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Gas chromatographic method for the assay of aliphatic and aromatic sulphonates as their *tert.*-butyldimethylsilyl derivatives

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ABSTRACT

A gas–liquid chromatographic procedure is described which permits analysis of aliphatic and aromatic sulphonates as their *tert.*-butyldimethylsilyl derivatives. The *tert.*-butyldimethylsilylation of sulphonic acids in their free or sodium salt form is accomplished in a single derivatization step with N-methyl-N-(*tert.*-butyldimethylsilyl) trifluoroacetamide and *tert.*-butyldimethylchlorosilane in acetonitrile. Stability results and mass spectral analysis of all *tert.*-butyldimethylsilyl sulphonates are presented. Each derivative displays a prominent and characteristic [M—57] fragment ion in its mass spectrum.

INTRODUCTION

Organic sulphonate compounds are important industrial chemicals used as surfactants, pigments and dye intermediates etc. They constitute a significant number of samples analyzed at the Canadian Customs Laboratory for Tariff Classification purposes. In particular, it is necessary for us to determine the identity and purity of these chemicals.

Sulphonates have been investigated by various chromatographic methods. Among these methods we are particularly interested in the technique of gas chromatography (GC). Since sulphonates are compounds of low volatility, they were converted to volatile derivatives to be amenable to GC analysis. GC methods have been developed to analyze sulphonic acids as their trimethylsilyl (TMS) derivatives[1,2], methyl esters[3] and thionyl chloride derivatives[4]. Another method of analysis involves desulphonation in a reaction precolumn followed by GC analysis[5].

All the derivatization methods other than silylation involve sample work-up and are not applicable to sulphonic acids containing other polar functional groups such as hydroxy and amino groups. In general, silylation enjoys the advantage over other derivatization methods in that it is a single-step procedure and does not require

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separation of the derivatives prior to GC analysis. It is also a more versatile derivatization method. If a proper silylating reagent is employed, other polar substituents can be derivatized along with the sulphonate group.

Previous work, however, indicates that TMS derivatives suffer from instability[1] and lack of response to flame ionization detection (FID)[2]. It was also noted that the trimethylsilylation involves mainly the free acids, and very little, if any, of sulphonate salts.

This paper reports the development of a *tert.*-butyldimethyl silylation (tBDMS) method that allows derivatization of sulfonates in their free acid or sodium salt form in a single step reaction. Polar substituents such as OH, COOH and NH_2 were also derivatized by this procedure. Most of the synthesized tBDMS derivatives were found to be stable for at least 25 days at room temperature in the reaction solution. Unlike the TMS derivatives, the tBDMS-sulfonate compounds were detected by FID. All tBDMS derivatives were also subjected to GC–mass spectrometry (MS) analysis. Fragmentation patterns of these derivatives are presented.

EXPERIMENTAL

Materials

N-Methyl-N-(*tert.*-butyldimethylsilyl)trifluroacetamide(MTBSTFA), *tert.*-butyldimethylchlorosilane (tBDMCS) and acetonitrile were purchased from Pierce (Rockford, IL, U.S.A.). Benzo-15-crown-5 was obtained from Aldrich (Milwaukee, WI, U.S.A.). *n*-Tetradecane was a product of Alltech (IL, U.S.A.). Dioctyl phthalate was a commercial sample of >99% purity.

All the sulphonates used in this study are listed in Fig. 1. They were all obtained from Aldrich except compounds 8, 9 and 10 which were commercial samples.

Derivatization

The tBDMS derivatives of all the sulphonates were prepared by adding 18 mg tBDMSCl, 100 μl of MTBSTFA and 100 μl of a 2% acetonitrile solution of dioctyphthalate into a PTFE-faced Reacti-vial containing 3–4 mg of the sulphonate. Derivatization of sodium isethionate in the presence of benzo-15-crown-5 was carried out the same way except that 6 mg of the polyether was added to the reaction mixture.

The reaction mixture was stirred at 70°C for a period of 24 h. Aliquots of 1 μl were injected into GC–FID system at 1, 3, 6 and 24 h reaction time. Peak ratio of the product to the internal standard (dioctyl phthalate) was plotted against reaction time, the point at which the curve started to level off is taken as the reaction completion time. In all cases, the reaction mixtures at the end of 24 h were analyzed by GC–MS to obtain the mass spectra of the derivatives.

The stability of the phthalate internal standard in the silylation reaction mixture was tested using the same derivarization procedure described above, except 1 mg of tetradecane was used in place of the sulfonates. Peak ratio of the phthalate and *n*-alkane was found to remain constant at 70°C for 24 h and later for 25 days at room temperature, indicating that the dioctyl phthalate was stable throughout the derivatization and stability study.

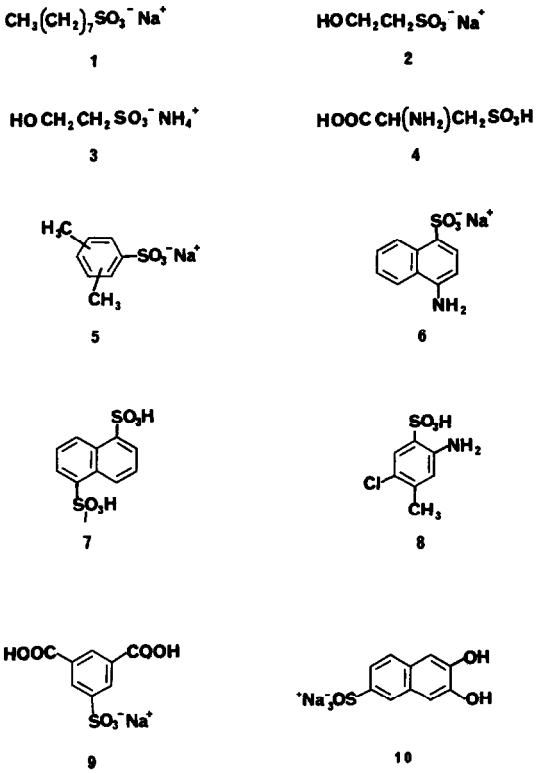

Fig. 1. Structures of sulphonates used in this study. 1 = Sodium octanesulphonate; 2 = sodium isethionate; 3 = ammonium isethionate; 4 = L-cysteic acid; 5 = sodium xylene sulphonate; 6 = sodium 4-amino-1-napthalenesulphonate; 7 = 1,5-napthalenedisulphonic acid; 8 = 2-amino-5-chlorotolenesulphonic acid; 9 = 5-(sodiosulfo)isophthalic acid; 10 = sodium 2,3-dihydroxy-6-naphthalenesulphonate.

Stability study

After 24 h at 70°C, the reaction mixture was allowed to stand at room temperature for at least 25 days. The mixture was analyzed by GC every 5 days and the peak ratio of the tBDMS derivative *vs.* the internal standard was plotted against time. A slope of zero from the plot and the absence of extraneous peaks in the chromatogram was interpreted as absence of decomposition of the derivative during the study period.

GC

A Hewlett-Packard Model 5840 A gas chromatograph equipped with a flame ionization detector was employed. The column used was a 15 m × 0.25 mm I.D., 0.25 μm thick DB5 fused-silica column. The injector temperature was 250°C and 1 μl of the reaction mixture was injected with a split ratio of 100:1 at an oven temperature of 80°C; after an initial hold time of 2 min at 80°C, the oven temperature was programmed at 10°C/min until 250°C; helium flow-rate was 1 ml/min.

GC–MS

The gas chromatograph-mass spectrometer (Finnigan Model 1020) was equipped with an electron impact source and a Nova 4 data system. The scanning rate was 1 s/scan in the range 40–650 a.m.u. The ion source temperature was held at 80°C. Electron impact (EI) spectra were obtained at 75 eV. The GC instrument (Perkin-Elmer Sigma-3B) was operated with the same column, the same oven and injector temperatures as described for GC–FID above. Helium flow-rate was 1 ml/min.

RESULTS AND DISCUSSION

Formulation of silylation cocktail

Previous work in our laboratory[6] has shown that sulfonic acids can be readily silylated by MTBSTFA in acetonitrile at 70°C. No reaction, however, was observed with various sodium salts of sulphonic acids using the same silylating reagent, even after prolonged heating. It is known that the reactivity of hexamethyldisilazane (HMDS) can be increased by the addition of a small amount of trimethylchlorosilane (TMCS), a chloride containing the same silyl group as HMDS[7]. In our laboratory, we have observed[8] that a silylation cocktail composed of a mixture of HMDS and TMCS in pyridine is able to derivatize metal salts of various carboxylic acids which fail to react with HMDS alone. Using the same reasoning, a silylation cocktail composed of MTBSTFA and tBDMCS, a chloride containing the same tBDMS silyl function as MTBSTFA, in acetonitrile were formulated as described in the Experimental section and used in this investigation.

Derivatization

As shown in Table I, among the four aliphatic sulphonates studied, sodium octanesulphonate and ammonium isethionate were completely silylated as mono- and disilylated derivatives, respectively, within the first hour.

TABLE I

DERIVATIZATION AND STABILITY RESULTS OF ALIPHATIC SULPHONATES

Compound	*Derivative*	*Degree of reaction after 1 h (%)*	*Minimum No. of days without decomposition*
1	$-SO_3$(tBDMS)	100	28
2	$-SO_3$(tBDMS) –O(tBDMS)	6[a], 75[b]	–
3	$-SO_3$(tBDMS) –O(tBDMS)	100	25
4	$-SO_3$(tBDMS) –COO(tBDMS) –NH(tBDMS)	70	Slow decomposition to yield an extraneous GC peak

[a] The degree of silylation was estimated from the GC response of the generated tBDMS derivative and that of the same derivative derived from the corresponding ammonium salt at the completion of reaction.

[b] In the presence of benzo-15-crown-5, added in equal molar amount as the substrate.

Unlike the ammonium salt, sodium isethionate was only 20% reacted after 24 h. It appears that the poor reactivity is due to a solubility problem. A macrocyclic polyether, benzo-15-crown-5, known to complex with the sodium cation and thus help to bring the anion into organic solvent[9], was added to the reaction mixture in a 1:1 molar ratio with respect to the substrate. A dramatic increase in reaction rate was observed. Sodium isethionate was 75% derivatized in the first hour. After 24 h reaction at 70°C, however, only 50% of the tBDMS derivative was detected, while no other extraneous peak was observed. We believe the complexing of sodium ion by the polyether renders the chloride ion generated from the silylation reaction more "naked". The activity of this anion is enhanced such that it is able to reverse the reaction as shown in the following equation. This postulate is presently under investigation in our laboratory.

$$\textit{tert.}\text{-butyl}(CH_3)_2SiCl + HOCH_2CH_2SO_3^- + \text{polyether-}Na^+ \rightleftarrows (\text{tBDMS})OCH_2CH_2SO_3(\text{tBDMS}) + \text{polyether-}Na^+ + Cl^-$$

Cysteic acid, a compound containing SO_3H, NH_2 and COOH functional groups, formed a trisilylated derivative. The silylation reaction appeared to be completed in 3 h but the response of the derivative started to slide as an unidentified new peak is formed. MS analysis indicates that this peak is not the tetrasilylated derivative in which both of the hydrogens on the primary amino group are replaced by the silyl groups. Degradation of the trisilylated derivatives, however, was slow, with 15% loss in response over a period of 18 h.

TABLE II

DERIVATIZATION AND STABILITY RESULTS OF AROMATIC SULPHONATES

Compound	*Derivative*	*Degree of reaction after 1 h (%)*	*Minimum No. of days without decomposition*
5	$-SO_3$(tBDMS)	100	27
6	$-SO_3$(tBDMS)	100[a]	32
7	$-SO_3$(tBDMS) $-SO_3$(tBDMS)	84	26
8	$-SO_3$(tBDMS) –NH(tBDMS)	16[b]	34
9	–COO(tBDMS) –COO(tBDMS) $-SO_3$(tBDMS)	–[c]	–

[a] The disilyl derivative in which one of the amino proton was replaced by a tBDMS group was observed only after 24 h of reaction.

[b] Mono- and disilyl derivatives were observed simultaneously, but the response of the disilyl derivatives grew at the expense of the monosilyl derivative. At the end of 24 h, the monosilyl peak almost disappeared, indicating silylation was close to completion.

[c] The extent of reaction was not estimated since reaction was not completed at the end of the 24-h study period.

TABLE III

RELATIVE INTENSITIES OF THE MAJOR FRAGMENT IONS IN THE MASS SPECTRA OF THE tBDMS DERIVATIVES OF SULPHONATES

Compound	*Derivative*	*Mol. wt.*	*Base peak*	*Relative intensity (%)*								
				m/e 73	*m/e 75*	*m/e 115*	*m/e 133*	*[M−15]*	*[M−57]*	*[M−121]*[a]	*[M−179]*[a]	*[M−195]*[a]
1	$-SO_3$(tBDMS)	308	251	22	82	4	1	1	100	2	0	0.3
2, 3	$-SO_3$(tBDMS) –O(tBDMS)	354	73	100	30	24	26	2	56	0	0.2	4
4	–COO(tBDMS) –NH(tBDMS) $-SO_3$(tBDMS)	511	73	100	46	8	9	0.3	6	0.8	0	5
5	$-SO_3$(tBDMS)	300	243	11	11	0.2	0	0.4	100	9	0.2	28
6	$-SO_3$(tBDMS)	337	280	7	20	48	0	0.7	100	50	41	50
6	$-SO_3$(tBDMS) –NH(tBDMS)	451	184	83	45	17	0.7	8	37	14	20	10
7	$-SO_3$(tBDMS) $-SO_3$(tBDMS)	516	185	79	50	6	6	0.6	79	0	2	3
8	$-SO_3$(tBDMS)	335	75	11	100	2	0	0	70	22	4	12
8	$-SO_3$(tBDMS) –NH(tBDMS)	449	73	100	12	4	4	0.5	24	0	0.4	0
9	–COO(tBDMS) –COO(tBDMS) $-SO_3$(tBDMS)	588	73	100	43	3	13	0	16	0	0	0
10	–O(tBDMS) –O(tBDMS) $-SO_3$(tBDMS)	582	525	99	7	2	2	2	100	0.2	0.2	0.4

[a] [m − 121], [M–179] and [M − 195] correspond to the fragment ions [$M - SO_2 - 57$], [$M - SO_2$(tBDMS)] and [$M - SO_3$(tBDMS)] respectively.

In general, no difficulty was experienced in derivatizing aromatic sulphonates, although derivatives of higher degree of silylation were formed slower than those of lower degree of silylation (Table II). In all cases except compound 8, only one derivative was detected during the 24-h study period. For compound 8, both mono - and disilylated derivatives were observed simultaneously, with the quantity of the latter growing at the expense of that of the former. A strong GC response was observed after overnight derivatization for compound 10, although no kinetic or stability studies were carried out for this compound.

In case where there are more than one active site reacting such as in compounds 6 and 8, the detected monosilyl derivative is assummed to be the one with the sulphonate group derivatized, since aromatic compounds containing an amino group attached to the ring can elute under the described GC conditions but underivatized organic sulphonic acids or salts are too polar to pass through the DB5 column[10].

Stability of the tBDMS-sulphonates as a function of time

Those sulphonates which were completely derivatized in less than 24 h were subjected to stability test as described under Experimental. As presented in Tables I and II, all these tBDMS derivatives demonstrated excellent stability for at least 25 days.

Mass spectrometry

Each synthesized tBDMS-sulphonate was subjected to GC–MS analysis and each displayed a very sharp single chromatographic peak except the monosilyl derivatives of the two amino sulphonates (compounds 6 and 8) which exhibited a slight peak tailing.

Table III shows the MS results for the aliphatic and aromatic sulphonates, respectively. Both groups of tBDMS derivatives produced the same general fragmentation. All yielded a singular unique [M − 57] fragment ion in the high mass spectral region. As is typical of tBDMS derivatives, this fragment ion results from the elimination of one *tert.*-butyl function from the molecule. In monosilylated derivatives, this ion was very intense and often served as the base ion. The relative intensity of this fragment decreased as the degree of silylation increased. Each derivative also displayed both a weak molecular ion (<0.1%) and a low relative intensity [M − 15] fragment (0–8%) which was produced by the loss of a methyl group from the derivative.

In general, all these derivatives displayed fragment ions *m/z* 73, 75 and 115.

$^{+}O\text{-}C(CH_3)_3$	$H\overset{+}{O}=Si(CH_3)_2$	$[Si(CH_3)_2\text{-}tert.\text{-}C_4H_9]^{+}$
m/e 73	*m/e 75*	*m/e 115*

In addition to the ions already mentioned, di- or trisilylated derivatives also yielded the ion *m/e* 133 containing two silicone atoms.

$$(CH_3)_2HSi\overset{+}{O}=Si(CH_3)_2$$

Fragments characteristic of tBDMS–sulphonate function are $[M - SO_2 - 57]^{+}$, $[M - SO_2(tBDMS)]^{+}$ and $[M - SO_3(tBDMS)]^{+}$ corresponding to loss of

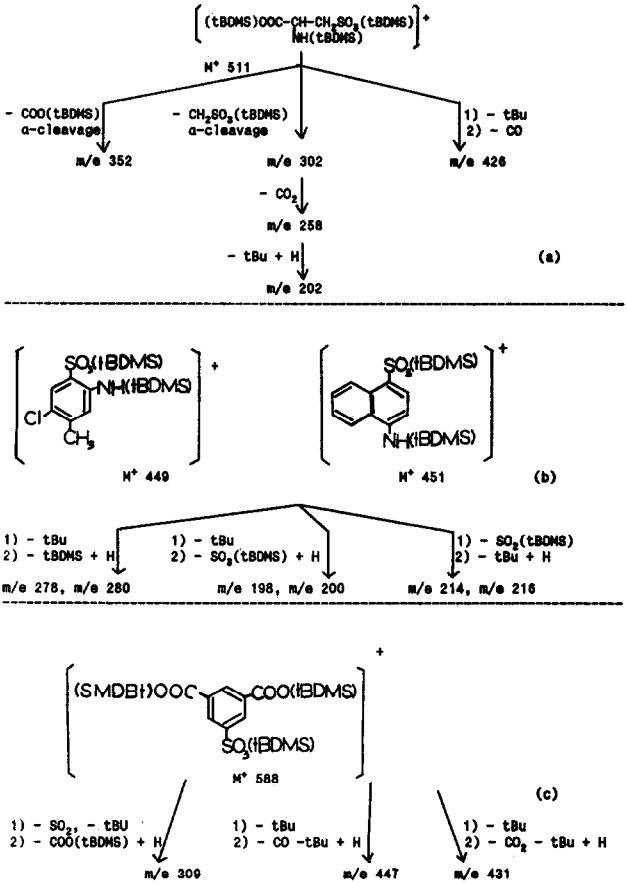

Fig. 2. Characteristic fragmentation patterns of tBDMS derivatives of (a) compound 4, (b) compounds 6 and 8 and (c) compound 9.

a.m.u. 121, 179 and 195 from the molecular ion. As shown in Table III, some or all of these fragments were observed in all of the derivatives except in the trisilylated derivative of compound 9, in which fragmentation involving the tBDMS–carboxylate function was competing with the cleavage at the tBDMS–sulphonate group.

Fig. 2 describes fragmentation patterns specific to the tBDMS derivatives of compounds 4, 6, 8 and 9.

Mass spectra of the trisilyl derivatives of compounds 4 and 9 are composed mainly of fragments of low intensities except the ions of *m/e* 73 and *m/e* 75. Ions resulting from the favorable cleavages α to the amino function were observed at *m/e* 302 and *m/e* 352 for compound 4 derivative as shown in Fig. 2a.

The disilylated derivative of compounds 6 and 8, both of which are aromatic aminosulphonates, share several similar fragmentation reactions as shown in Fig. 2b.

CONCLUSION

A method has been developed in which sulphonic acids or their sodium salts are derivatized to their respective tBDMS derivatives in a single-step reaction. These derivatives can be easily detected by FID. In addition, the tBDMS–sulphonates can be readily identified by their mass spectra characterized by the presence of [M − 57] fragment ion, and other ions resulting from cleavage at the SO_3(tBDMS) function.

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REFERENCES

1 K. A. Caldwell and A. L. Tappel, *J. Chromatogr.*, 32 (1968) 635.
2 O. Stokke and P. Helland, *J. Chromatogr.*, 146 (1978) 132.
3 J. J. Kirkland, *Anal. Chem.*, 32 (1960) 1388.
4 A. Amer, E. G. Alley and C. U. Pittman, Jr., *J. Chromatogr.*, 362 (1986) 413.
5 M. Nakada, A. Uzawa, S. Fukushi, H. Tomita and M. Hirota, *Nippon Kagaku Kaishi*, 5 (1984) 728.
6 L.-K. Ng, *U.S. Customs Bulletin*, 19 (1985) 40.
7 A. E. Pierce, *A Technique for Gas Phase Analysis, Silylation of Organic Compounds*, Pierce, Rockford, Il. 1968, ch. 1.
8 L.-K. Ng and M. Hupé, unpublished results.
9 C. J. Pedersen, *J. Am. Chem. Soc.*, 92 (1970) 386.
10 L.-K. Ng, unpublished results.