SHORT COMMUNICATION

Sulfonation with SO_3: Relative Reactivity of Commercial Alkylbenzene Components

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ABSTRACT: Commercial linear alkylbenzene components, such as linear alkylbenzene homologs and isomers, branched alkylbenzene and dialkyltetralins, have been synthesized and isolated. Equimolar mixtures have been prepared, and their relative velocities during the sulfonation reaction have been established.

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KEY WORDS: BAB, DAT, LAB, LAS, SO, sulfonation.

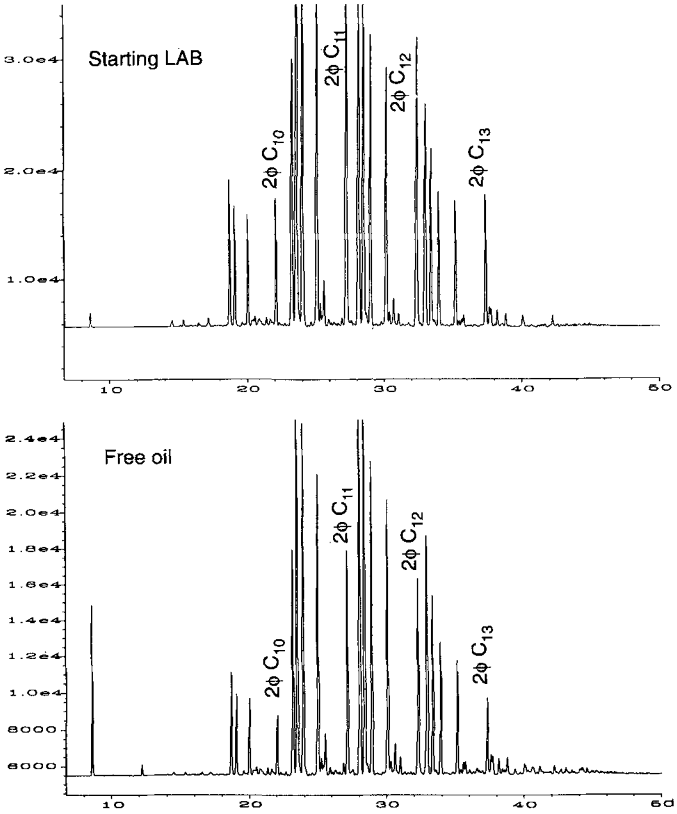

FIG. 1. Chromatograms of linear alkylbenzene (LAB) prior to and after sulfonation.

Commercial linear alkylbenzene (LAB) is a mixture of different homologs and isomers and contains some minor components, such as branched alkylates and tetralins. All these components have been isolated or synthesized, and their mixtures in different proportions have been prepared to determine their competitivity during sulfonation. This work completes earlier studies (1,2).

MATERIALS AND METHODS

Sulfonation. All the samples were sulfonated with SO_3 gas at a molar ratio of (with LAB) 1.04; temperature, 45°C; SO_3/N_2, 4.34 wt%.

Free oil extraction. The free oil was extracted according to ASTM D1568 (3). Linear alkylbenzene sulfonate was dissolved in 1:1 ethanol/water solution, and free oil was extracted with hexane.

Starting LAB and free oil analysis by gas chromatography (GC). The starting LAB is the material before sulfonation. Free oil analysis by GC (ISO 6841-88; Ref. 4) gives the LAB distribution of the material that has not been sulfonated. Briefly, the apparatus was HP-5880A (Hewlett-Packard, Palo Alto, CA) or similar; the column was a fused silica capillary column with cross-linked 5% phenyl methyl silicone; column length, 25 m; column i.d., .31 mm; film thickness, 0.17 mm; detector, flame-ionization detection; splitter, 1:200; carrier gas, helium at 2 mL/min; program, 80–230°C at 2°C/min.

LAB was quantitated by individual component calibration with a standard which was prepared by weighing each homolog and then checking the distribution by GC. Response factors obtained were: phenyl-C_{10}, 0.99; phenyl-C_{11}, 1.02; phenyl-C_{12} 0.97; phenyl-C_{13}, 1.02; and phenyl-C_{14}, 1.00.

As an example, chromatograms of a LAB prior and after sulfonation are given in Figure 1. For the sake of simplicity, only the two phenyl isomers for each homolog have been included. Figure 1 shows that the relative content of the two phenyl isomer decreases in the free oil as compared to the starting LAB.

RESULTS AND DISCUSSION

Mixtures of two components were prepared, and their behavior during sulfonation was studied by analyzing the free oil

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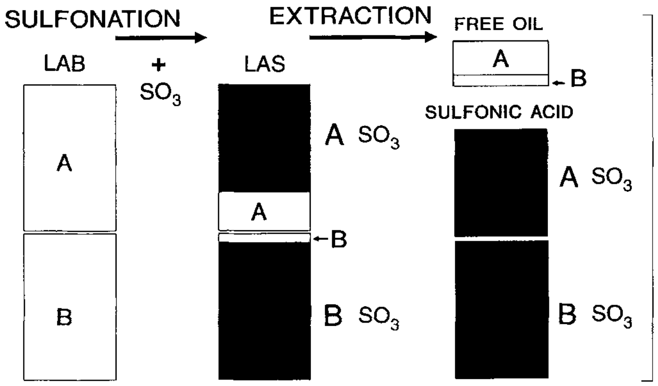

FIG. 2. Linear alkylbenzene (LAB) sulfonation and free oil extraction. LAS, linear alkylbenzene sulfonate.

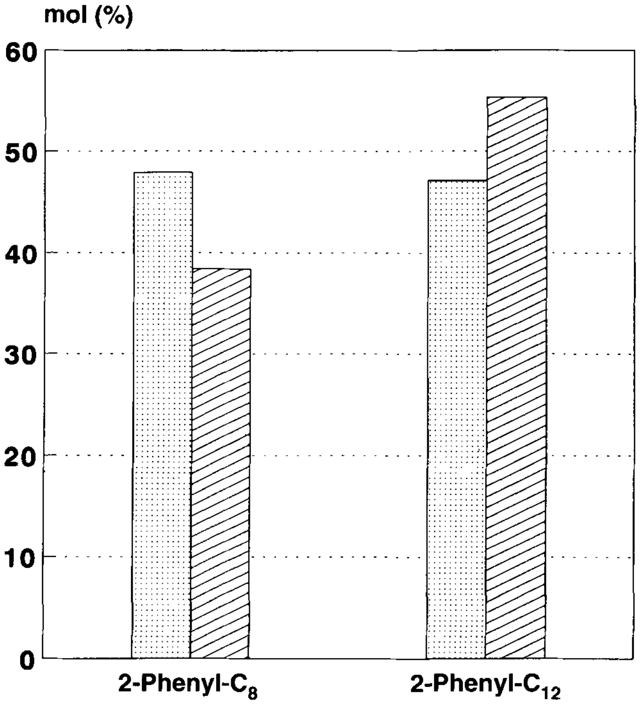

FIG. 3. Reactivity of 2-phenyl-C8 vs. 2-phenyl-C$_{12}$ during sulfonation. Dotted bar, starting product; hatched bar, free oil.

TABLE 1
Commercial LABs: 2-Phenyl Isomer Content in Each Homolog by Gas Chromatography[a]

	LAB HF (%)	LAB AlCl$_3$ (%)
2ϕ C$_{10}$	21.6	37.8
2ϕ C$_{11}$	19.1	33.1
2ϕ C$_{12}$	17.0	28.3
2ϕ C$_{13}$	16.0	23.7
2ϕ C$_{14}$	13.3	—

[a] LAB, linear alkylbenzene.

TABLE 2
Phenyl-C$_{10}$–Phenyl-C$_{12}$ Mixture Gas Chromatography Distribution[a]

	Starting Mixture A (mol%)	Free oil (mol%)
5ϕ C$_{10}$	12.5	11.0
4ϕ C$_{10}$	12.4	11.3
3ϕ C$_{10}$	12.6	12.7
2ϕ C$_{10}$	12.1	8.1
Total ϕ C$_{10}$	49.6	43.1
6ϕC$_{12}$	11.7	13.8
5ϕC$_{12}$	7.1	9.0
4ϕC$_{12}$	10.2	12.3
3ϕC$_{12}$	11.4	13.6
2ϕC$_{12}$	10.0	8.2
Total ϕC$_{12}$	50.4	56.9

[a] Before and after sulfonation of Mixture A.

by GC. The comparison between the LAB's composition, both prior to and after sulfonation, gave the relative reactivity of each component in the mixture (Fig. 2). When two components are studied during a reaction, two factors have to be taken into account—their molar concentration, which is related to the probability of collision between both reactants; and their relative reactivity, which is related to the affinity of each component for SO$_3$. Using an equimolar ratio allows us to eliminate the influence of the molar concentration.

Homologs and isomers. 2-Phenyl-C$_8$ and 2-phenyl-C$_{12}$ isomers were obtained by GC; and, at 3ϕ and 2ϕ, were, respectively, 3.0, 97.0 and 6.6 and 43.4. An equimolar mixture of both isomers was sulfonated, and the free oil was analyzed by GC. The result is shown in Figure 3. This result indicates that 2-phenyl-C$_8$ has a higher sulfonatability than 2-phenyl-C$_{12}$. In other words, for the same isomer, the longer the carbon chain of the homolog, the lower its reactivity during sulfonation.

When the relative reactivity of the different homologs that are present in commercial LAB is studied, it is important to remember that each homolog is a mixture of several isomers. The proportion of these isomers can modify the homolog behavior during sulfonation. It is already known (2) that external isomers are more reactive than internal isomers during SO$_3$ sulfonation (this greater reactivity can be explained in terms of steric effects). As far as commercial LABs are concerned, the external isomer concentration decreases as the carbon chain increases (Table 1). Therefore, it is not clear which of the two factors (isomer or chainlength contribution) has a greater impact on the sulfonation process. To clarify this point, two different mixtures of homologs, A and B, were prepared by changing the two phenyl isomer contents (Tables 2 and 3). As can be seen from Mixture A (Table 2), which is a phenyl-C$_{10}$–phenyl-C$_{12}$ mixture with almost the same isomer distribution, the phenyl-C$_{10}$ has a higher reactivity than phenyl-C$_{12}$. In Mixture B (Table 3), the 2-phenyl-C$_{12}$ isomer was increased from 10 up to 25.6% by doping Mixture A with 2-phenyl-C$_{12}$. The results after sulfonation show that the determining factor in the sulfonation reaction is the carbon chainlength over external isomer content.

TABLE 3
Phenyl-C_{10}–Phenyl-C_{12} Mixture Gas Chromatography Distribution[a] Before and After Sulfonation of Mixture B

	Starting Mixture B (mol%)	Free oil (mol%)
$5\phi C_{10}$	12.5	11.7
$4\phi C_{10}$	12.4	11.7
$3\phi C_{10}$	12.6	13.0
$2\phi C_{10}$	12.1	9.0
ϕC_{10}	49.6	45.4
$6\phi C_{12}$	5.4	7.7
$5\phi C_{12}$	5.4	6.4
$4\phi C_{12}$	6.0	7.7
$3\phi C_{12}$	8.0	9.9
$2\phi C_{12}$	25.6	22.8
ϕC_{12}	50.4	54.5

[a] Before and after sulfonation of Mixture B.

TABLE 4
Linear and Branched Alkylate Distribution

	Linear (wt%)	Branched (wt%)
ϕC_9	—	4.9
ϕC_{10}	—	3.6
ϕC_{11}	2.9	6.9
ϕC_{12}	84.2	81.6
ϕC_{13}	12.9	3.0
Molecular weight	247.3	242.3

TABLE 5
Tetralin, Linear and Branched Alkylate Mixture from Gas Chromatography/Mass Spectrometric Analysis Before and After Sulfonation

	Starting mixture (mol%)	Free oil (mol%)
Tetralin C_{10}	37.6	2.9
Phenyl-C_{10}	49.4	67.8
Branched	8.4	20.3
Others	4.6	9.0

Linear vs. *branched alkylbenzene.* A 1:1 molar mixture of linear and branched alkylbenzenes was sulfonated. The GC distribution of both alkylbenzenes is shown in Table 4. The composition of the mixture, prior and after sulfonation, was 50.5 and 49.5 for branched and linear starting oil (mol%), respectively; and 59.2 and 40.8 for branched and linear free oil, respectively. The experimental results show higher reactivity of LAB when compared to branched alkylbenzene.

Tetralins vs. *other components.* A C_{10} mixture of tetralin, LAB and branched alkylate was prepared and analyzed by GC/mass spectrometry before and after sulfonation as indicated in Table 5. Tetralins disappear rapidly during the sulfonation reaction, so that the tetralin content in the free oil is practically zero, while all other components in the free oil have increased their relative content as compared to the starting mixture. These results indicate that tetralin is the most reactive component during sulfonation.

The reason for the high tetralin reactivity can be explained by taking into account that the benzene ring in tetralin has two alkyl groups with an electron donor effect, whereas the other components have only one. Besides this, lower steric hindrance for tetralin could also help to explain its higher reactivity.

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