TABLE VII

Over-all Composition of the 9–15 Carbon Diester Fractions

No. of carbon atoms in dicarboxylic acid	Composition, mole %
9	56.1
10	0.9
11	0.6
12	25.3
13	0.0
14	0.0
15	17.1

fats. Depending on future price and availability of hydrazine, whether premium prices for C_{12} and C_{15} dibasic acids may be merited over those for C_9 acids, and a number of unnamed factors, this process may be worthy of further consideration. At present pilot-plant work may be justified to produce C_{12} and C_{15} dibasic acids in amounts sufficent to evaluate their properties and to determine the demand for them in commercial products, such as polymers, plasticizers, and possibly fibers.

Commercial production of C_{12} dibasic acid has been announced recently, and numerous outlets are antici-pated (14). If this dibasic acid and not the C_{15} acid were desired, it would be derived from linoleic acid (3) or from linoleic acid-rich sources in soybean, safflower, and tall oils.

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Investigations on the Side Reactions in Sulfonation Reactions—Hydrophobic Compounds in the Unsulfonated Oil Fraction.

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Abstract

Petroleum ether extracts of alkylbenzene sulfonates prepared by sulfur trioxide, oleum, and sulfuric acid were compared. These extracts contained by-products as well as unreacted material. Dialkylbenzene, originally existing in raw alkylbenzene, resisted against sulfonation, especially when sulfur trioxide was used as sulfonating agent. Sulfone formation seemed to occur in the early stage of sulfonation. Sulfonation with sulfuric acid gave different characteristics to the petroleum ether extract compared with two other means.

Introduction

THE SULFONATION REACTIONS of benzene and its alkyl derivatives have been studied extensively (10,11,12,15,17). The conventional sulfonating agents are oleum, sulfuric acid, and more recent, sulfur trioxide (2,5,6,7,8,9,13,14). These agents have been widely used, however, very little information is available on the by-products formed during the reaction. The known by-products are: sulfonic acid anhydride, dialkylphenyl sulfone, polysulfonates, and other dialkylated compounds (4,6,7,8,9,17). The authors believe that these compounds may seriously influence the sulfonation reaction.

It is the purpose of this paper to report our findings on the by-products, particularly the hydrophobic substances, formed in sulfonation reactions with sulfur trioxide, oleum, and sulfuric acid.

Experimental

Materials and Methods. Alkylbenzene and n-dodecylbenzene were used in the study. Alkylbenzene was a commercial product, Alkane 56, made by Oronite Chemical Co.; n-dodecyl benzene was synthesized in the laboratory from n-dodecanoyl chloride (10). Sulfur trioxide was distilled from 65% oleum. The sulfuric acid reagent was prepared from 22% oleum and 98% sulfuric acid. All solvents used were of reagent grade.

Sulfonation. The sulfonation reactions with sulfur trioxide were carried out as described by Gilbert et al. (7). Gaseous sulfur trioxide, mixed with dry air was bubbled through the sample. Eighteen separate sulfonations were carried out with sulfur trioxide at 40, 50, and 60C, for 1 and 2 hr reaction periods each. One sample each was also sulfonated with oleum and sulfuric acid for comparison with standard process (13). The conditions of the reaction are given in Table I.

Sample Preparation and Extraction. Sulfonic acid anhydride in the resulting reaction medium with sulfur trioxide was decomposed to sulfonic acid by adding 1% of water w/w and the acid was neutralized with 10% NaOH. The hydrophobic substances were then extracted with petroleum ether according to the standard AST method 1568-58T (1).

From the neutralized paste, 1.5–2.0 g of hydrophobic oils were obtained. The degree of reaction was calculated using the following equation:

$$\text{Degree of reaction \%} = \frac{\text{Combined Alkylbenzene}}{\text{Combined Alkylbenzene} + \text{Petroleum ether extract}} \times 100$$

where combined alkylbenzene = active ingredient with

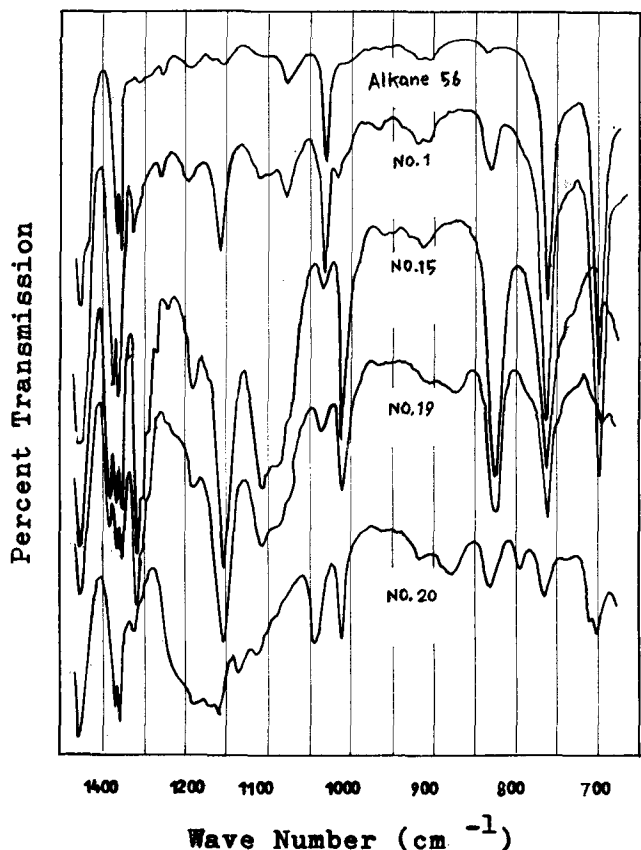Epton's titration method $(3,16) \times \dfrac{246}{348}$

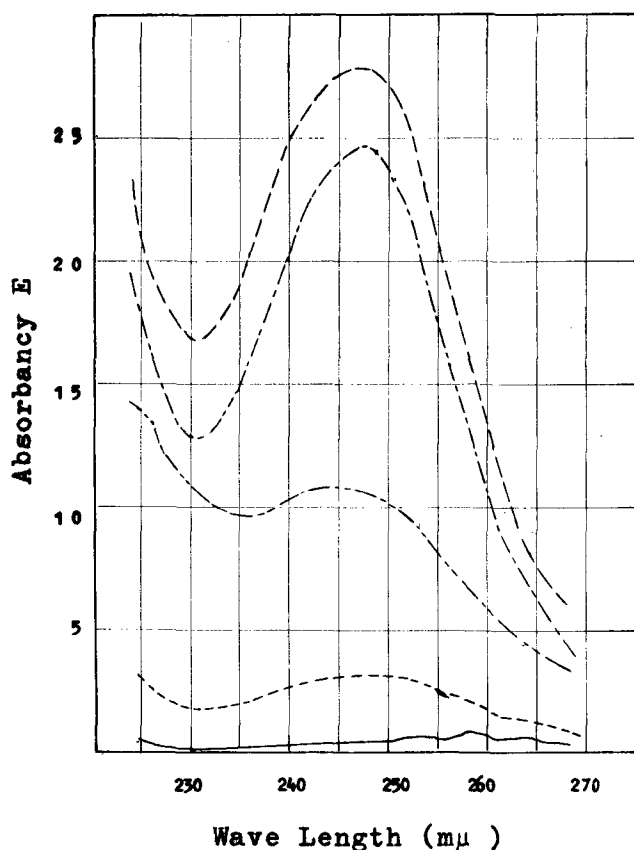FIG. 1. IR spectra of raw alkylbenzene and petroleum ether extracts.

FIG. 2. UV spectra of raw alkylbenzene and petroleum ether extracts. ———— Alkane 56, - - - - - - No. 1, — - — - — No. 15, — — — — No. 19, — - - — - - No. 20.

Fractionation on Alumina Column. One to 2 g each of the extracts fractionated on an 80 g alumina column (25 mm × 500 mm). Alumina (200 to 300 mesh) was activated at 200C for 2 hr. 200 to 300 ml of each of the solvents was used in the following sequence: petroleum ether, ethyl ether, chloroform and methanol. Twenty ml fractions were collected, solvents were distilled off and the dry residue weighed. The fractions for each solvent were pooled and analyzed by infrared (IR) and ultraviolet (UV) spectroscopy. The IR spectra were determined in liquid state on Nihon Bunko Spectrophotometer Type IRS. The UV spectra were determined in ethanol solutions on a Hitachi apparatus Type EPS-2.

Di-(p-Dodecyl Phenyl) Sulfone. The ethyl ether eluate of petroleum ether extract from n-dodecylbenzene sulfonated with sulfur trioxide was dried to obtain white solid. Recrystallization twice from n-hexane solution resulted in white crystal of M.P. 69.2–70.0C. Mol wt was 545.7 by cryoscopic method. Theoretical value for di-(p-dodecylphenyl) sulfone was 554.9. It had UV absorption maximum at 247

TABLE I
Results of Sulfonation Reactions

| Exp. No. | Sulfonating agents | Reaction | | | Added SO₃ mole | Reaction degree % | Refractive index[b] n_D^{25} |
		Period	Temp.	Mole ratio SO₃/H.C.[a]			
1			40	1.00	0.95	89.0	1.4860
2				1.15	1.07	97.5	1.4952
3				1.30	1.14	98.8	1.5058
4				1.00	0.94	89.0	1.4862
5		1 hr	50	1.15	1.04	98.5	1.5035
6				1.30	1.12	98.7	1.5091
7				1.00	0.92	88.6	1.4831
8			60	1.15	1.02	98.2	1.5039
9	SO₃			1.30	1.08	98.5	1.5091
10				1.00	0.94	89.8	1.4872
11			40	1.15	1.07	97.8	1.4971
12				1.30	1.19	98.2	1.4985
13				1.00	0.94	92.3	1.4876
14		2 hr	50	1.15	0.96	92.8	1.4887
15				1.30	1.21	99.0	1.5090
16				1.00	0.86	85.9	1.4857
17			60	1.15	0.91	91.7	1.4890
18				1.30	1.03	98.5	1.5081
19	22% Oleum			3.00	......	99.0	1.5129
20	100% H₂SO₄			4.00	......	99.3	1.4872

[a] Raw alkylbenzene (mean mol wt 246).
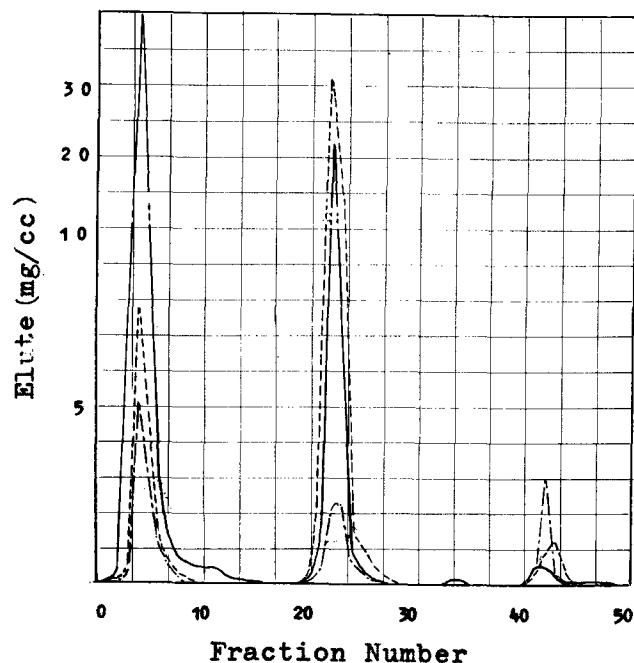[b] Refractive indices of petroleum ether extracts.

FIG. 3. Chromatographic separation of petroleum ether extracts. ———— No. 1, - - - - - - No. 19, — · — · — No. 20.

TABLE II

Chromatographic Separation of Petroleum Ether Extracts

Sample No.	Applied, g	Petroleum ether, g (%)	Ethyl ether g (%)	Chloroform and methanol, g (%)	Eluted amounts, g	Recovery, %
1	1.5884	1.4135 (92.9)	0.0886 (5.8)	0.0193 (1.3)	1.5224	95.8
2	1.0866	0.7064 (68.9)	0.3086 (30.1)	0.0100 (1.0)	1.0250	94.3
3	0.2535	0.0940 (36.1)	0.1588 (60.9)	0.0078 (3.0)	0.2606	102.9
8	1.5102	1.2752 (87.9)	0.1520 (10.5)	0.0228 (1.6)	1.4500	96.0
9	1.3758	0.5721 (42.9)	0.7402 (55.4)	0.0222 (1.7)	1.3345	97.0
11	0.6245	0.5399 (88.5)	0.0607 (9.9)	0.0087 (1.6)	0.6093	97.6
13	0.8948	0.7720 (90.0)	0.0758 (8.8)	0.0105 (1.2)	0.8583	95.9
14	1.8851	1.6142 (89.5)	0.1833 (10.1)	0.0073 (0.4)	1.8048	95.7
15	0.4518	0.1437 (34.4)	0.2653 (63.4)	0.0091 (2.2)	0.4181	92.5
17	1.0862	0.9445 (88.0)	0.1159 (10.8)	0.0125 (1.2)	1.0729	98.8
19	1.5914	0.2780 (20.4)	1.0107 (74.2)	0.0726 (5.4)	1.3613	85.5
20	0.6203	0.2034 (51.4)	0.1134 (28.7)	0.0786 (19.9)	0.3954	63.7

mμ in ethanol solution. The analysis showed:

	Calculated	Found
C %	77.92	78.05
H %	10.53	10.72
S %	5.78	5.87

Results

The IR spectra of the petroleum ether extracts for 4 representative samples, prior to the fractionation on the column, are shown in Figure 1 along with a spectrum of Alkane 56.

Characteristic bands were observed at 830 cm^{-1} and 1330 cm^{-1} which showed increased absorbancies in these regions with the increase in the degree of reaction (T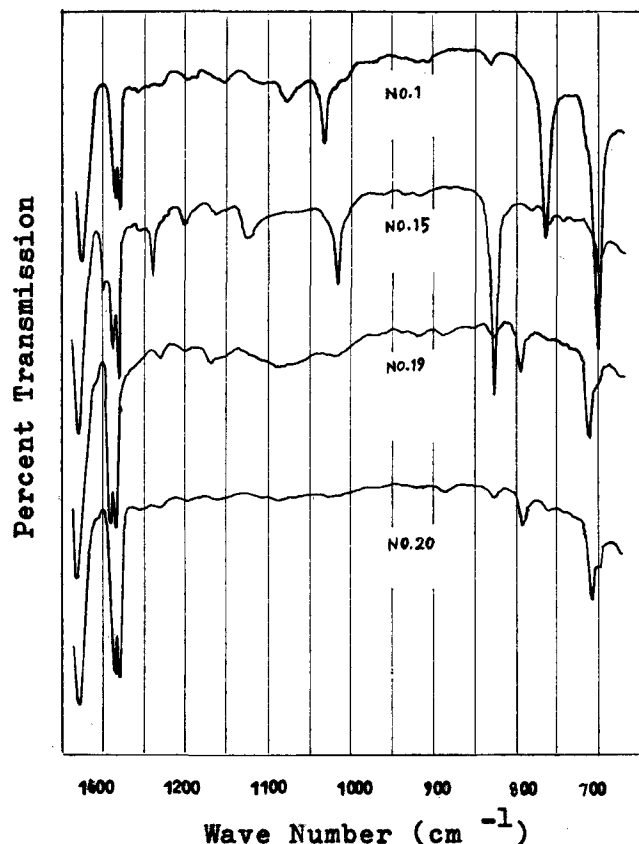able I). In the sample sulfonated with oleum and sulfuric acid (no. 19 and 20) the absorbancies were significantly lower in spite of the higher degrees of reaction.

The UV spectra of the same samples are shown in Figure 2. In general, they gave significantly different spectra with the spectrum of untreated monoalkylbenzene. Figure 3 shows the elution patterns obtained with 3 representative samples.

Ninety-seven to 99% of the sample applied to the column was eluted with petroleum ether and ethyl ether. Small quantities of a brownish yellow material was eluted with chloroform and methanol. The distribution of the fractions is shown in Table II. The material obtained with chloroform and methanol is combined for the sake of convenience. The petroleum ether eluates ranged from 34 to 80%. The quantity of the eluate seems to be influenced by the ratio of sulfur trioxide to the hydrocarbon used in the reaction.

Refractive indices (n_D^{25}) of the petroleum ether extracts also showed an increase with the degree of reaction (Table I).

The IR spectra of the petroleum ether eluates (Fig. 4) showed that the difference of the degree of reaction caused the significant difference in absorption, and the UV spectra (Fig. 5) showed that the spectra of sample reacted with oleum or sulfuric acid were significantly different from the one treated with sulfur trioxide which was similar to the spectra of untreated monoalkyl benzene and p-dialkyl benzene.

The UV spectra of the ethyl ether eluates were shown in Figure 6. The extinction coefficients at 247 mμ of all the eluates except No. 20 were found the same, i.e. $E_{1cm}^{g/l} = 41.2$.

Refractive indices of the eluates were 1.5243 (n_D^{25}).

Discussion

Petroleum Ether Eluates. If the petroleum ether extract is unsulfonated alkylbenzene, it should have the characteristics of monoalkylbenzene, that is of the raw materials. There was substantial monoalkylbenzene with low degree of reaction of alkylbenzene, but as the degree of reaction increased, the differences
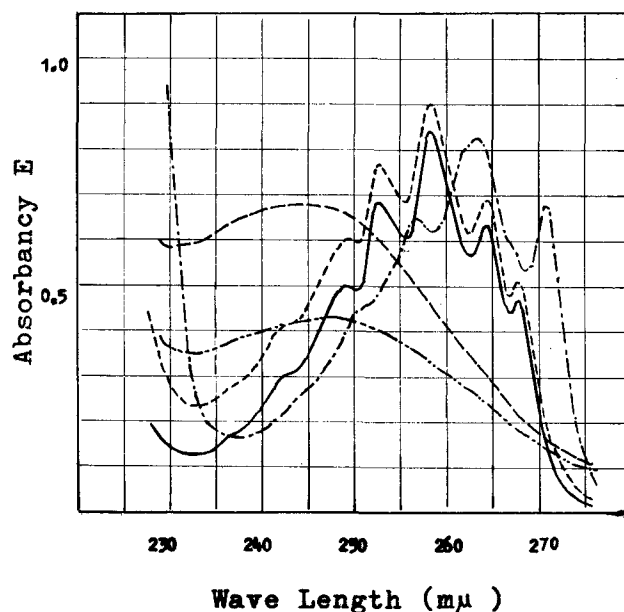

FIG. 4. IR spectra of petroleum ether eluates.

FIG. 5. UV spectra of petroleum ether eluates. ———— Alkane 56, ······· No. 1, —·—·— No. 15, ——— No. 19, —··—··— No. 20.

between petroleum ether extracts and raw alkylbenzene became marked. These differences were (a) the IR spectra of p-disubstituted benzene and sulfone exhibited stronger adsorption; (b) the UV spectrum absorption of alkylbenzene at 261 mμ became weaker; (c) they had higher refractive indices than raw alkylbenzene.

The increased IR absorption of p-disubstituted benzene might be attributed to the increased concentration of dialkyl benzene, which was contained in the raw alkylbenzene in small quantities. However, the absorption at 830 cm⁻¹ in the IR spectra, a band appearing at 247 mμ in the UV spectra and the refractive indices increased with the degrees of reaction of alkylbenzene. These changes indicated that the constituents of petroleum ether extracts not only included unsolfonated alkylbenzene but were seriously influenced by the by-products produced during the sulfonation reactions.

The degree of reaction of alkylbenzene correlated with the refractive indices. In other words, the petroleum ether extracts, obtained from the reactants having the same degrees of reaction, gave the same refractive indices, no matter what the reaction conditions were, indicating that the petroleum ether extracts, obtained from the reactant having the same degrees of reaction, resembled one with another in their constituents.

Petroleum ether eluates were composed of hydrocarbons containing unsulfonated alkylbenzene and possibly hydrocarbon fragments produced by side reactions.

This was substantially monoalkylbenzene as long as the degree of reaction was low, as IR, UV spectra were similar to the raw material and characteristic of monoalkylbenzene. However, in their IR spectra

FIG. 6. IR spectra of ethyl ether eluates.

absorbancies at 830 cm⁻¹ were generally larger than the raw material and increased with the degrees of reaction. This meant that dialkyl benzene, contained in raw material in small quantities, was not sulfonated more readily than monoalkylbenzene and was accumulated in petroleum ether extracts. This was in agreement with the observation that in the extremely high degrees of reaction, the IR and UV spectra of the petroleum ether eluate resembled that of p-dialkylbenzene with no absorption bands at 763 and 700 cm⁻¹, but with a band at 830 cm⁻¹, in the IR spectrum. The UV spectrum also resembled very closely that of p-dialkyl benzene. The fact that the extinction coefficient ($E_{1cm}^{1g/1}$) was not in agreement with that of raw material, even in low degree of reaction, meant that the unsulfonated alkylbenzene did not always have the same distribution of alkyl chain or alkyl chain branching as the raw material.

From IR spectra petroleum ether eluates obtained from oleum and sulfuric acid sulfonation seemed to have little dialkyl benzene in spite of their high degrees of reaction of alkylbenzene. This meant that dialkyl benzene was converted by sulfonating agents to some other material. Furthermore, the remarkable decreases in absorbancies attributed to substituted aromatic ring vibrations in the IR spectra indicated that alkylbenzenes (mono- and di-) and/or their sulfonates were degraded to the non-aromatic hydrocarbons by side reaction during the sulfonation reaction. This conclusion was also supported by UV spectra.

The differences in constituents of petroleum ether extracts between sulfur trioxide sulfonation products and oleum and sulfuric acid sulfonation products arose from differences of reactivities of sulfonating agents. It was well known that sulfur trioxide was the strongest sulfonating agent among these three. Sulfur trioxide was led into reactants as diluted gases, having very short contact period. On the other hand, in the sulfonation reaction with oleum and sulfuric acid, the two reactants had much longer reaction periods in the presence of excessive agents. Under these conditions, it was likely that both mono- and dialkyl benzene reacted to final stage, and moreover that different side reactions occurred in the sulfonation reactions.

The quantitative correlations of petroleum ether extracts in their constituents were affected seriously with the degrees of reaction of alkylbenzene. In conclusion, we did not consider calling the petroleum ether soluble material as "unreacted" adequate, because in the last stage of sulfonation, alkylbenzene did not remain to be sulfonated any more. These hydrophobic by-product unsulfonated materials might have some effects on the surface activities. Strictly speaking, this extract did not represent the exact unsulfonated material, but the summation of all hydrophobic substances in the reactant. Large amounts of sulfones were observed in the petroleum ether extracts with high degree of reaction of alkylbenzene. Therefore, it was more reasonable to determine the unsulfonated material by azeotropic distillation of hydrocarbons (true unsulfonated material plus by-product hydrocarbon) from the neutralized pastes or powders.

Ethyl Ether Eluates. Assuming that the di-(p-alkylphenyl) sulfone was formed by the reaction of alkylbenzene sulfonic acid with alkylbenzene, this reaction must have occurred in the early stage, while the degree of reaction of alkylbenzene was not high, and the unsulfonated alkylbenzene was abundant in the reactant.
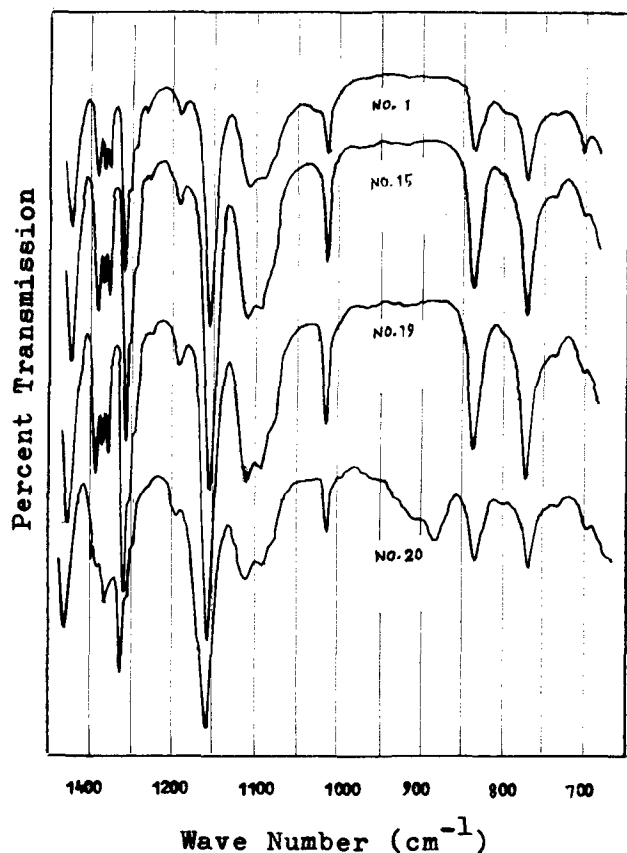
We considered that the formation of di-(p-alkyl-phenyl) sulfone began at about 85% of reaction of alkylbenzene. It was observed that the remarkable increases of refractive indices began at this point, and the viscosities were about 500 c.p.s. at 50C. It was assumed that the formation of sulfone was seriously affected by the viscosities of reactant—in other words, the formation began with poor stirring effect.

The amounts of sulfone formed during the sulfonation reaction were about the same under various reaction conditions, therefore, the formation of sulfone did not continue for a long period.

The abrupt increases in refractive indices of petroleum ether extract were due to the decrease of the concentration of alkylbenzene and increase of the concentration of di-(p-alkylphenyl)sulfone. Table III showed that the amount of alkylphenyl sulfone formed during the sulfonation reaction was not large, namely 0.6 to 0.8 g from 100 g of raw material. This value was small compared with the ones obtained by Gilbert et al. (7) with lower alkylbenzenes, and not in disagreement with their results. However, it should have been emphasized that sulfone was the main component in the by-products.

It was observed that the amount of sulfone produced during the oleum sulfonation was about the same as in the case of sulfur trioxide sulfonation, based on the fact that the free sulfur trioxide in the oleum could be attributed to the sulfonation of alkylbenzene. However, we could observe the formation of sulfone in the sulfuric acid sulfonation, although it was small compared with sulfur trioxide and oleum sulfonation.

Figure 2 showed that the absorbancies of petroleum ether extracts at 247 mμ increased with the degrees of reaction of akylbenzene, which in turn meant an increase in concentration of sulfone in the petroleum ether extracts with the degrees of reaction. It was therefore possible to obtain the amounts of sulfone in petroleum ether extracts by determining the absorptivity at 247 mμ, for this absorptivity of alkylbenzene ($E_{1cm}^{1g/1}$ = 0.5) was quite small compared with the one of sulfone ($E_{1cm}^{1g/1}$ = 41.2). We could determine the amount of sulfone in the petroleum ether extract by measuring the extinction coefficient of extract using ethanol as solvent, and comparing it with a standard sample (ethyl ether eluate). The ethyl ether eluate was not a pure substance in a strict sense, but we could consider it as a standard substance as its absorptivity was constant. Petroleum ether eluate, chloroform eluate, and methanol eluate might have some influence on the determination of sulfone, but the small absorptivity of petroleum ether eluate and the small amount of chloroform and methanol eluate did not seriously affect the determination. Absorbancies were measured with various mixtures of alkylbenzene and ethyl ether eluate. A straight line over a wide range crossing at an origin was obtained when plotting absorbancies against the concentrations of ethyl ether eluate, showing that the ethyl ether eluate obeyed the Lambert-Beer's law, and that the absorptivities with alkylbenzene might be neglected. Table III showed the results of the determination of sulfone with this procedure vs. chromatographic separation. Although the estimation of sulfone by measurement of the absorptivity in petroleum ether extracts was not too accurate, it was believed to be accurate enough to use as a handy method.

Chloroform and Methanol Eluates. The fraction was not thoroughly investigated. However, the IR

TABLE III
Percent Sulfone in the Petroleum Ether Extract

Sample No.	Reaction degree of Alkane, 56, %	With chromatographic separation	With UV Spectroscopy	Sulfone formed from 100 g of Alkylbenzene, g
1	89.0	5.8	8.0	0.6
2	97.5	30.1	31.2	0.8
3	98.8	60.9	67.5	0.7
13	92.3	8.8	8.5	0.7
14	92.8	9.7	10.3	0.7
15	99.0	63.4	59.7	0.6
17	91.7	10.8	12.9	0.9
19	99.0	74.2	67.5	0.7
20	99.3	28.7	25.8	0.2

and UV spectra showed the presence of sulfone, sulfonic acid, hydroxyl, and carbonyl group. Perhaps this fraction contained various by-products which was formed during sulfonation.

Conclusions

1. Petroleum ether extracts of neutralized alkylbenzene sulfonate contained sulfone, hydrocarbon and colored material as by-products together with unsulfonated alkylbenzene. Dialkylbenzene existed in small amount in raw alkylbenzene, was not readily sulfonated by sulfur trioxide in contrast to sulfonation by either oleum or sulfuric acid, and was found in petroleum ether extract. The observation was parallel to Gilbert et al. (9). However, when oleum or sulfuric acid was used, chemical change was observed probably because of long sulfonation period.

2. Di-(p-alkylphenyl) sulfone seemed to be formed at the earlier stage of sulfonation. The amount was 0.6 to 0.8 g for 100 g of raw alkylbenzene when sulfonated with sulfur trioxide or oleum. A smaller amount was formed by sulfuric acid treatment.

The amount of sulfone in the petroleum ether extract was roughly able to calculate by comparing absorption coefficient at 247 mμ with standard.

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