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GAS CHROMATOGRAPHIC METHOD FOR THE DETERMINATION OF 3-(TRIMETHOXYSILYL)PROPYLOCTADECYLDIMETHYLAMMONIUM CHLORIDE

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SUMMARY

A sanitary finishing agent, 3-(trimethoxysilyl)propyloctadecyldimethylammonium chloride (I), was easily degraded with potassium *tert.*-butoxide in benzene–dimethyl sulphoxide (8:2) under mild conditions to yield 1-octadecene and octadecyldimethylamine in the ratio 5:1. The volatile 1-octadecene was detected on a 5% SE-30 column by gas chromatography with a hydrogen flame ionization detector. The calibration curve was linear at levels ranging from 40 to 200 ppm of compound I. The proposed method was applied to the determination of compound I in commercial textile products.

INTRODUCTION

Dow Corning 5700, 3-(trimethoxysilyl)propyloctadecyldimethylammonium chloride (I) is a surface-bonding type of antimicrobial agent with organosilylating properties[1]. Recently, the compound has been widely used in Japan as a sanitary finishing agent and deodorant for cotton fabrics such as socks, towels, sportswear and sleepwear.

The trimethoxysilane of compound I reacts with the hydroxy group of cotton cellulose to form a silyl ether bond and to give a durable coating on the surface of cotton fabrics (Fig. 1)[2]. For gas chromatographic (GC) analysis, it is necessary to degrade compound I bonded on the cellulose surface and to convert it into some suitable chemical fragment by chemical reaction. However, there are no reports of the GC analysis of compound I. Although long-chain alkyltrimethylammonium salts are converted into alkyldimethylamine with lithium aluminium hydride[3] or by thermal decomposition[4–6], the problems described above cannot be overcome by demethylation methods because the tertiary amine corresponding to compound I is not released from the cellulose surface as a GC detectable fragment.

In a previous paper[7] we reported that alkyltrimethylammonium chlorides and dialkyldimethylammonium chlorides are degraded to 1-olefins corresponding to the alkyl group by Hofmann degradation in the presence of potassium *tert.*-butoxide. By

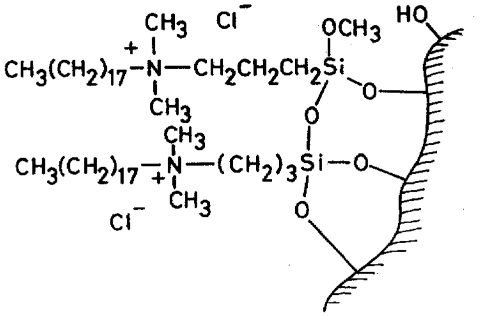


Fig. 1. Coating of cotton by compound I.

use of the degradation method, it is possible to convert the octadecyl group of compound I into volatile 1-octadecene. This paper describes a convenient method for the determination of compound I based on GC measurement of the 1-octadecene obtained by Hofmann degradation.

EXPERIMENTAL

Apparatus

Isothermal GC analyses were performed on a Shimadzu Model GC-4CM chromatograph fitted with a hydrogen flame ionization detector. Peak-area measurements were obtained by a Shimadzu Model C-RIB Chromatopac integrator. Gas chromatography–mass spectrometry (GC–MS) measurements were carried out with a JEOL Model JMS-D300 mass spectrometer equipped with an Hewlett-Packard Model 5710A gas chromatograph. Nuclear magnetic resonance (NMR) spectroscopy was carried out with a JEOL Model JNM-FX270 instrument. Chemical shifts, δ (ppm), are downfield from tetramethylsilane as an internal standard.

Reagents

Potassium *tert.*-butoxide was obtained from Wako Pure Chemical Industries (Tokyo, Japan). Dow Corning 5700, 42% (w/w) compound I in methanol, was obtained from Dow Corning (Midland, MI, U.S.A.). A standard solution was prepared by dissolving in benzene–dimethyl sulphoxide (DMSO) (8:2) the residues of Dow Corning 5700 obtained after removal of methanol by evaporation. All other reagents were of analytical-reagent grade.

Method

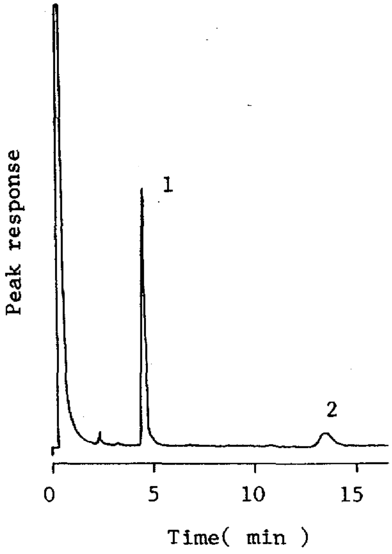
A textile sample, 200 mg of cotton fabrics cut into very small pieces ($< ca.$ 2 mm^2), or a standard solution containing 0.2–1 mg of compound I was placed in a 100-ml Kjeldahl flask. A 200-mg amount of potassium *tert.*-butoxide and 25 ml of benzene–DMSO (8:2) were added. The solution was heated under reflux on a water-bath for 30 min. After cooling the flask to room temperature, the solution was filtered through a glass filter and the filtrate was transferred to a 100-ml separating funnel. The flask and the filter were rinsed with two 5-ml portions of benzene. The rinsing solutions were added to the solution in the separating funnel. The pooled benzene solution was washed with two 20-ml portions of 5% hydrochloric acid and then with 20 ml of water. The benzene layer was separated and evaporated to dryness under reduced pressure at about 40°C. The residues were dissolved in 5 ml of hexane and 5 μl of the solution were injected into the gas chromatograph.

GC conditions

GC was carried out on a glass column (2 m × 3 mm I.D.) packed with 5% SE-30 on Chromosorb W AW DMCS (80–100 mesh) at 200°C with a nitrogen flow-rate of 40 ml/min. The injection port and detector temperatures were 250°C.

RESULTS AND DISCUSSION

It was shown previously that when alkyltrimethylammonium chlorides were degraded with potassium *tert.*-butoxide under reflux for 30 min in benzene–DMSO (8:2) they yielded the corresponding 1-olefin[7]. When degraded under the conditions described above, compound I yielded 1-octadecene (II) and octadecyldimethylamine (III), which had retention times of 4.9 and 14.5 min, respectively, in isothermal GC (Fig. 2). The identification of these degradation products was also supported by GC–MS and NMR spectroscopy. Compound II: m/z 252 (M^+); NMR(C^2HCl_3), ^1H, δ 0.88 (3 H, t, J = 6.6 Hz), 4.95 (2 H, m), 5.80 (1 H, m); ^{13}C, δ 14.2 (q), 114.1 (t), 139.3 (d) ppm. Compound III: m/z 297 (M^+); NMR ($C^2H_3O^2H$), ^1H, δ 0.88 (3 H, t, J = 6.6 Hz), 2.53 (6 H, s), 2.68 (2 H, m); ^{13}C, δ 14.4 (q), 44.3 (q), 59.7 (t) ppm. As shown in Scheme 1, it was confirmed that the formation of 1-octadecene and octadecyldimethylamine from compound I was based on elimination of hydrogen at



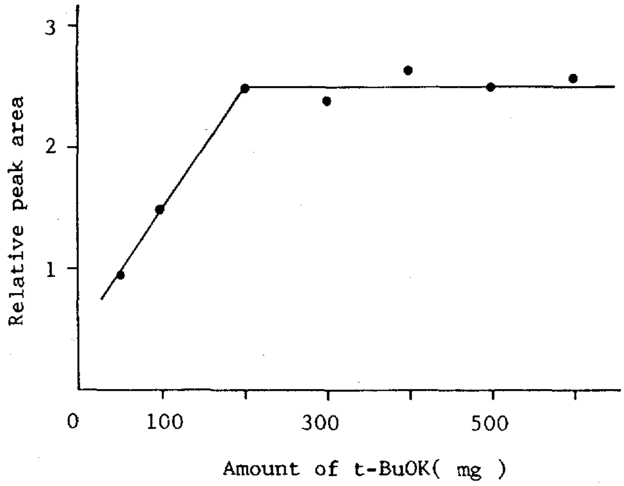
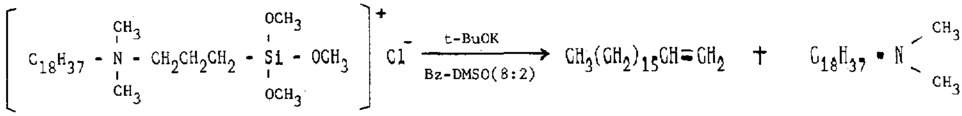


Fig. 2. Gas chromatogram of the degradation products of compound I. Peaks: 1 = 1-octadecene; 2 = octadecyldimethylamine.

Fig. 3. Effect of the amount of potassium *tert.*-butoxide on the formation of 1-octadecene from commercial I-bonded dish cloth. Sample size: 400 mg.



$$\left[C_{18}H_{37}-\overset{CH_3}{\underset{CH_3}{N}}-CH_2CH_2CH_2-\overset{OCH_3}{\underset{OCH_3}{Si}}-OCH_3\right]^{+}Cl^{-}\xrightarrow[Bz\text{-}DMSO(8:2)]{t\text{-}BuOK}CH_3(CH_2)_{15}CH{=}CH_2+C_{18}H_{37}-N\begin{matrix}CH_3\\CH_3\end{matrix}$$

I II III

Scheme 1. Degradation products of compound I. t-BuOK = potassium *tert.*-butoxide; Bz = benzene.

the *β*-carbon of the octadecyl and trimethoxysilylpropyl groups. The ratio of the yields of 1-octadecene and octadecyldimethylamine from peak-area measurements was 5:1. Therefore, GC analysis of compound I was carried out by using the peak of 1-octadecene obtained as degradation product.

The conditions for the degradation of compound I with potassium *tert.*-butoxide were examined. These experiments were carried out using a commercial dish cloth containing 0.26% of compound I. The effects of the amount of potassium *tert.*-butoxide, the concentration of DMSO in the reaction solvent and the reaction time on the formation of 1-octadecene from the dish cloth are shown in Figs. 3–5. When more than 200 mg of potassium *tert.*-butoxide were added to 400 mg of the dish cloth the formation of 1-octadecene was evidently constant (Fig. 3). Thus, the amount of potassium *tert.*-butoxide was set at 200 mg, the same as that of the sample size (200 mg) as described in the Experimental section. From the results in Figs. 4 and 5, the ratio of benzene/DMSO for the reaction solvent was chosen as 8:2 and the reaction time for the degradation was set at 30 min in the same manner as described in a previous paper[7].

As shown in Fig. 6, the calibration curve of peak heights *vs.* concentrations for compound I showed good linearity over the range of 40–200 ppm, although it did not pass through the origin.

Recovery tests were performed by adding known amounts of compound I to

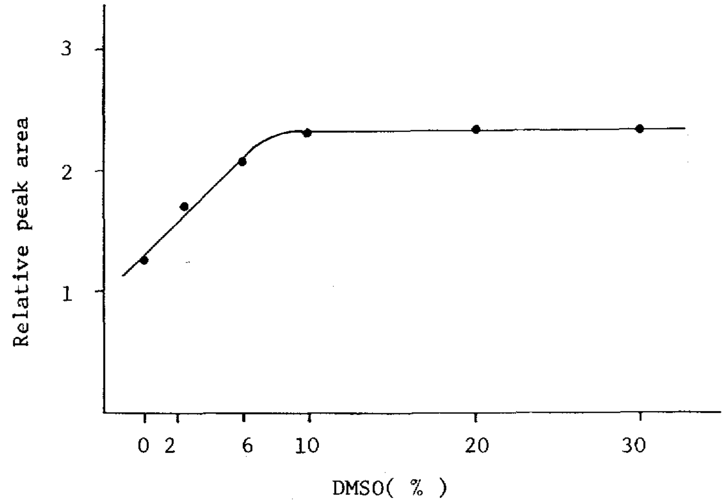


Fig. 4. Effect of the concentration of DMSO on the formation of 1-octadecene from commercial I-bonded dish cloth. Sample size: 200 mg.

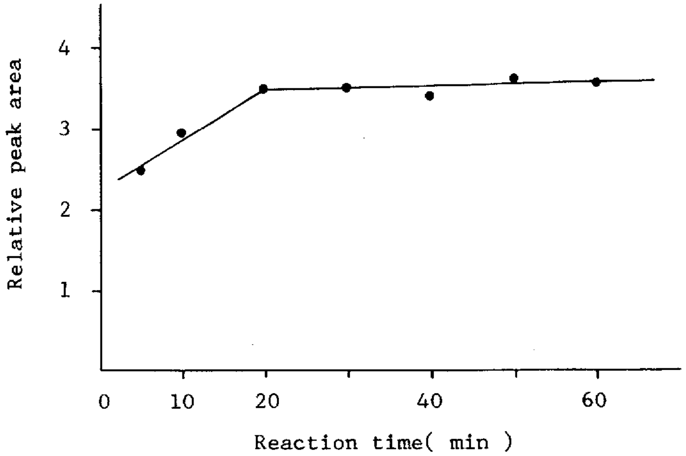


Fig. 5. Effect of the reaction time on the formation of 1-octadecene from commercial I-bonded dish cloth. Sample size: 200 mg.

a cotton fabric, *i.e.*, diaper, as shown in Table I. The results obtained were reproducible. Average recoveries in three experiments with 200–800 μg of compound I and 1584 μg of I-processed cotton fabric were 85.8–91.4% and the coefficient of variation (C.V.) was less than 4.0% for the entire procedure. The method was applied to the determination of compound I in commercial samples. The results in Table II show that these samples contained 0.10–0.74% of compound I.

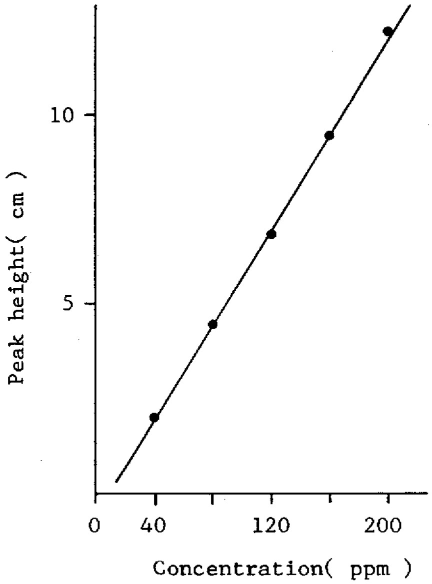


Fig. 6. Calibration curve for compound I.

TABLE I

RECOVERIES OF COMPOUND I FROM COTTON FABRICS

Sample	*Added (μg)*	*Av. recovery (n = 3) (%)*	*C.V. (%)*
Cotton fabric (diaper)*	200	91.4	2.2
	400	85.8	1.6
	600	89.6	1.2
	800	88.6	0.5
I-processed cotton fabric (diaper)**	1584	91.3	4.0

* Known amounts of compound I were added to 200 mg of the intact cotton fabric.

** Calculated amounts of compound I in 200 mg of cotton fabric were treated as described in ref. 2.

TABLE II

DETERMINATION OF COMPOUND I IN TEXTILE PRODUCTS

Sample	*Material*	*Content (%)*
Towel	100% Cotton	0.32
Dish cloth	100% Cotton	0.26
Dish cloth	100% Cotton	0.10
Socks	100% Cotton	0.74
Pajamas	70% Cotton 30% Polyester	0.18

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