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ANALYSIS OF ALKYLTRIMETHYL- AND DIALKYLDIMETHYLAMMONIUM COMPOUNDS BY GAS CHROMATOGRAPHY

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SUMMARY

A method for the determination of long-chain alkyltrimethylammonium chlorides (I–VII) and dialkyldimethylammonium chlorides (VIII, IX) by gas chromatography has been developed. The Hofmann degradation of I–IX with potassium *tert.*-butoxide in benzene–dimethyl sulphoxide (8:2) under reflux for 30 min gave quantitatively the corresponding 1-olefin. The 1-olefins obtained were measured by gas chromatography on a 5% SE-30 column. The proposed method could be applied to the analysis of these compounds in household products such as hair rinses, fabric softeners and antistatic aerosols.

INTRODUCTION

Cationic surfactants of the long-chain alkyltrimethylammonium and dialkyldimethylammonium types are widely employed in toiletry and household products such as hair rinses, hair treatments and fabric softeners. These ammonium compounds are usually homologous mixtures of C_{10}–C_{18} alkyl groups and are present at the level of 1–5% in hair rinses and many other commercial household products.

The determination of the type and homologous distributions of cationic surfactants is difficult due to their high polarities. Therefore, only a few analyses of these compounds have been reported. Kawase *et al.*[1,2] described the analysis of alkyltrimethylammonium compounds by flow injection analysis techniques and of dialkyldimethylammonium compounds by high-performance liquid chromatography. Metcalfe[3] attempted the determination of alkyltrimethyl- and dialkyldimethylammonium compounds by Hofmann degradation and with gas chromatography (GC) by direct injection on an alkali-treated column. Kojima and Oka[4] reported the lithium aluminium hydride reduction of these two types of ammonium compounds to alkyldimethylamines and dialkylmethylamines for GC analysis. However, the reduction products or thermal decomposition products obtained by such conversion methods were mainly the tertiary amines, not the corresponding 1-olefins.

This paper describes a new method for the convenient GC determination of

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cationic surfactants of the alkyltrimethylammonium and dialkyldimethylammonium types by Hofmann degradation. The non-volatile cationic surfactants were converted with potassium *tert.*-butoxide into the corresponding volatile 1-olefins amenable to GC.

EXPERIMENTAL

Apparatus

GC was carried out using an Hitachi Model 163 gas chromatograph fitted with an hydrogen flame ionization detector. Peak area measurements were obtained by a Shimadzu Chromatopac C-RIA digital integrator. Gas chromatography–mass spectrometry (GC–MS) was performed on a JEOL JMS-D300 instrument equipped with an Hewlett-Packard gas chromatograph. The mass spectra were recorded at 70 eV in the electron-impact ionization mode. Nuclear magnetic resonance (NMR) spectroscopy was carried out with a JEOL JNM-FX 270 instrument (^1H, 269.65 MHz; ^{13}C, 67.80 MHz). The spectra were recorded for solutions in deuterochloroform. Chemical shifts, δ (ppm), are downfield from tetramethylsilane as internal standard.

Reagents

Alkyltrimethylammonium chlorides with C_{12} (I), C_{14} (II), C_{16} (III) and C_{18} (IV) alkyl groups were purchased from Tokyo Kasei Kogio (Tokyo, Japan). Alkyltrimethylammonium chlorides with C_{20} (V), C_{22} (VI) and C_{24} (VII) alkyl groups and dialkyldimethylammonium chlorides with C_{16} (VIII) and C_{18} (IX) alkyl groups were obtained from Kao Soap Co. (Tokyo, Japan). Standard solutions were prepared by dissolving each ammonium compound in ethanol.

All other chemicals employed were of analytical grade.

Degradation procedure A for I–IX

An ethanolic solution containing 0.5–4 mg of compounds I–IX was placed in a 100-ml Kjeldahl type flask and evaporated to dryness under reduced pressure. A 100-mg amount of potassium *tert.*-butoxide and 25 ml of benzene–dimethyl sulphoxide (DMSO) (8:2) were added. The solution was refluxed on water-bath for 30 min. After cooling the flask to room temperature, the reaction solution was transferred to a 100-ml separating funnel. The flask was rinsed with two 5-ml portions of benzene. The rinsing solutions were added to the reaction solution and then washed with two 20-ml portions of 5% hydrochloric acid and with 10 ml of water. The benzene layer was separated, 1 ml of *n*-nonane was added and then evaporated to about 1 ml under reduced pressure. This residue was made up to 5 ml with hexane and 5 μl of the solution were injected into the gas chromatograph.

In the case of compounds VIII and IX, because alkyldimethylamine was obtained together with the 1-olefin, the hexane solution was subjected to further clean-up by silica gel column chromatography (silica gel 60, 2 g; 6 cm × 1 cm I.D.) with hexane to remove the alkyldimethylamine. The 1-olefin was eluted with 30 ml of hexane. To the hexane eluate was added 1 ml of *n*-nonane and then evaporated to about 1 ml under reduced pressure. This residue was dissolved in hexane as described above.

Degradation procedure B for samples such as hair rinse and fabric softener

All the samples containing the cationic surfactants I–IX were dissolved in a mixture of ethanol and benzene to yield 0.1–1.0% solutions of appropriate concentration for the GC determinations. Each solution (10 ml) was placed in a 100-ml Kjeldahl type flask, and degraded with potassium *tert.*-butoxide as described in procedure A. The reaction solution was evaporated under reduced pressure to remove the benzene, 10 ml of hexane were added and the mixture was transferred to a 100-ml separating funnel. The flask was rinsed with two 5-ml portions of hexane. The pooled hexane solutions were washed with 20 ml of 5% hydrochloric acid. The hexane layer was subjected to silica gel column chromatography, and the solution for the GC determinations prepared as in procedure A.

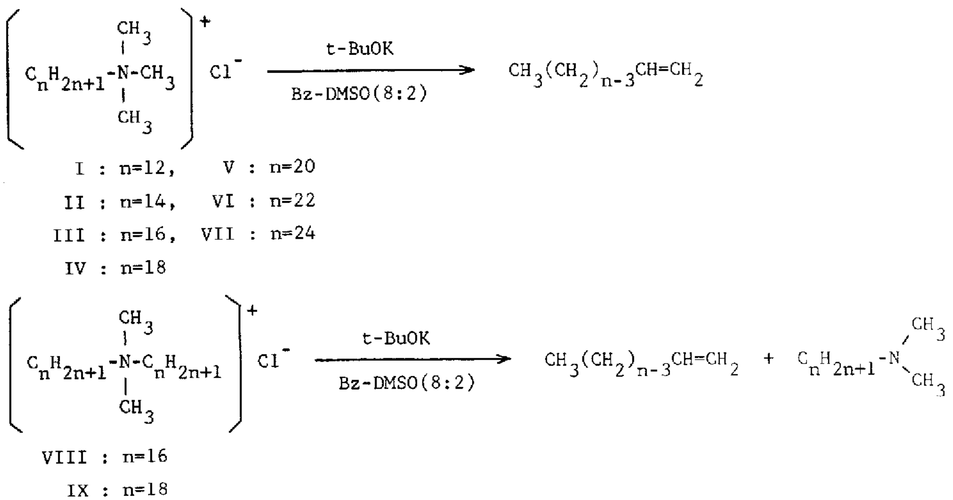
GC conditions

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) with a nitrogen flow-rate of 40 ml/min. The injection port and detector temperatures were 250°C. The column oven temperatures were as follows: (1) for identification of the degradation products, increased from 160 to 270°C at a rate of 6°C/min then isothermal until the end of the chromatogram; (2) for the examination of optimum reaction conditions, isothermal at 160°C; (3) for the construction of calibration curves, isothermal at 130°C (I), 150°C (II), 170°C (III, VIII), 190°C (IV, IX), 210°C (V), 230°C (VI) and 250°C (VII).

RESULTS AND DISCUSSION

Identification of degradation products

The ammonium compounds (I–IX, 30 mg) shown in Scheme 1 were degraded according to procedure A. The degradation products were identified by GC–MS and NMR spectroscopy after their isolation from the reaction mixture by silica gel col-

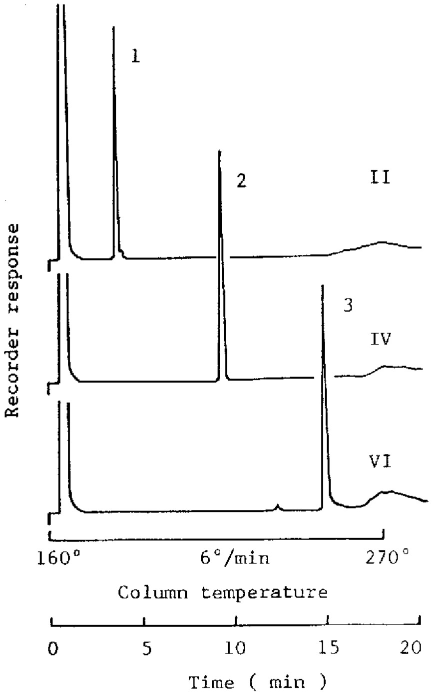


Scheme 1. t-BuOK = potassium *tert.*-butoxide; Bz = benzene.

umn chromatography. Each product from compounds I–VII gave one peak on the temperature-programmed gas chromatogram. Typical gas chromatograms of II, IV and VI are shown in Fig. 1. The mass spectra of the degradation products corresponding to peaks 1, 2 and 3 exhibited molecular ion peaks, M^+, at *m/z* 196, 252 and 308, respectively. The ^1H NMR spectra of the degradation products indicated the presence of methyl (δ 0.88 ppm, 3H, t, J = 6.6 Hz) and $-CH=CH_2$ groups (4.95, 2H, m; 5.80, 1H, m). These were also suggested by the signals at δ 14.2 (q), 114.1(t) and 139.3(d) ppm, and the signals of long-chain alkyl group were observed at 22.7(t), 29.0(t), 29.2(t), 29.4(t), 29.6(t), 29.7(t), 32.0(t) and 33.8(t) ppm in the ^{13}C NMR spectra. Therefore, the degradation products of compounds II, IV and VI were identified as 1-tetradecene, 1-octadecene and 1-docosene. The yield was 92–107% for 1-olefins.

On the degradation of compounds I, III, V and VII, each product was identified as 1-dodecene, 1-hexadecene, 1-eicosene and 1-tetracosene based on GC–MS and NMR spectral data, respectively.

The degradation products of compounds VIII and IX gave two peaks on the gas chromatograms as shown in Fig. 2. Peaks 4 and 5 were identified as 1-hexadecene and 1-octadecene by GC–MS and NMR spectroscopy. On the other hand, the degradation products corresponding to peaks 6 and 7 gave M^+ at *m/z* 269 and 297 in



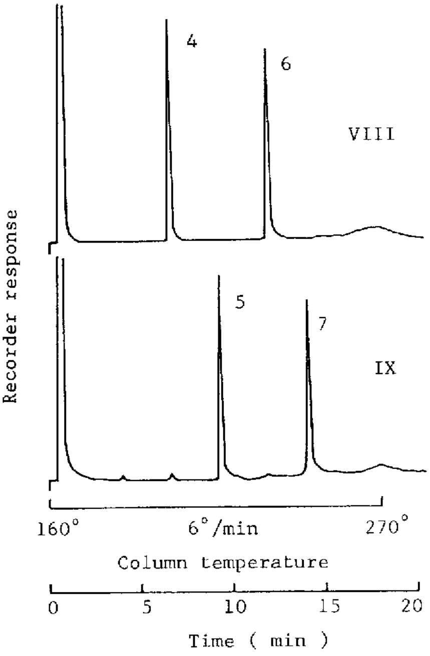


Fig. 1. Temperature-programmed gas chromatograms of 1-olefins derived from alkyltrimethylammonium chlorides (II, IV and VI). Peaks: 1 = 1-tetradecene; 2 = 1-octadecene; 3 = 1-docosene.

Fig. 2. Temperature-programmed gas chromatograms of 1-olefins and alkyldimethylamines derived from dialkyldimethylammonium chlorides (VIII and IX). Peaks: 4 = 1-hexadecene; 5 = 1-octadecene; 6 = hexadecyldimethylamine; 7 = octadecyldimethylamine.

the mass spectrum, and showed ^{1}H NMR signals due to a methyl group (0.88, 3H, t, J = 6.6 Hz) and two equivalent methyl groups bonded to a nitrogen atom (2.21, 6H, s). The ^{13}C NMR spectra also showed the presence of a methyl group at 14.2(q) ppm, long-chain alkyl group at 22.8(t), 27.7(t), 28.0(t), 29.6(t), 29.9(t) and 32.1(t) ppm and methyl and methylene groups bonded to a nitrogen atom at 45.5(q) and 60.1(t) ppm. Therefore, the degradation products were identified as hexadecyldimethylamine for peak 6 and octadecyldimethylamine for peak 7. The yield was 96–98% for 1-olefins and 93–98% for alkyldimethylamines.

In the Hofmann degradation of compounds I–IX, the corresponding 1-olefins were formed as the main product with release of tertiary amine based on β-elimination as shown in Scheme 1. Tanaka *et al.*[5] reported that alkyltrimethyl- and dialkyldimethylammonium salts yielded the 1-olefin and the tertiary amine, *i.e.*, alkyldimethylamine and dialkyldimethylamine, upon Hofmann degradation involving demethylation in the presence of sodium methoxide in dimethylformamide. The described method involving potassium *tert.*-butoxide provided a more selective β-elimination reaction than that with sodium methoxide as attempted by Tanaka *et al.*[5] It was confirmed that this mechanism consisted exclusively of the olefin-forming β-elimination at the nitrogen-bonded alkyl chain in compounds I–IX.

Optimum reaction conditions

The conditions for Hofmann degradation with potassium *tert.*-butoxide were examined. GC analysis of 1-olefins formed from 2 mg of compounds I–IV was performed under isothermal conditions at 160°C. Fig. 3 shows the effect of amount of potassium *tert.*-butoxide on the degradation. The results indicated that the 1-olefins were formed quantitatively when more than 60 mg of potassium *tert.*-butoxide were employed. Thus, the amount of potassium *tert.*-butoxide was set at 100 mg for the degradation of compounds I–IX. In the presence of this amount, the formation of 1-olefins was slightly increased by increasing the concentration of DMSO in benzene

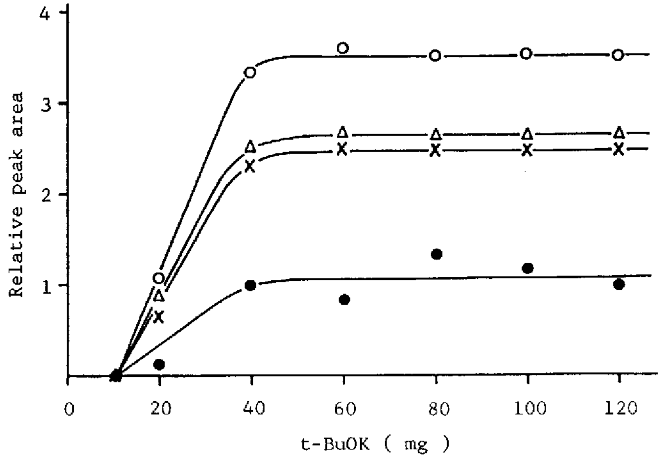


Fig. 3. Effect of the amount of potassium *tert.*-butoxide on the formation of 1-olefins from alkyltrimethylammonium chlorides. GC column temperature: 160°C. ●–●, I; ×–×, II; △–△, III and ○–○, IV.

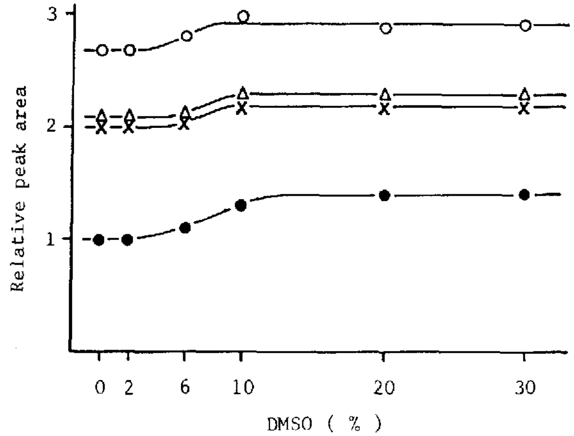


Fig. 4. Effect of DMSO concentration on the formation of 1-olefins from alkyltrimethylammonium chlorides (I–IV). GC column temperature and symbols as in Fig. 3.

and fairly constant on the addition of more than 10% of DMSO (Fig. 4). Benzene–DMSO (8:2) was chosen as the reaction solvent. As shown in Fig. 5, the reaction time for the degradation with 100 mg of potassium *tert.*-butoxide in 25 ml of benzene–DMSO (8:2) solution was 20 min. From these results, the recommended reaction conditions were as follows: 100 mg potassium *tert.*-butoxide; 20% DMSO in benzene; reaction time, 30 min.

Modification of analytical procedure

The procedure was modified for application to the determination of compounds I–IX in hair rinses and fabric softeners.

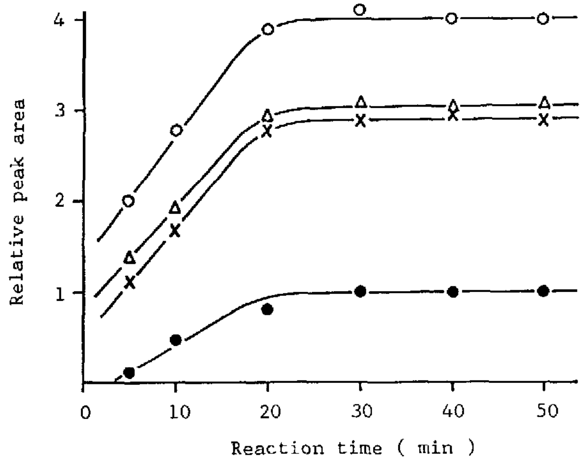


Fig. 5. Effect of reaction time on the formation of 1-olefins from alkyltrimethylammonium chlorides (I–IV). GC column temperature and symbols as in Fig. 3.

The potassium *tert.*-butoxide was inactivated by the presence of water contained in hair rinses or in ethanol used as solvent for the preparation of the sample solution, and the yield of 1-olefins was decreased. Thus, the sample solution made up with ethanol was completely evaporated to dryness under reduced pressure before degradation and freed from water and ethanol.

When the reaction solution was directly washed with 5% hydrochloric acid as in procedure B, shaking of the two phases frequently caused emulsification. The benzene layer was extremely difficult to separate from the aqueous emulsion of the examined hair rinses. Therefore, the reaction solution was freed from benzene under reduced pressure. The 1-olefin formed was extracted with hexane. However, the gas chromatograms of the hexane extracts were complicated with alkyldimethylamine derived from compounds VIII and IX and by interference, *e.g.*, from long-chain fatty alcohols such as cetyl alcohol and stearyl alcohol contained as emulsifier in hair rinses. Thus, the extracts were subjected to silica gel column chromatography for the removal of the tertiary amines and alcohols, as in procedure B.

Calibration curve

As shown in Fig. 6, the calibration curves of peak heights *vs.* concentration for compounds I–IX treated as in procedure B passed through the origin and showed good linearity over the range of 100–800 ppm. The GC measurements were carried out under isothermal column conditions where the 1-olefin appeared at a retention time of about 5 min. The detection limit for each ammonium compound from I–IX was approximately 40 ppm.

Application to practical product analysis

Recovery tests were performed by adding known amounts of compounds II, IV, VII and IX to a laboratory-made hair rinse as shown in Table I. Average recoveries in three experiments were 96.3–102.0% for II, IV and VI, and 96.3–101.6% for

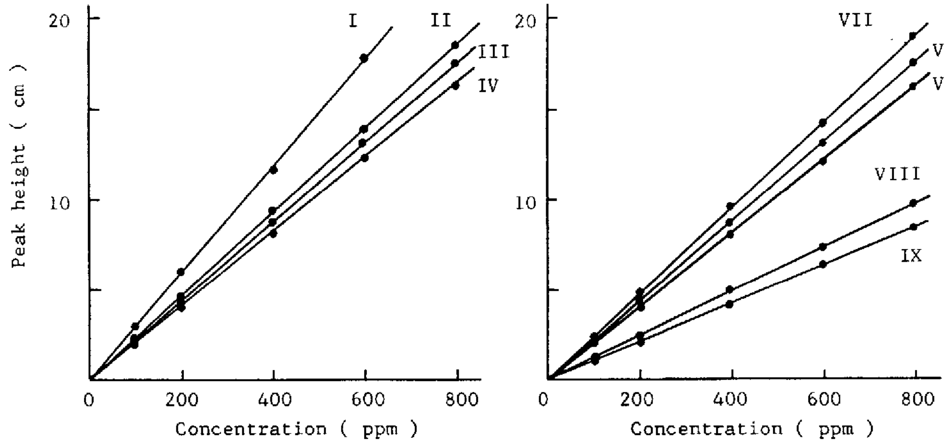


Fig. 6. Calibration curves for alkyltrimethyl- and dialkyldimethylammonium chlorides. Column temperatures: I, 130°C; II, 150°C; III, 170°C; IV, 190°C; V, 210°C; VI, 230°C; VII, 250°C; VIII, 170°C; IX, 190°C.

TABLE I

RECOVERIES OF ALKYLTRIMETHYL- AND DIALKYLDIMETHYLAMMONIUM CHLORIDES FROM HAIR RINSE

The quaternary ammonium chlorides were added to 0.5 g of laboratory-made rinse, the composition of which is as follows: 0.5% cetyl alcohol; 4% propylene glycol; 1% methylcellulose (mol.wt. 4000), colour and perfume q.s.; made up with purified water.

Compound	*Added (mg)*	*Average recovery (n=3) (%)*	*C.V. (%)*
II	1.0	97.0	2.9
	2.0	102.0	1.0
	3.0	97.0	3.0
IV	1.0	98.1	1.5
	2.0	96.4	1.7
	3.0	96.9	2.0
VI	1.0	101.7	1.7
	2.0	98.3	1.0
	3.0	98.3	1.0
VIII	1.0	98.7	1.9
	2.0	96.3	2.7
	3.0	101.6	1.6
IX	1.0	101.0	1.0
	2.0	100.0	1.4
	3.0	100.0	1.0

VIII and IX using the entire procedure B. A good reproducibility was obtained, and the coefficient of variation (C.V.) was less than 3.0%. Table I demonstrates that the proposed method can be applied to commercial product analysis.

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