

biological role of these compounds? Third, what is the optimum incubation time, temperature, and medium for the production of these metabolites?

Registry No. I, 90108-63-7; II, 90108-64-8.

Supplementary Material Available: Fractional coordinates and temperature factors (Table I), bond distances (Table II), and bond angles (Table III) (4 pages). Ordering information is given on any current masthead page.

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Thermal Degradation of Sodium Dodecyl Sulfate

John M. Patterson,* Zbigniew Kortylewicz, and Walter T. Smith, Jr.

Pyrolysis at 700 °C of a technical grade of sodium dodecyl sulfate that contained an alkyl group distribution of 56.7% dodecyl, 37.5% tetradecyl, and 5.8% hexadecyl resulted in a 65% weight loss and produced 47% of condensable material and 18% of noncondensable gases (largely SO₂). The condensable products consisted of the corresponding isomeric alkenes, primary alcohols, and ethers. A substantial amount of the mixed ether, dodecyl tetradecyl ether, was formed along with didodecyl and ditetradecyl ethers. In a cytotoxicity screening procedure using cultured Hamster embryo cells, some of the condensable pyrolyzate components were found to be more toxic than aniline.

Sodium dodecyl sulfate, a widely used surfactant, may be found in the chemical residues on certain crops as a result of the application of agricultural chemical formulations. In the case of tobacco crops, these residues will be subjected to high temperatures during the use of the tobacco (smoking) and may be expected to undergo pyrodegradation. In related work we have found that the nature of the "inert" ingredient in commercial formulations of agricultural chemicals can make a significant difference in the cell toxicity of the pyrolyzate obtained on thermo-

lysis of the formulation. The thermal decomposition of sodium dodecyl sulfate (SDS) and homologues has been investigated extensively under a variety of conditions. Aqueous solutions of SDS are converted completely to the corresponding alcohols at 270 °C in a GC injection port (Malin and Chapoteau, 1981) while pyrolysis alone at 650 °C is reported to produce 1-alkenes and the corresponding alcohols (Liddicoet and Smithson, 1965). When the SDS is mixed with phosphorus pentoxide and pyrolyzed at 400 °C, only 1-alkenes and internal alkenes of the same carbon number are obtained (Lew, 1967). The pyrolysis of sodium octyl sulfate in mixture with KOH at 400 °C leads to isomeric alkenes, alcohols, and ethers (Nakagawa, 1968), and it is stated without details that the same kinds of

*Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055.

products were obtained without the use of the alkali metal hydroxide.

In this report, we describe the behavior of a technical grade of sodium dodecyl sulfate under controlled pyrolysis conditions (700 °C) that simulate smoking and examine the cell toxicities of the pyrolyzate fractions.

EXPERIMENTAL SECTION

General. Gas chromatographic analyses were carried out on a 12 ft × 0.375 in. 10% SE-30 column kept at 80 °C for 3 min and then programmed at 4 °C/min to 256 °C. The final temperature was maintained for 25 min. Infrared spectra were measured on a Beckman IR-8 spectrophotometer, mass spectra were taken on a Hitachi Perkin-Elmer RMU-6E mass spectrometer or a VG Instruments ZAB-2F Micro Mass mass spectrometer, and NMR spectra were taken on a Varian Model T-60 spectrometer.

Material. A technical grade of sodium dodecyl sulfate [mp 172–179.5 °C; NMR (Me₂SO) δ 0.72 (t, 3 H), 0.87–1.63 (br s, 20 H), 3.53 (t, 2 H)] was used in the pyrolysis experiments as obtained. Heating the sample in vacuo at 185 °C for 72 h produced less than a 0.2% weight loss and extraction with hot acetone and chloroform followed by gas-liquid phase chromatography (GLPC) examination of the concentrated extracts showed no organic impurities. Treatment of the sample with 1-methyl-3-(*p*-tolyl)triazine in ether followed by GLPC analysis of the residue obtained after workup revealed no impurities.

Alkyl Group Distribution in Technical Sodium Dodecyl Sulfate. Hydrolysis was accomplished by refluxing 2.5 g of the sodium dodecyl sulfate sample in 1:1 H₂O–H₂SO₄ for 6 h. The cooled mixture was neutralized with 30% NaOH and extracted with chloroform, and the CHCl₃ extracts were dried over molecular sieves. Evaporation of the solvent produced 1.44 g (87%) of alcohol mixture, which was analyzed by GLPC. The mixture consisted of 56.7% dodecanol, 37.5% tetradecanol, and 5.8% hexadecanol.

Methods. *Pyrolyses.* The pyrolyses were carried out in the controlled pyrolysis apparatus previously described (Smith et al., 1975) connected to a pair of water traps and equipped with a valve so that gas samples could be diverted into an IR gas cell (100 mm).

In a typical pyrolysis, 5.213 g of the sodium dodecyl sulfate was spread evenly over a 60-cm length of the quartz pyrolysis tube and the tube was swept with a stream of nitrogen (200 mL/min). The furnace was heated to 700 °C and driven along the pyrolysis tube at a rate of 5.4 cm/min. The pyrolyzate, a mixture of yellow oil and white solid, 2.460 g (47%), migrated in front of the moving furnace leaving behind 1.830 g (35%) of black residue. The weight loss was assumed to be due to gases produced—0.923 g, (18%). The percent yields from five similar experiments were within ±2% of the values reported above.

Product Analysis. (1) *Gases.* The infrared spectrum showed bands typical of SO₂, SO₃, and CO₂ [2350, 1600 (w), 1380 (s), 1355, 1365 (s), 1180 (w), 1190 (w) cm⁻¹]. (2) *Residue.* The black residue was dissolved in water (solution pH 9–10) and filtered to remove a small amount of insoluble material. The filtrate was tested for the presence of sulfite, sulfate, and thiosulfate (Evans et al., 1942). Only sulfite was present.

Water Traps. The water in the traps had a pH of 5 and contained sulfate and sulfite anions. A small amount of unidentified oily liquid was present.

Pyrolyzate. The mixture of the yellow oil and white solid was dissolved in CHCl₃ and analyzed by infrared spectroscopy and GLPC. The infrared spectrum showed

Table I. Pyrolyzate Composition from Technical Sodium Dodecyl Sulfate

fraction	component	concn, wt %
1	dodecene mixture	18
2	tetradecene mixture	13
3	1-dodecanol	29
4	hexadecene mixture	4
5	1-tetradecanol	8
6	mixture ^a	<2
7	didodecyl ether	13
8	dodecyl tetradecyl ether	11
9	ditetradecyl ether	3
10	unknown ether	<1

^a Mixture consisted of at least four components, one of which was 1-hexadecanol.

no absorption due to S–O, and thus probably very little if any undecomposed starting material is present in the pyrolyzate. Analysis of the pyrolyzate solution by GLPC showed 10 peaks that were separated into 10 fractions by preparative GLPC. The fractions thus collected were examined by IR, NMR, and mass spectroscopy. The results of the GLPC analysis are summarized in Table I.

Properties of Pyrolyzate Fractions. *Fraction 1.* Partially resolved into at least three components, one with a retention time corresponding to that of 1-dodecene: IR (neat) 3080, 3020, 2960, 2920, 2860, 1970, 1695, 1385, 1000, 975, 920, 820, 730 cm⁻¹; NMR (CDCl₃) δ 1.00 (t), 1.45 (s), 1.78 (t), 2.15 (q), 4.96–5.27 (three m), 5.48–5.60 (m), 5.66–6.20 (m); mass spectrum *m/e* 168 (M⁺). The IR spectrum is identical with that of 1-dodecene ("Sadtler Standard Spectra", 1972, 1974) except for peaks at 975 and 820 cm⁻¹. These latter peaks are attributable to internal alkenes. The NMR spectrum is identical with that reported for 1-dodecene (Pouchert and Campbell, 1974) except for resonances appearing at 5.48–5.60 ppm.

Fraction 2. Partially resolved by GLPC into two components: IR (neat) is essentially the same as that from fraction 1, a band at 975 cm⁻¹ suggesting the presence of 2-alkene; NMR (CDCl₃) δ chemical shifts and resonance shapes the same as those from fraction 1 [the NMR spectra of literature 1-alkenes are essentially the same; see spectra in Pouchert and Campbell (1974)]; mass spectrum *m/e* 196 (M⁺); a tetradecene mixture.

Fraction 3. The GLPC retention times and the IR and NMR spectra were identical to those obtained from an authentic sample of 1-dodecanol: mass spectrum *m/e* 168 (M⁺ – 18).

Fraction 4. The IR and NMR spectra of this fraction were similar to those of fractions 1 and 2. The mass spectrum, *m/e* 224 (M⁺), suggests that the fraction is a hexadecene mixture.

Fraction 5. The GLPC retention time and the IR and NMR spectra were identical with those obtained from an authentic sample of 1-tetradecanol: mass spectrum *m/e* 196 (M⁺ – H₂O).

Fraction 6. According to the GLPC analysis this fraction consisted of at least four partially resolved components. The GLPC retention time of one of the peaks corresponded to that of 1-hexadecanol. The IR spectrum of the fraction was identical in every respect (band position and intensity) with that obtained from an authentic sample except for additional peaks occurring at 1650, 820, and 815 cm⁻¹.

Fraction 7. This fraction, a white solid melting at 31–33 °C [lit. mp 32–33 °C (Ueno et al., 1949)], gave GLPC retention time and IR and NMR spectra that were identical with those obtained from authentic didodecyl ether. The mass spectrum (15 eV) gave a cluster of peaks around the parent ion, *m/e* (rel intensity for peaks in cluster) 354

Table II. Preliminary Mammalian Toxicities in Me₂SO

fraction	component	toxic dose
1	dodecenes	nontoxic at 292 ppm
2	tetradecenes	nontoxic at 140 ppm
3	1-dodecanol	TD ₇₅ = 55
4	hexadecenes	TD ₂₅ = 65
5	1-tetradecanol	TD ₅₀ = 62
6	hexadecanol mixture	TD ₅₀ = 80
7	didodecyl ether	TD ₂₅ = 33
8	dodecyl tetradecyl ether	nontoxic at 150 ppm
9	ditetradecyl ether	TD ₂₅ = 36
	aniline ^a	TD ₅₀ = 200
	carbaryl ^a	TD ₅₀ = 8
	1-naphthol ^a	TD ₅₀ = 8

^aSubstances included for comparison of toxicities.

(3, M⁺), 355 (100, M⁺ + 1), and 356 (27, M⁺ + 2). The M + 1 peak was the most intense peak in the 70-eV mass spectrum.

Fraction 8. This solid fraction was 92% pure as determined by analytical GLPC and melted at 39–41 °C. The IR spectrum was essentially the same as those reported for ditetradecyl ether (Sadler, 1972, 1974) and for didodecyl ether (fraction 7): NMR (CCl₄) δ 0.92 (t, ~6 H), 1.30 (br s, ~44 H), 3.32 (t, ~4 H). The mass spectrum gave a cluster of peaks around the parent ion, *m/e* (rel intensity for peaks in cluster) 381 (22, M⁺ - 1), 382 (12, M⁺), 383 (100, M⁺ + 1), and 384 (31, M⁺ + 2).

Fraction 9. This fraction, 97% pure as indicated by GLPC analysis, melted at 40–42 °C with some softening and gave IR and NMR spectra and a GLPC retention times that were identical with those obtained from an authentic sample of ditetradecyl ether. The mass spectrum showed a cluster of peaks around the parent ion: *m/e* (rel intensity) 408 (16, M⁺ - 2), 409 (29, M⁺ - 1), 410 (13, M⁺), 411 (100, M⁺ + 1), and 412 (35, M⁺ + 2). Authentic ditetradecyl ether gave a similar cluster about the parent ion: 408 (5, M⁺ - 2), 409 (14, M⁺ - 1), 410 (6, M⁺), 411 (100, M⁺ + 1), and 412 (12, M⁺ + 2).

Fraction 10. The amount of material collected in this fraction was too small for positive identification. The IR and NMR spectra were similar to those obtained for the ether fractions described above.

RESULTS AND DISCUSSION

An investigation of the technical sodium dodecyl sulfate sample showed that it did not contain free water or water of hydration and that impurities such as alkanes, alkenes, alcohols, and carboxylic acids were absent. The alkyl group distribution in the sample as determined by hydrolysis and GLPC analysis of the hydrolysate was 56.7% dodecyl, 37.5% tetradecyl, and 5.8% hexadecyl.

Under controlled pyrolysis conditions at 700 °C the sodium alkyl sulfate was converted into a mixture of isomeric alkenes, primary alcohols, and ethers whose alkyl groups corresponded to those present in the pyrolyzand mixture. These results parallel those observed in the batch pyrolysis of potassium ethyl sulfate at 350 °C (Nef, 1901) and of sodium octyl sulfate at 400 °C (Nakagawa et al.,

1968) in which alkenes, alcohols, and symmetrical ethers were produced. In the present report, it has been demonstrated that more complex mixtures arise during pyrolysis of technical grades of SDS as evidenced by the appearance of unsymmetrical ethers. Thus substantial amounts of dodecyl tetradecyl ether were formed along with didodecyl and ditetradecyl ethers.

The pyrolyzate fractions were screened for cytotoxicity by using cultured Hamster embryo cells. This system is reported (Smith et al., 1963; Christian et al., 1977) to give good correlations between cytotoxicity in vitro and toxicity in the whole animal for a wide variety of organic and inorganic chemicals.

The results (Table II) are reported as the toxic dose (TD) in ppm that resulted in inhibition of cell growth by the designated percent. For example, the TD₇₅ = 55 for 1-dodecanol means that a concentration of 55 ppm inhibited growth of 75% of the cells relative to a control.

The observation that certain pyrolyzate fractions produced in the thermal degradation of sodium dodecyl sulfate possess toxicities comparable to that of aniline suggests that the pyrolytic properties of the inert ingredient of agricultural formulations should be investigated when the end use of the agricultural product involves high temperatures (as in smoking). In addition, it would be desirable to determine the level and distribution of residues derived from the inert ingredients used in agricultural formulations.

Registry No. Dodecyl tetradecyl ether, 59012-60-1; didodecyl ether, 4542-57-8; ditetradecyl ether, 5412-98-6; 1-dodecene, 112-41-4; tetradecene, 26952-13-6; 1-dodecanol, 112-53-8; hexadecene, 26952-14-7; 1-tetradecanol, 112-72-1.

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