-dimethyl thiotrifluoroacetate.

5. References

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