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Note

Petrochemical analytical problems

IV.* Gas–liquid chromatographic–mass spectrometric investigation of the desulphonation of dodecylbenzenesulphonic acids**

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Biodegradability and other important characteristics of alkylbenzenesulphonates (ABS) are strongly, sometimes decisively, influenced by the structure of the alkyl chain[1]. The structure of the remainder of the hydrocarbon skeleton cannot be analyzed in the sulphonates, while gas–liquid chromatography (GLC)[2–13], especially in combination with mass spectrometry (MS)[14], was shown to be a good method for the analysis of the corresponding alkylaromatic hydrocarbons. Therefore, the desulphonation of ABS products (or of their salts) is of primary importance in this field.

The most reliable desulphonation procedure was suggested by Knight and House[15], using orthophosphoric acid as desulphonation agent. They found that (i) the yield of the desulphonated alkylbenzene (AB) is nearly quantitative and (ii) the gas chromatogram and (iii) the mass spectrum of the product AB mixture are very similar to those of the starting (before sulphonation) AB mixture. Nevertheless, they used packed columns for GLC and their MS measurements were performed with a mixture of isomeric ABs. As the desulphonation with orthophosphoric acid is a rather difficult procedure, changes in the remainder of the hydrocarbon skeleton cannot be excluded. Therefore, it seemed necessary to reinvestigate the desulphonation reaction using capillary columns in combination with on-line MS analysis of each individual peak.

EXPERIMENTAL

Linear alkylbenzenes were tested where almost all the components are eluted

* For Part III, see I. Ötvös, I. Martinusz and G. Pályi, *J. Chromatogr.*, 93 (1974) 413.
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as separate peaks. Sulphonation was performed with a 10% excess of 20% oleum at 60° for 1 h, followed by neutralization with 15% sodium hydroxide solution. The ABS content of the neutral product was determined* by the methylene blue method[16–18]. Desulphonation was carried out by the method of Knight and House[15]. Yields* from the desulphonation reaction were 100 ± 4.8%. GLC–MS experiments were performed as described earlier[14].

RESULTS AND DISCUSSION

Experimental results obtained with Marlikan (Hüls, Marl, G. F. R.) and Dobane JN (Shell, Rotterdam, The Netherlands) are shown in Tables I and II. Comparison of the analysis of the starting and recovered AB mixtures provides unequivocal evidence that the desulphonation of linear ABS leaves the remainder of the hydrocarbon

TABLE I

GLC–MS ANALYSIS OF STARTING AND DESULPHONATED MARLIKAN
FID and electron ionisation detector (EID) response factors were taken as 1.00.

Compound[a]	*Starting sample* (%)	*Desulphonated sample* (%)	*Compound*[a]	*Starting sample* (%)	*Desulphonated sample* (%)
$5C_{10}LB$	1.9	1.9	$5-6C_{12}LB$[f]	6.9	7.3
$4C_{10}LB$	1.9	2.0	$4C_{12}LB$	4.7	5.0
$3C_{10}LB$	2.8	2.8	$3C_{12}LB$	5.4	5.4
AB[b]	0.9	0.7	AB[g]	0.5	—[k]
AB[b,c]	0.7	0.7	$C_{17}H_{26}$[h]	0.2	—[k]
$2C_{10}LB$	4.2	4.6	$C_{17}H_{26}$[i]	0.5	0.5
$6C_{11}LB$	5.1	5.3	$7C_{13}LB$[j]	0.3	0.1
$5C_{11}LB$	10.2	10.6	$6C_{13}LB$[j]	0.2	0.7
$4C_{11}LB$[d]	8.0	8.1	$2C_{12}LB$[j]	7.3	8.2
$3C_{11}LB$	8.3	8.3	$5C_{13}LB$	2.0	2.3
AB[e]	0.9	0.7	$4C_{13}LB$	1.6	1.9
$2C_{11}LB$	22.4	21.7	$3C_{13}LB$	1.5	1.5
			$2C_{13}LB$	1.4	0.8

[a] Abbreviated formulae (as in ref. 14) are used: first, a number indicates the position of the phenyl group on the alkyl chain, then the carbon number (n) of the alkyl group is indicated as C_n followed by the LB notation of linear-chain alkylbenzenes; for example, $3C_{11}LB$ = 3-phenylundecane.

[b] Unidentified alkylbenzene(s); mole peak: $C_{17}H_{28}$.

[c] Most probably this GLC peak contains two components.

[d] Identified on the basis of retention time.

[e] Unidentified alkylbenzene(s). Most probably two components: $C_{17}H_{28}$ and $C_{18}H_{30}$.

[f] Might be only $5C_{12}LB$.

[g] Unidentified alkylbenzene(s), mole peak: $C_{18}H_{30}$.

[h] Probably indenyloctane(s).

[i] Unidentified hydrocarbon(s), alkylaromatic.

[j] These components give one GLC peak with 7.8 and 9.0%. The distribution was calculated on the basis of mass spectra.

[k] These two components could not be detected in the desulphonated sample.

* Mean molecular weights used in these calculations were averages of the osmometric and GLC–MS molecular weights determined previously[14]. These agree well with the data reported[3] for Dobane JN.

TABLE II

GLC–MS ANALYSIS OF STARTING AND DESULPHONATED DOBANE JN
FID and EID response factors were taken as 1.00.

Compound[a]	*Starting sample (%)*	*Desulphonated sample (%)*	*Compound*[a]	*Starting sample (%)*	*Desulphonated sample (%)*
$5C_{10}LB$[b]	6.1	7.3	X[c]	0.7	0.9
$4C_{10}LB$	5.1	5.6	$4C_{12}LB$	4.5	4.5
$3C_{10}LB$	4.0	4.0	$3C_{12}LB$	4.7	4.7
AB[c]	1.3	0.9	2-Me-2-Ph-undecane	1.7	1.8
$2C_{10}LB$	6.5	6.8	AB[f]	0.9	0.4
$6C_{11}LB$	2.7	3.8	$6C_{13}LB$[g]	3.0	2.5
$5C_{11}LB$	6.7	6.8	$2C_{12}LB$[g]	8.4	9.1
$4C_{11}LB$	5.1	3.9	$5C_{13}LB$	3.1	3.3
$3C_{11}LB$	5.6	5.5	$4C_{13}LB$	3.2	3.3
2-Me-2-Ph-decane[d]	1.5	1.3	$3C_{13}LB$	3.5	3.0
$2C_{11}LB$	5.3	5.0	2-Me-2-Ph-dodecane[d]	1.0	2.1
$6C_{12}LB$	5.7	5.6	$2C_{13}LB$[b]	3.9	3.7
$5C_{12}LB$	5.5	5.8			

[a] Abbreviations as in Table I.
[b] Identified on the basis of retention time.
[c] Unidentified alkylbenzene(s); mole peak: $C_{16}H_{26}$.
[d] The MS assignment of the structure is not fully certain; well defined mole peaks at $C_{17}H_{28}$, $C_{18}H_{30}$ and $C_{19}H_{32}$.
[e] Unidentified alkylaromatic hydrocarbon, most probably $C_{18}H_{30}$.
[f] Unidentified alkylbenzene(s); mole peak: $C_{19}H_{32}$.
[g] These components were eluted in one GLC peak of 11.4 and 11.6%. The peak may also contain $7C_{13}LB$.

skeleton intact and thus the conclusions from the analysis of a desulphonated AB are valid also for the parent ABS.

As reported earlier, branched-chain AB mixtures cannot be resolved even with capillary columns because of the large number of possible isomers. Therefore, only the type of component could be determined. Similar observations were made with a branched-chain AB product (hard dodecylbenzene: Isorchem, Liquichimica, Milan, Italy), but these results cannot be regarded as conclusive as those obtained with the linear-chain products. Therefore, this problem should be reinvestigated if the chromatographic resolution of "hard" ABs could be improved, as the tertiary and quaternary carbons in the branched chains could be expected to be the most sensitive points against chemical attack during the desulphonation.

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