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Note

Degradation and analysis of oligooxyethylene glycol mono(4-*tert.*-octylphenyl) ethers in the presence of acetyl chloride

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Polyoxyethylene glycol mono(4-alkylphenyl) ethers, $RC_6H_4O(CH_2CH_2O)_nH$, are important non-ionic surfactants used in different fields of industry. Up to now these surfactants have been uniquely those in which the alkyl group is not straight-chain but branched. Moreover, this alkyl group is usually obtained by oligomerization of branched alkenes, usually propene or isobutene. The composition of such commercial products is very complex owing to the presence of several so far unidentified compounds in alkylphenols. For this reason, it is difficult to carry out direct analysis and it is impossible to separate and identify all components. Homologues having different numbers of the oxyethylene group can be separated but they elute in the form of broad multi-component peaks.

The aim of this work was to study the degradation of model oligooxyethylene glycol mono(4-*tert.*-octylphenyl) ethers and the application of this degradation to the determination of the average degree of ethoxylation.

EXPERIMENTAL

The following reagents were used for degradation: model oligooxyethylene glycol mono(4-*tert.*-octylphenyl) ethers (ICSO "Blachownia", Kędzierzyn-Koźle, Poland) obtained by the reaction of 4-*tert.*-octylphenol with ethylene oxide; acetyl chloride, pure for analysis (Fluka, Buchs, Switzerland); and anhydrous iron(III) chloride, pure for analysis (POCh, Gliwice, Poland).

Degradation of oligooxyethylene glycol mono(4-*tert.*-octylphenyl) ethers in the presence and obsence of iron(III) chloride was carried out according to the procedures given in previous papers[1–3], based on Waszeciak and Nadeau's method[4].

The following three different gas chromatographic (GC) columns were used: column I (0.9 m × 2.7 mm I.D.), filled with silicone resin OV-17 (3%) on Chromosorb G AW DMCS, 60–80 mesh; column II (0.9 m × 2.7 mm I.D.), filled with silicone resin

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OV-101 (3%) on Chromosorb G AW DMCS, 60–80 mesh; and column III (1.6 m × 2.7 mm I.D.), filled with Carbowax 20M–TPA (12%) on Chromosorb W AW DMCS, 80–100 mesh. The temperature of column I was 80°C for 1 min, then increased to 290°C at 6°C/min. The temperature of column II was 100°C for 1 min, then increased to 300°C ay 8°C/min. The temperature of column III was 100°C for 1 min, then increased to 220°C at 5°C/min.

The identification of the separated components was carried out by means of a mass spectrometer coupled to a gas chromatograph (GC-MS 2091; LKB, Bromma, Sweden). Columns I and II were used to identify components formed from the alkylphenyl groups and oligooxyethylene chains, respectively. The separation conditions were the same as in the GC analysis. The mass spectra were taken at the tops of the chromatographic peaks. An ionization energy of 70 eV and an ion-source temperature of 250°C were employed.

The degree of degradation (α_d) was calculated according to

$$\alpha_d = \frac{\sum_{n=1}^{m} x_n}{\sum_{n=1}^{m} x_n + \sum_{i=1}^{j} x_i} \cdot 100\% \tag{1}$$

where x_n denotes the content of component n (%, w/w) formed during degradation and x_i the content of homologue i of polyoxyethylene glycol mono(4-*tert.*-octylphenyl) ether remaining in the post-reaction mixture after degradation.

The average degree of ethoxylation (α) was calculated according to eqn. 2 and the mass of the oligooxyethylene chain (m_{EO}) in the investigated sample according to eqn. 3.

$$\alpha = \frac{m_{EO} M_H}{44(m - m_{EO})} \tag{2}$$

$$m_{EO} = \sum_{i=1}^{j} \frac{44 m_s A_i K_{s,i} n_i}{A_s M_i} \tag{3}$$

where M_H and M_i denote the average molecular mass of the hydrophobic alkylphenyl groups and the molecular mass of a component i formed by degradation of the oligooxyethylene chains, respectively, m and m_s are the mass of the analysed sample and the mass of n-hexadecane used as the internal standard, respectively, A_s and A_i are surface areas of peaks of the standard and a component i formed by degradation of the oligooxyethylene chains, respectively, n_i is the number of oxyethylene groups needed to form a component i and $K_{s,i}$ denotes the relative correction factor of a component i in comparison with the internal standard.

A differential microcalorimeter (TA-2000A; Mettler, Greifensee, Switzerland) was used. A sample (0.002 g) of oligooxyethylene glycol mono(4-*tert.*-octylphenyl) ether and acetyl chloride (1:15, w/w) on silicon carbide was heated in an aluminium crucible covered with a perforated lid to 350°C at 25°C/min.

A mini-autoclave of capacity 0.5 cm^3 (Mettler) was used to register differential thermal analysis (DTA) curves under isochoric conditions. Samples (0.04 g) of oligooxyethylene glycol mono(4-*tert.*-octylphenyl) ether, acetyl chloride and iron(III) chloride (1:15:1, w/w/w) were heated from 60 to 200°C at 2°C/min. Benzene was used as a standard.

RESULTS AND DISCUSSION

4-*tert.*-Octylphenol, used as a reagent to obtain polyoxyethylene glycol mono-(4-*tert.*-octylphenyl) ethers (henceforth abbreviated to E), contains about 91% (w/w) of 4-(1,1,3,3-tetramethylbutyl)phenol. Using packed chromatographic columns, three additional components were separated and identified as 4-(1,1,4-trimethylpentyl)-phenol, 4-(1,1,3-trimethylpentyl)phenol and [2-(*tert.*-butyl)-4-(1,1,3,3-tetramethylbutyl)]phenol[5]. However, eleven components were separated as a capillary column was used. As a result, chromatograms of E, in addition to the main peaks of polyoxyethylene glycol mono[4-(1,1,3,3-tetramethylbutyl)phenyl] ethers having different numbers of oxyethylene groups, also contain polyoxyethylene derivatives of other alkylphenols[5].

Retention indices and the contents of successive homologues having different numbers of oxyethylene groups are given in Table I.

Thermograms of mixtures of E with acetyl chloride and/or without iron(III) chloride are presented in Figs. 1 and 2. Fig. 1 demonstrates that an endothermic effect is observed at temperatures of 30–110°C as a result of acetyl chloride evaporation. An exothermic effect above 110°C is caused by the acylation of E. A weak exothermic effect at 250–340°C observed for the system which do not contain iron(III) chloride is caused by slow degradation.

The DTA curve obtained under isochoric conditions (Fig. 2) demonstrates that in the presence of iron(III) chloride an exothermic effect is already observed at temperatures of 60–220°C and a significant increase in heat formed during degradation is observed above 150°C. Thus, in the presence of iron(III) chloride degradation proceeds much quicker and at lower temperatures. This is supported by chromatographic data, which demonstrates that complete degradation is impossible without the

TABLE I

RETENTION INDICES AND CONTENTS OF SEPARATED HOMOLOGUES IN OLIGOOXYETHYLENE GLYCOL MONO(4-*tert.*-OCTYLPHENYL) ETHERS

No. of oxyethylene groups	*Retention index, I_p*			*Content (%, w/w)*[a]
	OV-101	*OV-17*	*Carbowax 20M–TPA*	
0	1215–1638	1730–2114	2100–2592	2.75 ± 2.99
1	1759[b]–1843	2248[b]–2407	2668[b]–2835	90.25 ± 2.97
2	1991–2074	2549–2698	3062	7.00 ± 2.42
3	2237–2302	–	–	0.00

[a] Confidence limits for a significance level of 0.05 and 5 analyses.

[b] Main component, $(CH_3)_3CCH_2C(CH_3)_2$-p-$C_6H_4OCH_2CH_2OH$.

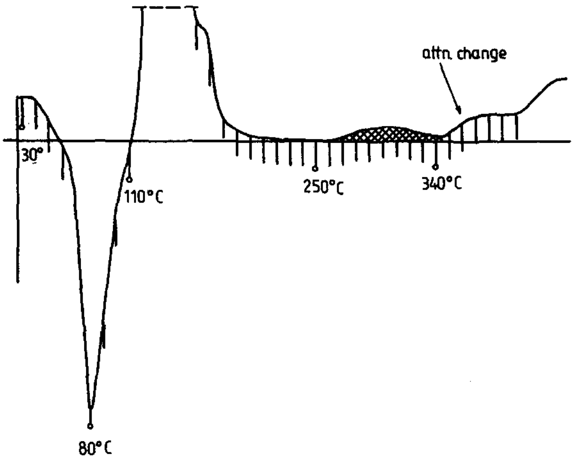

Fig. 1. DTA curve for a mixture of oligooxyethylene glycol mono(4-*tert*.-octylphenyl) ethers and acetyl chloride.

catalyst (Figs. 3 and 4). At 250°C the degradation of E is only about 45%. The degradation of polyoxyethylene glycol mono(4-nonylphenyl) ethers having an average degree of ethoxylation of 8 is even lower (30%). However, although the degradation is not complete, the products formed can be easily separated and identified. The degradation of the polyoxyethylene chain proceeds in the same way as was previously

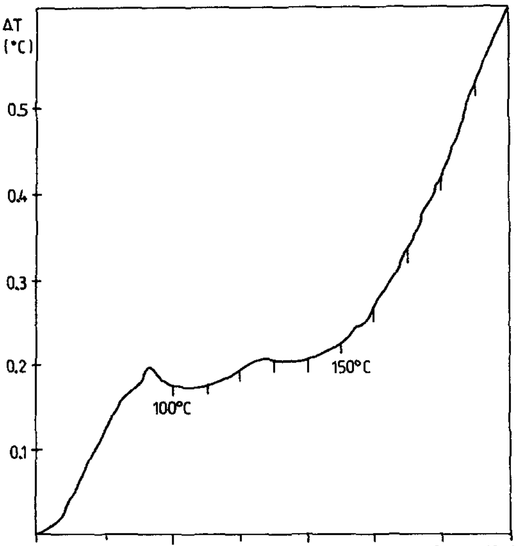

Fig. 2. DTA curve for a mixture of oligooxyethylene glycol mono(4-*tert*.-octylphenyl) ethers, acetyl chloride and iron(III)chloride (isochoric conditions).

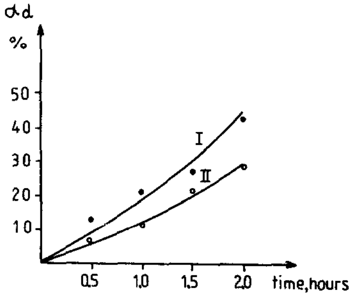

Fig. 3. Effect of time on the degradation of polyoxyethylene glycol mono(4-alkylphenyl) ethers in the absence of iron(III) chloride. (I) Oligooxyethylene glycol mono(4-*tert*.-octylphenyl) ethers; (II) polyoxyethylene glycol mono(4-nonylphenyl) ethers having an average degree of ethoxylation of 8. α_d = Degree of degradation calculated from eqn. 1.

demonstrated for polyoxyethylene glycols and their monoalkyl ethers[1–3]. 2-Chloroethyl acetate (retention index I_p = 1318) is the main degradation product and 1,2-dichloroethane (I_p = 1065), bis(2-chloroethyl)ether (I_p = 1536), 5-chloro-3-oxapentyl acetate (I_p = 1757) and dioxyethylene glycol diacetate (I_p = 1970) are formed in small amounts. Their mass spectra are similar to those reported previously[1].

In the presence of iron(III) chloride the degradation of E is complete at 150°C in 30 min (Figs. 5 and 6). Only three compounds formed from the polyoxyethylene chain were identified: 2-chloroethyl acetate (I_p = 1318 and 926 on Carbowax 20M–TPA and OV-17, respectively), bis(2-chloroethyl)ether (I_p = 1536 and 1220 on Carbowax 20 M–TPA and OV-17, respectively) and dioxyethylene glycol diacetate (I_p = 1970

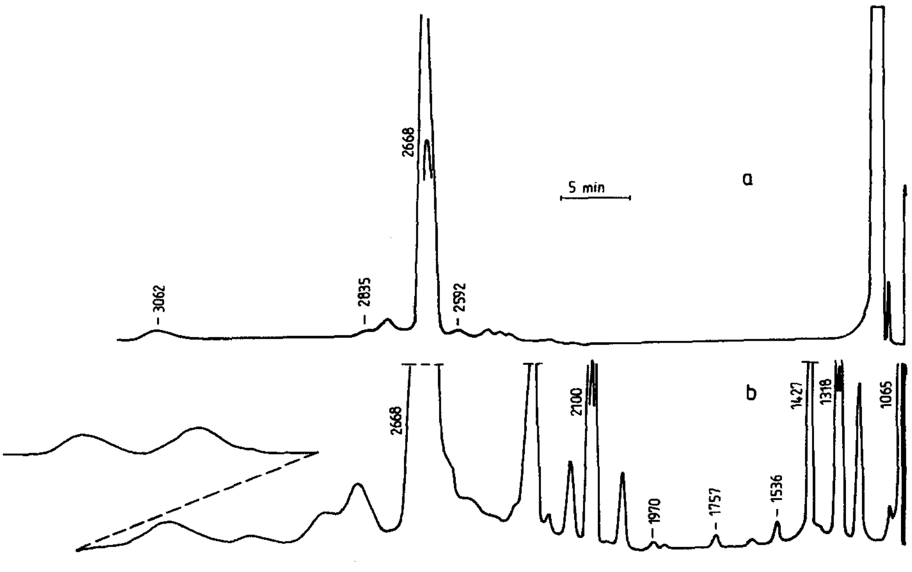

Fig. 4. Chromatogram of oligooxyethylene glycol mono-(4-*tert*.octylphenyl) ethers, (a) before and (b) after degradation without iron(III)chloride (column III, Carbowax 20M–TPA).

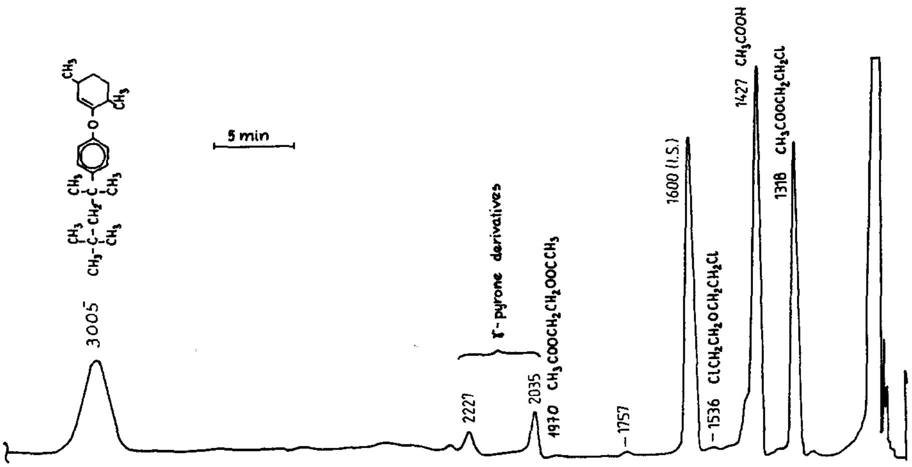

Fig. 5. Chromatogram of the degradation products with column III, Carbowax 20M-TPA.

and 1491 on Carbowax 20M–TPA and OV-17, respectively). As in previous work[1–3], peaks of acetic acid (I_p = 1427 on Carbowax 20 M–TPA) and of γ-pyrone derivatives (I_p = 2035 and 2227 on Carbowax 20 M–TPA) were observed. Acetic acid was formed from acetyl chloride, whereas γ-pyrone derivatives were formed from acetic acid. Hexadecane was used as the internal standard. All other peaks separated on OV-17 correspond to compounds obtained from alkyl phenyl groups (I_p = 2035, 2180, 2494, 2574, 2661, 2830, 3032 and 3085). Some of them were identified by their mass spectra (Fig. 7), which have lines of molecular ions and those formed by typical splitting of alkyl groups. Structures of other components were suggested taking into account their

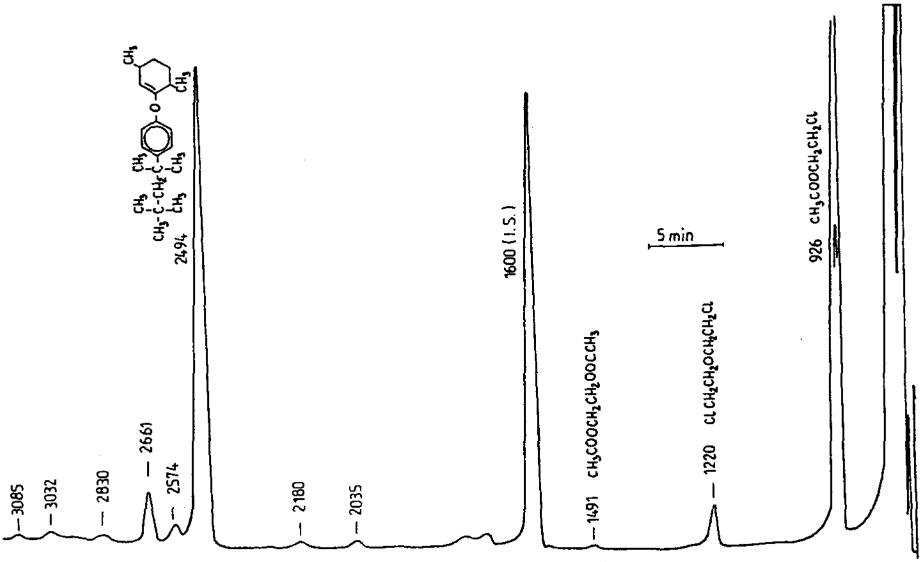

Fig. 6. Chromatogram of the degradation products with column I, OV-17.

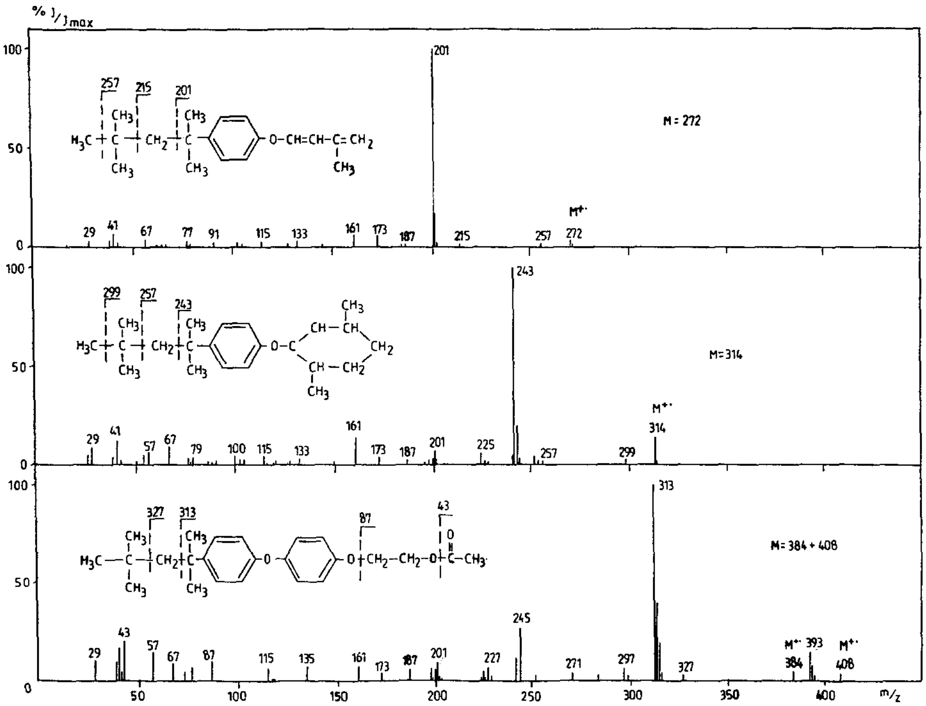

Fig. 7. Mass spectra of the products formed from alkylphenyl groups.

retention indices and those predicted from the group increments determined previously[6].

The compositions of the degradation products and their retention indices are given in Table II. The results demonstrate that 4-(1,1,3,3-tetramethylbutyl)phenyl-3,6-dimethyl-1-cyclohexenyl ether is the main compound formed from alkylphenyl groups. However, most of the alkylphenyl groups react towards unidentified resins which do not elute from the column.

Values of the average degree of ethoxylation calculated from the direct chromatographic analysis, *i.e.*, without degradation and by means of degradation, are presented in Table III. Good agreement between the results obtained by means of these two methods is observed, the average difference being only about 4%. Hence, the proposed method of degradation can be used to determine the average degree of ethoxylation of oligooxyethylene glycol mono(4-alkylphenyl) ethers. Its application to complex industrial preparations will be considered in the near future.

CONCLUSIONS

Oligooxyethylene glycol mono-(4-alkylphenyl) ethers can be degraded with an excess of acetyl chloride in the presence of anhydrous ion(III) chloride at 150°C in 0.5 h. Oligooxyethylene chains are degraded mainly to 2-chloroethyl acetate, while unidentified resins are mainly formed from alkylphenyl groups. 4-(1,1,3,3-Tetra-

TABLE II

COMPOSITION OF PRODUCTS OBTAINED BY DEGRADATION OF OLIGOOXYETHYLENE GLYCOL MONO(4-*tert.*-OCTYLPHENYL) ETHERS

Type of product[a]	*Component*	*Retention index*		*Content (%, w/w)*
		OV-17	*Carbowax 20M–TPA*	
I	2-Chloroethyl acetate	926	1318	16.21
	Bis(2-chloroethyl)ether	1220	1536	0.46
	Dioxyethylene glycol diacetate	1491	1970	0.19
II	4-(1,1,3,3-Tetramethylbutyl)phenyl-3-methyl-1,3-butadienyl ether	2035	2546	0.20
	4-(1,1,3,3-Tetramethylbutyl)phenyl-3-methyl-1-cyclobutenyl ether	2180	2726	0.45
	4-(1,1,3,3-Tetramethylbutyl)phenyl-3,6-dimethyl-1-cyclohexenyl ether	2494	3005	22.31
	4-Octylphenyl-3,6-dimethyl-1-cyclohexenyl ether	2574	3107	1.23
	4-(1,1,3,3-Tetramethylbutyl)phenyl-2-(3,6-dimethyl-1-cyclohexenyl)ethyl ether	2661	3206	2.70
	4,4′-Di(1,1,3,3-tetramethylbutyl)biphenyl	2830	–	0.49
	4-(1,1,3,3-Tetramethylbutyl)phenyl-4′-	3032	–	0.20
	(1,1,3,3-tetramethylbutyl)methylphenyl ether	3032	–	0.20
	4-(1,1,3,3-Tetramethylbutyl)phenyl-4′-(2-acetoxyoxyethyl)phenyl ether	3085	–	0.15
	High-boiling resins	–	–	55.11

[a] I and II denote components obtained from the polyoxyethylene chains and alkylphenyl groups, respectively.

TABLE III

AVERAGE DEGREE OF ETHOXYLATION OF OLIGOOXYETHYLENE GLYCOL MONO-(4-*tert.*-OCTYLPHENYL) ETHERS

Parameter	*Direct chromatographic analysis (a)*	*Analysis after degradation (b)*	*b – a*	$\Delta(\%) = \frac{b-a}{a} \cdot 100$
Degree of ethoxylation (individual values)	0.98	0.96	–0.02	–2.04
	0.98	0.93	–0.05	–5.10
	0.98	0.90	–0.08	–8.16
	0.98	1.03	+0.05	5.10
	1.01	0.92	–0.09	–8.91
Average degree of ethoxylation	0.99	0.95	–0.04	–3.82
Standard deviation	0.01342	0.05070		
Confidence limits[a]	±0.02	±0.07		

[a] For a significance level of 0.05 and 5 analyses.

methylbutyl)phenyl-3,6-dimethyl-1-cyclohexenyl ether is the main low-molar-mass component formed from alkylphenyl groups. The contents of the compounds obtained by degradation of oligooxyethylene chains can be precisely determined and used to calculate the average degree of ethoxylation. Good agreement is observed between the average degree of ethoxylation determined by direct chromatographic analysis and after degradation.

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