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# Short Communication

# Simultaneous gas chromatographic analysis of heptyl chloride–heptanesulphonyl chloride isomeric mixtures

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ABSTRACT

Gas chromatographic analyses of several sulphonyl chlorides were performed without derivatization. Optimized conditions for this analysis were selected and the results controlled by gas chromatography–mass spectrometry. The results obtained were compared with data reported for gas chromatography using derivatization. This method was extended to the simultaneous analysis of isomeric mixtures of *n*-heptyl chlorides and *n*-heptanesulphonyl chlorides obtained by the photochemical sulphochlorination of *n*-heptane.

## INTRODUCTION

Photochemical sulphochlorination with sulphur dioxide–chlorine (eqn. 1) is an efficient method for the functionalization of alkanes to alkanesulphonyl chlorides [1]. This method is used on an industrial scale [2] with higher *n*-alkanes and leads, after alkaline hydrolysis, to secondary alkanesulphonate (SAS) surfactants. However, undesirable alkyl chlorides are simultaneously produced in this process, and the composition of the reaction mixture needs to be controlled at all times.

$$\mathrm{RH} \xrightarrow[(\mathrm{R}=\text{alkyl})]{h\nu,\ \mathrm{SO_2},\ \mathrm{Cl_2}} \mathrm{RSO_2Cl} + \mathrm{RCl} + \mathrm{HCl} \quad (1)$$

Gas chromatographic (GC) analysis of the distribution of the sulphochlorinated isomers ($C_5$–$C_{16}$ saturated hydrocarbons) has been reported [3,4]. Packed silicone grease columns were used and the alkanesulphonyl chlorides were derivatized to the corresponding fluorides, esters or amides. The amides were recommended as being the most convenient derivatives. The distribution of the alkanesulphonyl chloride isomers was established. The chloroalkane content was not measured in the same photolysis mixture. Kirkland [5] had previously reported the GC analysis of sulphonyl chlorides or ester derivatives of the sulphonic acids (or acid salts) of aliphatic, aromatic and alkylaryl hydrocarbons. The chromatographic separation was carried out under reduced pressure in order to prevent sample decomposition. The esterification approach was used in the analysis of toluene–sulphonic acid isomers on short columns made of glass or stainless steel [6]. Aliphatic sulphonyl chlorides were also converted into their *tert.*-butyldimethylsilyl derivatives, in order to avoid their decomposition to alkyl

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halides in the injection port [7,8]. The sulphonamide method seems to be the most convenient when compared with other more time-consuming derivatizations [9].

In the frame of our work, devoted to the study of a new sulphochlorination process, we were interested in optimizing a method for the complete and quantitative analysis of the reaction mixture. In this work, the direct GC analysis of sulphonyl chlorides was studied and conditions were defined for the simultaneous analysis of chlorides and sulphonyl chlorides of *n*-heptane.

## EXPERIMENTAL

### *Sulphochlorination of N-heptane*

A 50-ml volume of *n*-heptane was photolysed at 360 nm for 90 min with continuous bubbling of sulphur dioxide and chlorine in a 2:1 flow-rate ratio. Two samples of 5 ml were removed. The first sample, used in the direct GC analysis, was washed with water until neutral. The volume was adjusted to 5 ml with heptane. Standards were added to 100 $\mu$l of this sample, making it ready for injection. The second sample was derivatized to the corresponding amide by addition of diethylamine, using the Berthold method [3]. After the reaction, the volume was again adjusted to its initial value, and standards were added to 100 $\mu$l of this solution.

### *Synthesis of 1-heptanesulphonyl chloride*

Grignard reagent, prepared from 1 mol of 1-chloroheptane and 1.1 mol of magnesium [10], was added at 0°C to 2 mol of sulphuryl chloride dissolved in *n*-hexane. After hydrolysis with sodium hydrogencarbonate solution, the mixture was extracted with diethyl ether. The organic phase was dried and filtered and the solvent evaporated, yielding a yellow oil. Distillation (80°C, 0.3 mmHg) gave 1-heptanesulphonyl chloride as a colourless oil (65% yield). IR (film): 1360, 1160 $cm^{-1}$. $^1H$ NMR ($CC:_4$):$\delta$ (ppm) 3.67 (t, 2H), 2.04 (q, 2H), 1.5 (m, 8H), 0.9 (t, 3H). $^{13}C$ NMR ($CCl_4$):$\delta$ (ppm) 65.5 (C-1), 31.36 (C-2), 28.57, 27.53, 24.31, 22.48 (C-3–C-6), 13.98 (C-7).

### *Synthesis of cyclohexanesulphonyl chloride*

The same method as above yielded cyclohexanesulphonyl chloride as a colourless oil. Boiling point: 134°C (1 mmHg). IR (film): 1370, 1170 $cm^{-1}$. $^1H$ NMR ($CCl_4$):$\delta$ (ppm) 3.5 (m, 1H), 2.6–0.87 (m, 1-OH). $^{13}C$ NMR ($CCl_4$):$\delta$ (ppm) 74.9, 27.2, 24.95, 24.7.

### *Reagents*

Methane-, trichloromethane-, 1-naphthalene-, 2-naphthalene-, 1-octane- and benzenesulphonyl chlorides, 1-chloroheptane and dibenzyl were purchased from Janssen, *p*-toluenesulphonyl chloride, *tert.*-butylbenzene and dimethoxynaphthalene from Aldrich and methoxynaphthalene from Fluka.

### *Gas chromatography*

Analyses were performed using either an Intersmat IGC 120 or Hewlett-Pckard 5730 A gas chromatograph equipped with a flame ionization detector. The injector and detector temperatures were 270°C unless specified otherwise. The carrier gas was nitrogen at a flow-rate of 0.7 ml/min. The columns used were as follows: SE-54, 5% diphenyl–95% dimethylsiloxane bonded DB-5 stationary phase, 30 m × 0.25 mm I.D., 0.25 $\mu$m film thickness, fused-quartz capillary column; OV-1, 100% polydimethylsiloxane (gum) bonded DB-1 stationary phase, 30 m × 0.32 mm I.D., 0.25 $\mu$m film thickness, fused-quartz capillary column; OV-101, 100% polydimethylsiloxane (fluid) with a bonded DB-1 stationary phase, 25 m × 0.32 mm I.D., 0.25 $\mu$m film thickness, fused-quartz capillary column; Carbowax 20M, 100% poly(ethylene glycol) with a bonded DW-Wax stationary phase, 30 m × 0.32 mm I.D., 0.25 $\mu$m film thickness, fused-quartz capillary column; and SE-30, 100% methylsilicone (gum) on Chromosorb P AW, 80–100 mesh, 2 m × 2 mm I.D. packed column.

### *Gas chromatography–mass spectrometry (GC–MS)*

A Finnigan MAT TSQ 70 mass spectrometer was used with a Varian 3400 gas chromatograph equipped with an SE-54 column. The conditions were trap current 200 $\mu$A, ionizing voltage 70 eV, ion-source temperature 150°C, helium flow-rate 1.5 ml/min, and vacuum $10^{-7}$ mmHg.

### *IR and NMR*

A Perkin-Elmer Model 457 IR spectrophotometer was used and $^1H$ and $^{13}C$ NMR analyses were performed on a Varian Gemini 200 spectrometer at

200 MHz. Tetramethylsilane (TMS) was used as an internal standard.

## RESULTS AND DISCUSSION

*Direct gas chromatographic analysis of sulphonyl chlorides*

Table I gives the retention time of 1-heptanesulphonyl chloride, showing that this isomer may be analysed on several capillary or packed non-polar columns. With the polar Carbowax columns, the sulphonyl chloride was no longer detected. This is probably due to on-column reaction between the sulphonyl chloride and the hydroxyl groups of the stationary phase.

On the other hand, comparison between the retention times given in Table I shows that the direct analysis is time saving when compared with the sulfonamides analysis.

For the remainder of this work, an OV-1 column was used. Direct and isothermal (180°C) GC analysis of the heptanesulphonyl chloride isomers (prepared by photolysis of *n*-heptane with $SO_2$–$Cl_2$) shows four peaks in the following order: 8.4 min (isomer 4), 8.6 min (isomer 3), 8.9 min (isomer 2), 9.5 min (isomer 1). Peak attribution for isomer 1 of heptanesulphonyl chloride was established by crossed injection. Analyses were also made after conversion to sulphonamide derivatives (see below). The elution order is well known for these compounds [3]. A quantitative comparison between the direct sulphonyl chloride analysis and indirect sulphonamide analysis allowed us to establish the identity of isomers 2, 3 and 4. GC–MS with electron impact ionization showed for each of the four isomers the fragment at *m/z* 163 corresponding to chlorine loss $[C_7H_{15}SO_2]^+$. The moleculr ions t *m/z* 199 and 201 $[MH]^+$ with the characteristic chlorine isotopic ratio were observed using GC–MS with chemical ionization.

These results show that under the conditions used, heptanesulphonyl chlorides are not decomposed into the corresponding chlorides, as stated by some workers [6,7].

The linearity of the detection was measured with the help of commercial 1-octanesulphonyl chloride and dibenzyl as a standard. No significant deviation from linearity was found in the concentration range examined (the injected solutions had concentrations between 0.1 and $5 \cdot 10^{-4}$ *M*).

The scope of the method was examined with the help of several other aliphatic and aromatic sulphonyl chlorides (Table II).

Sulphonyl chlorides were easily detected with reasonable retention times. However, with benzenesulphonyl chloride, two peaks were observed, with a ratio depending on the injector temperature. The first peak ($t_R$ = 6.8 min) was identified as benzyl chloride, as shown by crossed injection. The second peak was benzenesulphonyl chloride, as demonstrated by GC–MS. Trace amounts of dibenzyl were also found, showing that an increase in the temperature favoured a radical bond rupture, leading to a stable benzyl radical, precursor of benzyl chloride and dibenzyl:

$$C_6H_5CH_2SO_2Cl \xrightarrow{T \text{ increasing}} Cl^{\cdot} + C_6H_5CH_2^{\cdot} + SO_2$$

$C_6H_5CH_2^{\cdot}$ → $C_6H_5CH_2Cl$

$C_6H_5CH_2^{\cdot}$ → $(C_6H_5CH_2)_2$

TABLE I

RETENTION TIMES OF 1-HEPTANESULPHONYL CHLORIDE AND 1-HEPTANESULPHONIC ACID DIETHYLAMIDE ON VARIOUS STATIONARY PHASES

| Compound | Retention time (min) | | | | |
|---|---|---|---|---|---|
| | SE-54[a] | SE-30[b] | OV-101[a] | Carbowax 20 M[a] | OV-1[a] |
| $C_7H_{15}SO_2Cl$ | 9.8 | 4 | 10 | | 9.5 |
| $C_7H_{15}SO_2NEt_2$ | 15 | 13 | 21 | 35 | 20 |

[a] Injector 270°C; column 180°C.
[b] Injector 210°C; column 160°C.

TABLE II

RETENTION TIMES ($t_R$) OF SULPHONYL CHLORIDES ($RSO_2Cl$)

| Parameter | R | | | | | | |
|---|---|---|---|---|---|---|---|
| | $CH_3$ | $CCl_3$ | *p*-Tolyl | 1-Naphthyl | 2-Naphthyl | Cyclohexyl | Benzyl |
| $t_R$ (min) | 5 | 6.7 | 6.7 | 10.9 | 11.2 | 7.7 | 7.3 |
| $T$ (°C)[a] | 130 | 130 | 220 | 220 | 220 | 180 | 140 |

[a] Column temperature.

These results demonstrate that direct GC analysis is suitable for sulphonyl chlorides. However, compounds leading to stable radicals may decompose in the injector (and not in the column). In that event, the method needs to be standardized, taking into account the decomposition products.

*Gas chromatographic identification of N*-heptyl chloride isomers

The isomeric mixture of *n*-heptyl chlorides obtained as side-products in the photochemical sulphochlorination of *n*-heptane was analysed by GC using the same column at 70°C. The added standard was *tert.*-butylbenzene ($t_R$ = 19.6 min).

Three peaks were observed on the chromatogram. Isomer 4 (11.5 min), isomers 3 nd 2 (12 min) and isomer 1 (15 min) were identified by crossed injection with authentic samples prepared by an already published method [11].

*Comparison between amide derivatization and direct analysis of heptanesulphonyl chlorides*

An isomeric mixture of *n*-heptanesulphonyl chlorides prepared by the photochemical sulphochlorination of *n*-heptane was analysed by GC and the results were compared with those obtained after derivatization (Table III).

Considering the results obtained previously with

TABLE III

DISTRIBUTION (%) AND CONCENTRATIONS [C (mmol/l)] OF UNDERIVATIZED AND DERIVATIZED HEPTANESULPHONYL CHLORIDE ISOMERS AT DIFFERENT INJECTION TEMPERATURES

| Compounds | Injector temperature (°C) | Isomer 1 | | Isomer 2 | | Isomer 3 | | Isomer 4 | |
|---|---|---|---|---|---|---|---|---|---|
| | | % | C[a] | % | C[a] | % | C[a] | % | C[a] |
| Heptanesulphonyl chlorides | 180 | 19.5 | 91 | 34.9 | 162 | 30.2 | 140 | 15.4 | 71 |
| | 210 | 20.2 | 89 | 34.1 | 160 | 31.1 | 138 | 14.6 | 69 |
| | 240 | 20.2 | 91 | 34.5 | 155 | 30.8 | 138 | 14.5 | 65 |
| | 270 | 20.4 | 90 | 33.9 | 149 | 30.9 | 136 | 14.8 | 64 |
| | 300 | 25.1 | 80 | 35.5 | 114 | 26.4 | 85 | 13.0 | 41 |
| Heptanesulphonyl diethylamides | 180 | 22.9 | 94 | 32.8 | 135 | 30.3 | 125 | 14.0 | 57 |
| | 210 | 23.9 | 100 | 32.6 | 136 | 29.6 | 123 | 13.9 | 58 |
| | 240 | 23.6 | 99 | 32.4 | 139 | 30.1 | 130 | 13.9 | 59 |
| | 270 | 23.2 | 99 | 32.9 | 140 | 29.8 | 127 | 14.1 | 60 |
| | 300 | 24.3 | 111 | 32.8 | 137 | 29.3 | 122 | 13.6 | 57 |
| Heptanesulphonyl diethylamides (from ref. 3) | —[b] | 20.4–21.7 | | 31.8–33.2 | | 45.4–47.3[c] | | | |

[a] Relative accuracy and reproducibility between measurements made on different samples are ±2%.
[b] Not mentioned.
[c] Isomers 3 and 4 were unresolved.

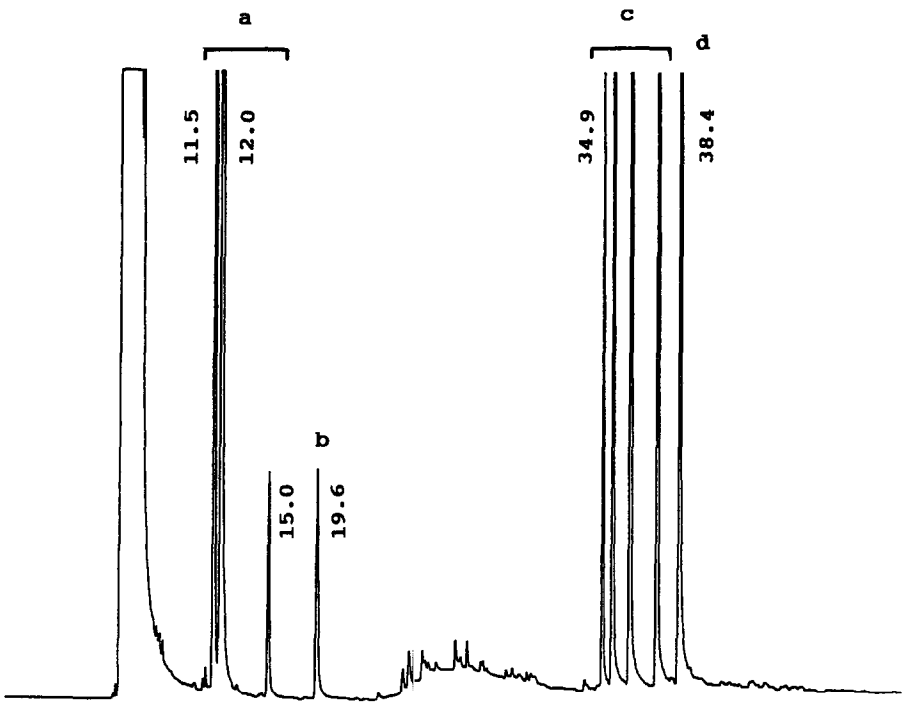


Fig. 1. GC analysis of heptyl chloride–heptanesulphonyl chloride mixtures. (a) Heptyl chloride isomers; (b) *tert.*-butylbenzene as standard; (c) heptanesulphonyl chloride isomers; (d) dimethoxynaphthalene as standard. Numbers at peaks indicate retention times in min.

benzenesulphonyl chloride, the influence of injector temperature was studied in the range 180–300°C. Methoxynaphthalene and dibenzyl were used as added standards for *n*-heptanesulphonyl chlorides and dimethoxynaphthalene for the corresponding *n*-heptanesulphonic acid diethylamides. The same temperature was used in the two analyses (180°C).

The isomeric distribution results given in Table III do not show any influence of the injection temperature for diethylamide derivatives and this was also the case for the sulphonyl chlorides between 180 and 270°C. However, at 300°C, some degradation of sulphonyl chlorides takes place. This degradation is less important for isomer 1 than for the others.

Good agreement with the literature results was observed with injection temperatures between 180 and 270°C. Below 180°C, the *n*-heptanesulphonic acid diethylamides are not efficiently vaporized in the injector. It is worth mentioning that the separation between isomers 3 and 4 of the sulphonamide was not reported in the derivatization method [3].

The GC conditions for the simultaneous analysis of the heptanesulphonyl chlorides and heptyl chlorides are a column temperature of 70°C (isothermal) for 19 min (in order to observe the *n*-heptyl chlorides), then increased at 10°C/min to 180°C, and isothermal detection of *n*-heptanesulphonyl chlorides. The injector temperature is fixed at 270°C. A typical chromatogram is shown in Fig. 1.

The determination of the heptyl chlorides was unaffected by the method used for the sulphonyl chlorides.

As shown by the concentrations obtained with the two methods, the direct analysis of sulphonyl chlorides is in very good agreement with the sulphonamide analysis. The comparison between the two procedures indicates that the direct technique is a valuable, convenient and simple method for a complete analysis of this type of reaction mixture.

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