The results of the solubility of Resin B in alkanes were used to calculate the values of μ against temperature (Figure 10). Again flat plots were obtained, but no regular changes of the α and β values (Table I) were found.

TABLE I. RESIN B IN SOLVENTS

$(\mu = \alpha + \beta/T)$

Solvent	α	β
Decane	0.90	790
Tetradecane	0.70	780
Octadecane	0.89	910
80% decane-20% toluene	0.602	600
70% decane-30% toluene	0.652	600
60% decane-40% toluene	0.87	640
50% decane-50% toluene	1.54	800

The treatment of Flory (*1*) predicts the type of solubility shown in Figure 11, where the numbers of the curves refer to the number of segments in the polymer. This maximum resin concentration is expected to fall at progressively lower resin concentration with increase in molecular weight and to occur at $1/(1 + \sqrt{x})$ where x is the degree of polymerization. The author has found maxima occurring at much higher resin concentrations than predicted by this treatment. The maxima for the same resin may vary with the solvent, occurring at progressively higher concentration as better solvents are used.

APPLICATION

This work was initiated to measure the solubility of various samples of polystyrene in hydrocarbon solvents to serve as a model for resin-plasticizer systems. The work has shown the type of solubility relationships that may be encountered in such systems and how solubility diagrams change with better solvents.

It has been suggested (*5*) that better physical properties are often obtained in plasticized systems where the resin is not too well dissolved. In many instances, such systems are unstable and tend to lose plasticizer by exudation, extraction, or volatilization. These studies suggest that systems may exist in which phase separation may occur at high resin concentration in both phases. Such systems would not be expected to lose plasticizer readily. Whether such systems are possible with nonvolatile plasticizers remains to be seen.

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Alkanesulfonic Acids as Catalysts in Polymerization and Alkylation

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The alkanesulfonic acids, containing one to four carbon atoms, have been studied as catalysts for the polymerization of olefins and the alkylation of aromatics. Alkylation ordinarily proceeds in preference to polymerization when conditions are favorable to both. In general, these acids are effective catalysts at temperatures above approximately 60° C. Below this temperature the sulfonic acids react with normal olefins to form stable secondary esters, and data are presented indicating that such ester formation is an intermediate in both polymerization and alkylation. The alkanesulfonic acids appear to be particularly suitable as catalysts for the study of polymerization and alkylation because side reactions such as hydrogen transfer and oxidation are essentially absent.

ALKANESULFONIC acids containing one to four carbon atoms have recently become available, and some general information as to the scope of their utility has been published (*5*). Included in the reactions previously reported was some work on the behavior of these acids as catalysts in polymerization and alkylation. This work has recently been considerably extended, and the object of this report is to present the results obtained.

Technical grades of methanesulfonic, ethanesulfonic, and mixed alkanesulfonic acids, now being produced on a pilot plant scale, were employed in this work, as well as methane- and ethanesulfonic acids which had been purified by distillation under reduced pressure. The technical grades of the sulfonic acids, typically, contained 2 to 5% of water and 3% of sulfuric acid. The exact composition of the mixed alkanesulfonic acids is uncertain, but the chief components are methane-, ethane-, and the two isomeric propane- acids, with an average molecular weight equal to the ethane- acid. Inasmuch as the mixed acid was the most readily available, and as early studies (*5*) had shown its behavior to be similar to that of the individual acids, most of the work was carried out with mixed acid. The presence of small amounts of sulfuric acid as an impurity in the technical grades of alkanesulfonic acids appears to have no appreciable effect on their characteristic behavior, except that in some cases traces of sulfonated materials are formed.

Alkanesulfonic acids are rather mild catalysts for polymerization of olefins and for the alkylation of aromatics. Under the conditions tried, they are not sufficiently strong catalysts to effect the alkylation of tertiary paraffins with olefins. The nature of the reaction of olefins in the presence of these acids, alone and in mixtures with aromatic compounds, depends upon the conditions employed. The olefins investigated include most of the lower olefins up to pentene and a few of higher molecular weight, and were sufficiently varied to indicate that representative behavior was being studied. Of those studied, ethylene was unreactive with alkanesulfonic acids; under the conditions used, it could not be polymerized or made to alkylate aromatic compounds.

ESTER FORMATION

In general, the primary reaction of the olefins with sulfonic acids is addition to form esters, and at ordinary temperatures these esters are stable. At higher temperatures the esters are unstable in the presence of free acid, and polymerization occurs unless an aromatic is present, in which case alkylation takes place preferentially.

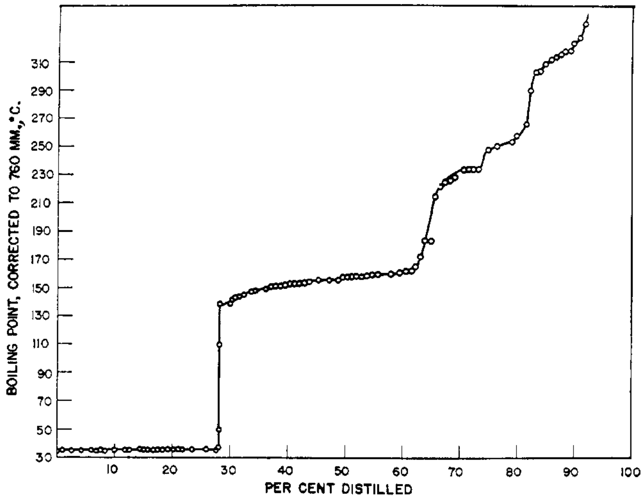


Figure 1. 1-Pentene Polymer

The only two unsaturated hydrocarbons studied that do not form esters with alkanesulfonic acids are ethylene and acetylene. Ethylene does not react with anhydrous methane- or ethanesulfonic acid at room temperature under pressures up to 40 pounds per square inch or at temperatures up to 110° C. at one atmosphere. Under these conditions ethylene does not alkylate aromatic hydrocarbons or phenol. Ethylene may prove to be more reactive in the presence of alkanesulfonic acid at elevated temperature under superatmospheric pressures; these conditions have not yet been investigated.

Acetylene does not react with alkanesulfonic acids under atmospheric pressure over a temperature range of 20° to 110° C. and does not alkylate benzene under these conditions.

Other primary and secondary olefins will form sulfonic esters, which at more elevated temperatures can be made to undergo reactions of polymerization and alkylation. Consequently, it seems likely that ester formation with the sulfonic acid catalyst is the necessary and primary step in both polymerization and alkylation, regardless of the mechanism of the subsequent course of the reactions. In the case of tertiary olefins, such as isobutene, a stable ester does not form at room temperature or above, polymerization or alkylation occurring instead.

The esters, formed according to Markownikov's rule, are stable only when pure and free of acid. Under conditions of formation from olefins, they are reasonably stable only in the temperature range 0–60° C., the stability depending somewhat on the olefin concerned. Ester formation proceeds according to the reaction

$$RSO_2OH + RCH{=}CH_2 \longrightarrow RSO_2O\text{—}\overset{\overset{\displaystyle R}{|}}{CH}\text{—}CH_3$$

The esters, when free of unreacted sulfonic acid, can be distilled under reduced pressure without decomposition. The results of the reaction of various alkanesulfonic acids on different types of olefins are summarized in Table I. Experimental conditions and techniques are illustrated by the following preparation of ester from liquid olefin; preparation from a gaseous olefin was previously described (*5*).

FORMATION OF ESTER FROM LIQUID OLEFINS. Ten milliliters (0.07 mole) of pure 2-octene were placed in a graduated cylinder with 10 ml. (0.11 mole) of 96% mixed alkanesulfonic acid. The immiscible mixture was shaken for a few minutes and allowed to separate. The acid phase increased to 13 ml. Several hours of further reaction, with shaking at 15-minute intervals, increased this to 18 ml. out of 19.3 ml. total volume. When the mixture was allowed to stand overnight, the volume of the acid phase decreased to 15 ml. 2-Octene polymerizes slowly, therefore, even at room temperature. In a separate experiment the acid phase obtained after 4-hour reaction was poured on ice, and about 15 ml. of crude ester were recovered.

VACUUM DISTILLATION OF ALKYL ALKANESULFONIC ESTERS. Crude isopropylethanesulfonate (100 grams, 0.66 mole), prepared in the manner described (*5*), was chilled to 0–5° C., and 25 ml. of ice water were added. The mixture was shaken and settled, and the acid phase was withdrawn at once. Chilled aqueous 10% ammonia (25 ml.) was added to the oil phase, the mixture was shaken and settled, and the aqueous phase was removed from the ester layer. The ester was dried by percolation through 5 grams of activated granular clay and stored over 2 grams of finely powdered calcium oxide. A distillation flask was charged with the dry ester, and the flask was slowly heated under reduced pressure. The ester distilled at 62° C. under 1.7 mm. pressure. The product was a water-white distillate, stable on storage as long as water was kept out. In following this procedure, care must be taken to avoid distilling too large a batch at once, as traces of acid in the charge may cause autocatalytic decomposition and result in a sudden violent surge of polymer formation. Isopropyl mixed alkanesulfonates and *unsym-sec*-amylethanesulfonate have also been vacuum-distilled.

POLYMERIZATION

Two methods of polymerizing olefins in the presence of alkanesulfonic acids have been studied: (1) formation of the alkanesulfonic esters as described above and subsequent heating to a temperature in the range 60–120° C. in the presence of free acid, and (2) passage of the olefin under atmospheric pressure into acid maintained at a temperature high enough to cause polymerization without appreciable ester formation.

In the first method a relatively long induction period (10 to 60 minutes) occurs, followed by a rapid rate of polymerization. Once started, the reaction is complete in a few minutes and is accompanied by a sharp rise in temperature of 30–80° C. A possible explanation for the observed induction period is that, as the ester breaks down, the catalysis is accelerated by the increase in the concentration of the sulfonic acid. In the case of isopropyl alkanesulfonates, however, it was noted that the induction period could not be eliminated by increasing the free acid content of the mixture up to 40% of the total.

In the second method the temperature required to cause polymerization varies with the olefin used. Isobutene polymerizes rapidly at room temperature, whereas 1-butene and other primary and secondary olefins require a temperature of 60–120° C. to react readily.

Broadly, two types of polymers are produced by sulfonic acid polymerization. One, which we have termed "homogeneous," consists of a series of well defined multiples of the monomer (dimer, trimer, tetramer, etc.). The other, or "heterogeneous" type, consists of compounds so diverse that few or no recognizable plateaus are obtained on fractional distillation. The homo-

TABLE I. ESTERIFICATION OF OLEFINS WITH ALKANESULFONIC ACIDS

Technique[a]	Olefin	Pressure, Lb./Sq. In. Gage	Sulfonic Acid, % Strength	Temp., ° C.	Yield[b], %
1	Propylene	40	96 mixed	30	60
1	Propylene	40	100 methane	30	80%
2	Propylene	0	96 mixed	30	20–30%
2	Propylene	0	91 mixed	30	Low
1	Propylene	40	100 ethane	30–40	90%
1	Propylene	40	93 mixed	30–40	
1	2-Butene	15	100 methane	30	100%
1	2-Butene	15	96 mixed	30	100%
2	Isobutene	0	91 mixed	30	Only polymer
2	Isobutene	0	96 mixed	30	Only polymer
3	Isobutene	0	100 ethane	−15	None
2	1-Pentene	0	96 mixed	25	60–80%
4	1-Pentene	0	100 methane	10	90%
2	1-Pentene	10	91 *n*-butane		90%
4	2-Octene	0	96 ethane	30	50–65%
4	2-Pentene	0	96 mixed	30	90%
4	Diisobutene	0	96 mixed	30	20–30%
4	1-*n*-Hexadecene	0	91 mixed	30	None
4	Allyl chloride	0	96 mixed	30	Trace
4	Methallyl chloride	0	96 mixed	30	Trace

[a] Technique: (1) Parr shaker glass bomb, (2) stirred three-necked flask reactor, (3) shaken by hand in flask under dry ice reflux, (4) acid and olefin shaken by hand in a graduated cylinder.

[b] Based on sulfonic acid.

geneous polymers may contain a number of isomers in each series, but the polymers of a given molecular weight are well defined. The two classes are illustrated in Figures 1, 2, and 3. The first two show the homogeneous polymers formed from 1-pentene and from diisobutene, and the third shows the heterogeneous polymer formed from 2-butene.

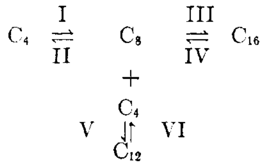
Many of the homogeneous polymers appear to be unusually pure. Tetraisobutene from the dimerization of diisobutene has a very narrow boiling range and behaves chemically as an unusually pure C_{16} polybutene, in contrast with polybutene of equivalent molecular weight made with aluminum chloride as catalyst, for example.

Heterogeneous polymers are obtained from propylene and *n*-butenes. The polymers from propylene are composed of unsaturated hydrocarbons ranging from about C_6 to above C_{20}. The plateaus, on distillation through an efficient column packed with wire gauze are poorly defined and numerous, and indication that compounds of all carbon numbers in that range (C_7, C_8, C_9, etc.) are present, as well as various degrees of branching. No hydrogen-transfer reaction appears to occur, since the polymers obtained are essentially 100% olefinic, and no appreciable quantity of the highly unsaturated oil typical with other catalysts can be isolated from the acid phase on dilution with water. Table II indicates the type of products obtained from various olefins.

Polymerization of Diisobutene. The alkanesulfonic acids have been useful catalysts for the study of the polymerization of isobutene and diisobutene because conditions may easily be set so that essentially no polymer above the tetramer is formed, and no side reactions take place. Diisobutene (2,4,4-trimethylpentene) was treated with alkanesulfonic acid at various temperatures and with various contact times. The composition of the products obtained under the different conditions is shown in Table III.

The data show that longer reaction times or higher temperatures give predominantly trimer, moderate amounts of tetramer, and small amounts of unchanged dimer. Shorter reaction times, more dilute acid, or lower temperatures lead almost entirely to tetramer and unchanged dimer. Table II and other data (*1*) indicate that the direct polymerization of isobutene yields chiefly trimer.

The preceding data indicate that the course of the reaction of isobutene in simple polymerization, under conditions where isomerization of the carbon skeleton does not occur, is as follows:



$$\begin{array}{ccccc} & \text{I} & & \text{III} & \\ C_4 & \rightleftarrows & C_8 & \rightleftarrows & C_{16} \\ & \text{II} & + & \text{IV} & \\ & & C_4 & & \\ & \text{V} & \downarrow\uparrow & \text{VI} & \\ & & C_{12} & & \end{array}$$

When isobutene is passed into the catalyst, reaction V predominates because it is much faster than III. Starting with diisobutene, the only reaction which can occur at a rapid rate is III, because no isobutene is present initially and the depolymerization reaction II is much slower. Since the tetramer does not polymerize further, a point is finally reached where the rates of reactions III and IV become equal. Then the slow reaction II and the fast reaction V become controlling, and the equilibrium shifts, with increasing reaction time, in favor of trimer as the major and most stable polymer.

The ultimate result of a prolonged reaction time is illustrated in Figure 4, which shows the distillation curve for "equilibrium" isobutene polymer. Additional reaction time changed the composition of the "equilibrium" polymer only slightly. Re-

Table II. Polymerization of Olefins

Method	Sulfonic Acid, % Strength	Olefin	Temp., ° C.	Yield[a], %	Polymer Type
Ester	Methane, 100	Propylene	100	70	Heterogeneous
Ester	Methane, 100	Propylene	100	73	Heterogeneous
Ester	Methane, 100	Propylene	93	50	Heterogeneous
Hot acid	Mixed, 97	Propylene	95-100	100	Heterogeneous
Hot acid	Mixed, 97	2-Butene	100	100	Heterogeneous
Ester	Methane, 100	2-Butene	60-90	100	Heterogeneous
Hot acid	Mixed, 96	Isobutene	100	100	Homogeneous
Ester	Mixed, 96	1-Pentene	100	43	Homogeneous

[a] Based on total absorbed olefin.

Table III. Polymerization of Diisobutene

Sulfonic Acid, % Strength[a]	Temp., ° C.	Time, Hr.	Product Composition, Vol. %			
			Dimer	Trimer	Tetramer	Heavier
95 mixed	30	2.0	95	...	Traces	..
91 mixed	60-70	2.5	31.9	1.1	65.9	.
95 mixed	100	1.25	27	11	59	.
95 mixed	60-70	10.0	25	...	70	.
99 ethane	100	0.25	11	56	29	5
99 ethane	100	2.0	12	48	34	6
99 ethane	66	0.25	11	13	76	<2

[a] Amount used equals 17 wt. %.

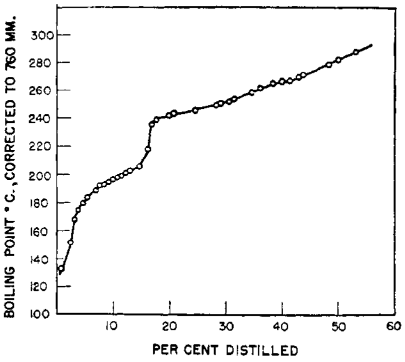


Figure 3. 2-Butene Polymer

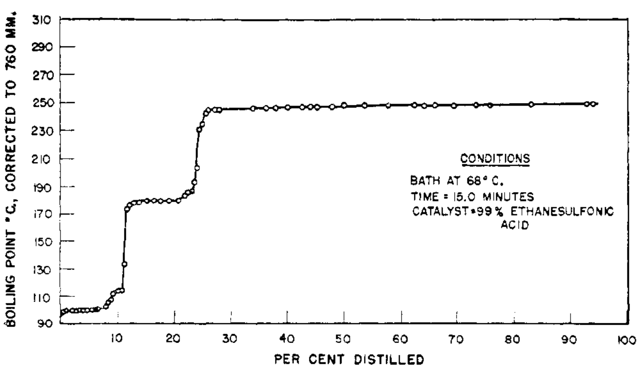


Figure 2. Diisobutene Polymer

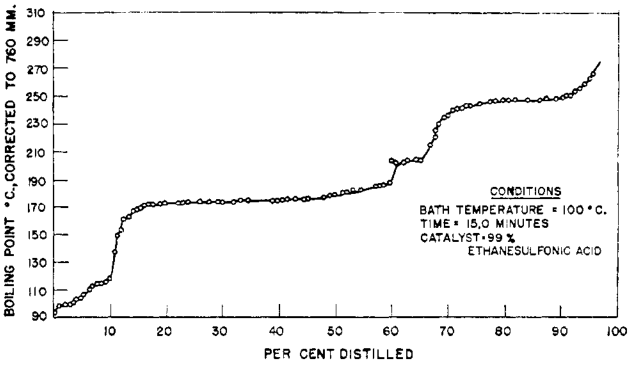


Figure 4. "Equilibrium" Diisobutene Polymer

TABLE IV. ALKYLATION OF AROMATICS WITH OLEFINS

Olefin, Moles	Aromatic, Moles	Sulfonic Acid, % Strength	Temp., ° C.	Pressure, Lb./Sq. In. Gage	Product Composition, %
Propylene[a], 1.06	Benzene, 3.6	Mixed, 96	100	0	70 benzene, 24 cumene, 6 polyalkylated benzenes
Propylene[b], 1.35	Benzene, 1.12	Methane, 100	65–75	40	20 benzene, 46 cumene, 28 diisopropylbenzene, 6 triisopropylbenzene
Propylene[b], 3.9	Benzene, 2.93	Methane, 100	50–55	40	Some ester, 1.5 benzene, 21 cumene, 42 diisopropylbenzene, 31 triisopropylbenzene
Propylene[c], 3.0	Benzene, 2.91	Mixed, 97	80–100	0	21 benzene, 35 cumene, 35 diisopropylbenzene, 9 heavier
Propylene[c], 5.1	Toluene, 1.9	Methane, 100	104–130	0	72 triisopropyltoluene, 28 lower boiling
Propylene[c], 1.5 (approx.)	Toluene, 5.5	Mixed, 96	100	0	63 toluene, 32 cumenes, 5 polyisopropyltoluenes
2-Butene[b], 2.0	Benzene, 0.58	Methane, 100	60–100	15	Mixture of polymer and alkylbenzenes
Crude octenes[b], 0.7	Toluene, 1.1	Mixed, 96	100–104	0	48 mono-octyltoluene, 52 unreacted toluene and octenes
Diisobutene[c], 1	Toluene, 2	Methane, 100	116	0	60% *tert*-butyltoluene, 18 heavier and 22 unreacted

[a] Ester method. [b] Glass shaker bomb apparatus. [c] Stirred flask with hot acid.

TABLE V. COMPOSITION OF ALKYLATE

				Product, Mole Fraction				
Method	Temp., ° C.	Propylene, Mole	Benzene, Mole	Benzene	Cumene	Diisopropylbenzenes	Triisopropylbenzenes	Tetraisopropylbenzenes
Ester	80–110	1.0	3.0	0.79	0.18	←0.03→		0
Ester	77 max.	1.0	0.93	0.29	0.46	0.21	0.085	0
Ester	77 max. (approx.)	1.0	0.28	0.03	0.29	0.43	0.25	0
Hot acid	100	1.0	<0.5[a]	0.027	0.10	0.37	0.37	0.13

[a] Uncertain because some benzene was lost by vapor carry-over with rejected propane.

fractive indices on trimer cuts suggest that the usual three groups of trimer isomers are present (*6*), two boiling at 177–179° and one at 183–185° C. Considerable information as to the catalytic redistribution of isobutene polymers has already been published, but the polymer of greatest stability has not been previously indicated (*3, 6*).

POLYMERIZATION OF 2-BUTENE. According to the ester method, vacuum-distilled (100%) methanesulfonic acid (12 grams, 0.12 mole) was placed in a glass Parr bomb and shaken with 2-butene at 15 pounds per square inch gage. After 11 minutes the acid had gained 7 grams in weight. Several batches of crude *sec*-butylmethanesulfonate, prepared in this way, were combined in a flask, which was then immersed in boiling water. After a short induction period a temperature rise occurred and 2-butene polymer separated as a white oil.

According to the hot acid method, a 1-liter three-necked flask with ground joints was fitted with a glass stirrer, gas-inlet tube, thermometer, and condenser. Mixed 96% alkanesulfonic acid (250 grams) was put in the flask and stirred so as to throw a spray against its upper walls. The temperature was raised to 100° C. and a rapid stream of 2-butene was introduced. Rapid polymerization occurred, and a polymer layer formed. External cooling was used to hold the temperature in the range 100–120° C. The polymer was separated, washed with water, dried over sodium sulfate, and vacuum-distilled.

ALKYLATION OF AROMATICS

Alkylation of aromatics proceeds over the same temperature range as polymerization. Only the most active olefins (isobutene) will alkylate at an appreciable rate at room temperature. In general, alkylation occurs in the temperature range in which the ester is thermally unstable. Once the proper conditions for alkylation are established, it will proceed in preference to polymerization in almost all cases. A previous report (*5*) gave some early data on alkylation with isobutene, and more recent work has shown that the alkylation reaction extends to all simple olefins above ethylene.

Two methods are available for alkylating aromatics with alkanesulfonic acids. The first is to stir the aromatic vigorously in a three-necked flask or other suitable reactor in the presence of catalytic amounts of alkanesulfonic acid at 80–120° C., and add the olefin either as a gas stream or as liquid feed. The second method is to heat the alkyl alkanesulfonate, prepared from the olefin and the alkanesulfonic acid at a lower temperature, with the aromatic to be alkylated; above 60° C. the ester breaks down and alkylation proceeds; at 100–120° C. the rate of alkylation is quite rapid. By either method an upper limit of the reaction temperature of about 150° C. is advisable because of decomposition of the acids.

The scope of the alkylation reaction includes only aromatics (benzene, phenol, etc.) and olefins, to yield alkyl aromatics. Alkanesulfonic acids have not yet been used successfully as catalysts for the alkylation of isopentane. Table IV gives data on a number of typical alkylations.

The alkanesulfonic acids are particularly suitable as catalysts where di- or trisubstituted benzenes are the desired end products. The introduction of a fourth alkyl group does not appear to take place, even if the ratio of olefin to benzene is quite high, provided a proper temperature is selected. At moderate temperatures (about 75° C.) good yields of triisopropylbenzenes can be obtained and no tetraisopropylbenzene is observed, although it has been reported with some other acid catalysts. The latter should be detectable in amounts greater than 2% (*2*). At higher temperatures (110–125° C.), however, tetraisopropylbenzene is formed. The material has been identified as the 1,2,4,5 derivative by its melting point of 116–117° C., after recrystallization from alcohol, compared with the literature value of 118° C. (*4*). Attempts to form the picrate have failed, a saturated alcoholic solution yielding only individual crystals of the hydrocarbon and picric acid at room temperature. Table V shows the effect of the propylene-benzene ratio on the composition of the alkylate.

The monoalkylation of toluene with propylene was also studied briefly. The cymene formed was analyzed by ultraviolet absorption spectroscopy, which showed it to consist of 44% *p*-cymene and 56% of *o*- plus *m*-cymene.

An extended study of higher olefins has not been made. It appears, however, that the tendency for polyalkylation diminishes as the olefin increases in molecular weight. This is shown by experiments in which 1 mole of propylene treated with 3.6 moles of toluene yielded 6.4 times as much monoalkylated product as polyalkylated product, whereas in the reaction of 1 mole of octene and 3.14 moles of toluene the ratio of mono- to polyalkylated product was more than 48 to 1.

Alkylations with isobutene and isobutene polymers contrast with alkylations using other olefins. The depolymerization already mentioned occurs when an attempt is made to alkylate toluene with either diisobutene or tetraiosbutene; the products are *tert*-butyltoluene plus some triisobutene. Cleavage of the diisobutene has been reported for other acid-condensing catalysts (*1*). Similarly, the alkylation of toluene with isobutene results in a product consisting of triisobutene and *tert*-butyltoluene. This alkylation is the only one observed in which polymerization is a successful competitor with alkylation under conditions favorable for both.

When phenol is treated with diisobutene or tetraisobutene in the presence of alkanesulfonic acids, octylphenol is obtained. The depolymerization of the tetraisobutene needs only to proceed as far as the dimer in order to yield an olefin sufficiently active to react with phenol (*5*).

Synthesis of Isopropylbenzene. By the ester method isopropylmethanesulfonate (1.06 moles), benzene (3.6 moles), and methanesulfonic acid (0.5 mole) were heated to 80° C. After an induction period of 10 minutes a sudden reaction occurred, and the mixture separated abruptly into two phases. The temperature was held at 80–100° C. for an additional 20 minutes, after which the hydrocarbon layer was separated, washed with dilute aqueous sodium hydroxide, and distilled under reduced pressure. The distillation curve showed no polymer and indicated the following yields, in volume per cent: recovered benzene, 70; isopropylbenzene, 24; diisopropyl- and triiospropylbenzene, 6 (predominantly diisopropylbenzene).

By the hot acid method mixed 97% alkanesulfonic acid (49 grams, 0.45 mole) and 223 grams (2.9 moles) of c.p. benzene were placed in a three-necked flask provided with a gas inlet tube, reflux condenser, and stirrer. The contents were stirred so as to spray the flask walls and were heated to 70° C. Propylene was then passed in at a moderate rate. Temperature was held at 75–85° C. for 4 hours, and the alkylation was completed during an additional 3 hours at 75–100° C. The product was washed, treated with alcoholic potassium hydroxide, dried, and fractionated. The composition was 21% benzene, 35% cumene, 35% diisobutene, and 9% heavier.

CONCLUSIONS

The alkanesulfonic acids of lower molecular weight are effective catalysts for the polymerization of olefins and the alkylation of aromatics with olefins. Specific thermal conditions apply to each of these processes. Ester formation between the catalyst acid and the olefin occurs at 0–60° C., and alkylation or polymerization at 60–150° C.

Polymerization of some olefins, such as isobutene and 1-pentene, yields products containing all multiples of the monomer through tetramer; other olefins, such as 2-butene and propylene, yield polymers which are more heterogeneous in nature. In general, the type of polymer appears to depend to some extent upon the molecular weight of the monomer.

These olefins that form alkanesulfonic esters undergo polymerization (and alkylation) only at temperatures at which the esters become thermally unstable. This fact, and the absence of either alkylation or polymerization with olefins which do not form esters, suggests that ester formation may be the primary step in both alkylation and polymerization. The alkanesulfonic acids are particularly suitable for use as catalysts in polymerization and alkylation because such side reactions as hydrogen transfer, sulfonation, and complex formation are essentially absent.

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Adsorption of Fatty Acids from Solvents

DUOLITE A-2 ANION EXCHANGE RESIN

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The adsorption on Duolite A-2, anion exchange resin, of a homologous series of carboxylic straight-chain acids from acetone, water, and Shell solvent is reported. The adsorption increases in the order given. The bearing of these results on various theories of the adsorption of acids by resinous anion exchange materials is indicated. Some qualitative and semiquantitative results for the adsorption of a variety of acids from hydrocarbon solution on the same adsorbent are given, with a few suggestions for practical application and reports of such applications.

In view of the various opinions (*2, 4, 7*) as to the mechanism of acid adsorption on anion exchange resins, the investigation of these adsorbents was extended to solvents other than water. Such an investigation also may open additional fields of application for these interesting adsorbents. Earlier work in this field by Myers (*6*) using Amberlite IR-4 anion exchange resin indicated that some water was required for effective adsorption of the fatty acids from solvents such as benzene. Amberlite IR-4B dries to hard glassy solid which apparently is largely impervious to solvents such as benzene and thus presents little active surface for acid adsorption when completely dry. Duolite A-2, on the other hand, remains relatively porous on drying and it has long been known that with this resin no water is necessary for the adsorption of fatty acids from nonaqueous solvents. In this study attention is directed to the straight-chain carboxylic acids. For comparative purposes the adsorption of carboxylic acids from aqueous media also is shown. The adsorption of these acids from nonaqueous media may be either greater or smaller than the adsorption of the corresponding acids from water.

EXPERIMENTAL

Materials. The resin chosen for this study was Duolite A-2, manufactured by the Chemical Process Company. The Duolite A resins differ from most other commercial anion exchange resins in that they remain relatively porous on drying and thus present a much larger active surface than do resins which shrink greatly in