The Thermal Alkylation of Phenol With Olefins

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ABSTRACT

Linear alkylphenols from α-olefins can be made by reaction at 260-425 C without added catalyst. By proper choice of conditions, up to 95% monoalkylphenol having the phenol moiety attached at the 1- and 2-carbon of the side chain (primarily *ortho* orientation) can be obtained.

INTRODUCTION

The alkylation of phenol with olefins is well represented in the literature (1-8). There is, however, very little information on the position of attachment of the phenolic moiety to the side chain in products resulting from such reactions. It appears that most alkylation techniques lead to mixtures containing a predominance of isomers in which the aromatic group is attached near the end of the chain, but substantial amounts of the internally attached counterparts are characteristically found. We therefore decided to try to find a means to control product orientation.

Our primary objective was to optimize attachment at the 1- and 2-carbons of the side chain. Both catalytic and thermal reactions were investigated. We found that ethoxamer sulfate surfactants made from thermal products are considerably richer in near end-attached isomers and more biodegradable than those prepared from alkylphenols relatively rich in internally attached isomers.

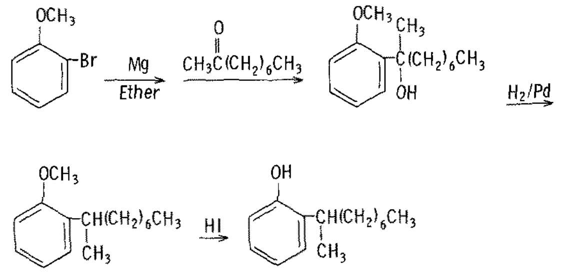
EXPERIMENTAL PROCEDURES

Die-Away Test

The die-away test used was similar to the river die-away test of the Soap and Detergent Association (T.E. Brenner, written communication, August 1965) with a few modifications. The bacterial source for the test was the effluent from a continuous activated sludge sewage test unit (9) fed with synthetic sewage (10). To a 90/10 mixture of tap water-effluent, which served as the medium, 5 ppm of the surfactant to be tested was added. Analyses were carried out by a modified American Public Health Association (APHA) methylene blue method (11). In some cases, a stronger bacterial system was made by the addition of 0.1% activated sludge.

Model Compounds

Three model compounds were synthesized by a series of steps typified as follows:



2-(o-Methoxyphenyl)nonanol-2

A 1 liter round bottom three-neck flask was charged with 13 g (0.54 mole) of magnesium turnings and flushed with nitrogen. Ten milliliters of *o*-bromoanisole [Eastman white label, >98% by gas liquid chromatography (GLC)] in 15 ml of dry ether was added. The reaction was started and kept at reflux by dropwise addition of the remainder of the *o*-bromoanisole (total: 100 g; 0.54 mole). 2-Nonanone (71 g; 0.5 mole, K and K Laboratories Lot No. 32324X, 98% by GLC) was added over a period of 0.5 hr under gentle reflux. The mixture was worked up according to Fieser's method (12). Yield of crude product: 108 g (86.5%).

2-(o-Methoxyphenyl)nonane

2-(*o*-Methoxyphenyl)nonanol-2 (81 g; 0.32 mole), 140 ml of absolute ethanol, and 1.4 g of 10% palladium on carbon were placed in an autoclave, pressured up to 1000 psig with H_2, and shaken at room temperature for 4.5 hr. Vacuum distillation of the filtered product afforded 68 g (90%) of a white oil. Redistillation gave a product 97% pure by GLC.

2-(o-Hydroxyphenyl)nonane

2-(*o*-Methoxyphenyl)nonane (24.3 g; 0.10 mole), 50 ml of 47.5% aqueous HI and 150 ml of glacial acetic acid were refluxed for 21 hr. Workup of the reaction mixture gave a crude material (20 g, 87.5% yield) which was 88-90% pure by GLC. Purification by vacuum distillation at 134-138 C (3 mm) gave 14 g of 2-(*o*-hydroxyphenyl)nonane which showed only one GLC peak.

Analysis calculated for: C, 81.8, H, 11.0. Found: C, 81.4, 81.2; H, 10.8, 10.7.

Catalytic Alkylation

The following example is typical of all catalytic alkylation experiments: A 500 ml round bottom three-neck flask

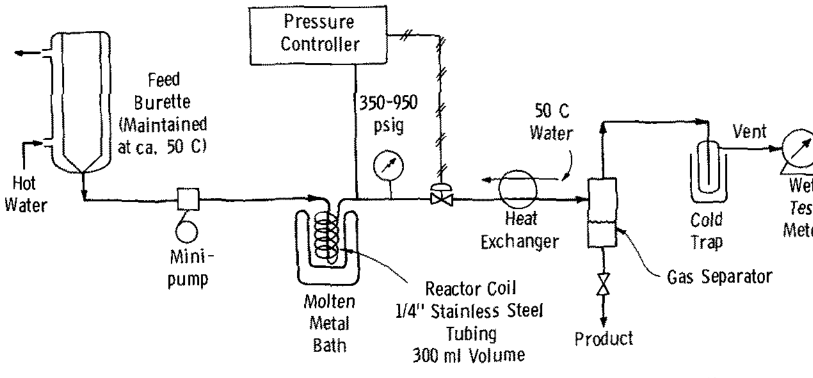


FIG. 1. Continuous unit for thermal alkylation of phenol with olefins.

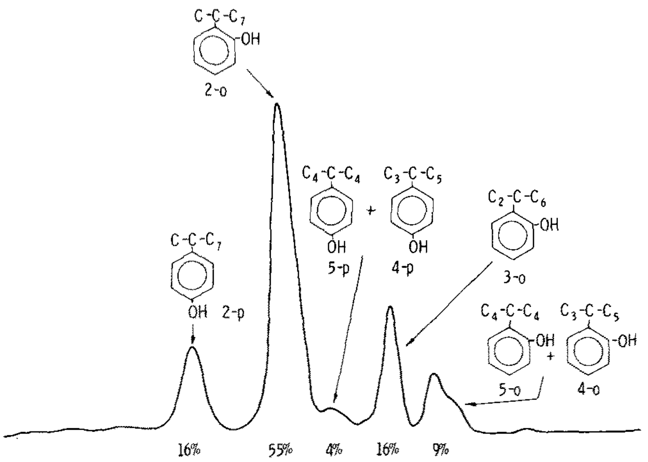


FIG. 2. GLC, Lewis acid-catalyzed alkylation. No alkylphenyl ethers present.

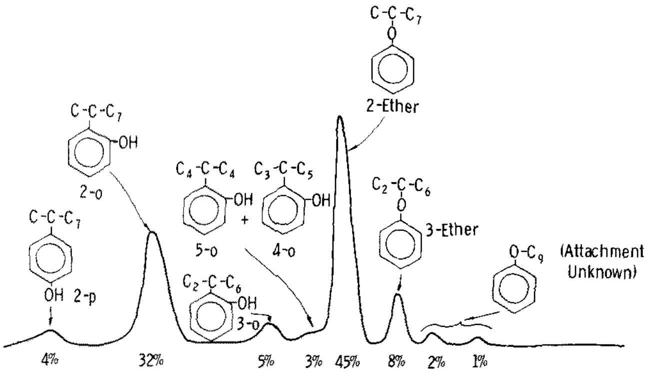


FIG. 3. GLC, Lewis acid-catalyzed alkylation. Alkylphenyl ethers present.

equipped with stirrer, thermometer, dropping funnel and nitrogen inlet was flushed with nitrogen and charged with 94 g (1 mole) of phenol and 4.6 g (0.018 mole) of anhydrous stannic chloride. The mixture was stirred and heated to 65 C. 1-Nonene (12.6 g; 0.1 mole) was added over a period of 2 min. Periodically a sample was withdrawn, washed thoroughly with water, dried over anhydrous calcium sulfate, and analyzed by GLC.

An Aerograph 350 C chromatograph containing 10 ft, 1/4 in. dual columns packed with 10% Apiezon L on 60-80 mesh Chromosorb W was used. Temperature was programmed at 10 C/min from 100-250 C.

Glass Capillary Tube Reactions

Glass tubes, 2 mm i.d., 15 cm long, were half filled with a 5:1 weight ratio of phenol (Baker, reagent) and 1-nonene (Chevron Alpha Olefin) and sealed under nitrogen. The tubes were placed in a muffle furnace at the desired temperature. Tubes were periodically withdrawn, quenched in a glycerol bath, and the contents analyzed by GLC.

Stainless Steel Tube Reactions

These reactions were performed in 8 mm i.d., 15 cm long, 1 mm wall thickness, 316 stainless steel tubes, capped at both ends with 316 stainless steel Swagelok fittings. After filling, the tubes were sealed and kept warm. They were immersed in a stirred molten sodium nitrite-potassium nitrate bath maintained at the desired temperature. Individual tubes were removed at appropriate times, quenched and analyzed by GLC.

Continuous Reaction

Figure 1 shows the flow diagram of the continuous equipment.

RESULTS AND DISCUSSION

Analytical Technique

Studies were conducted using 1-nonene, 1-decene, or mixtures thereof, as the olefin reactant. The principal analytical tool used was gas liquid chromatography. Figure 2 shows the GLC trace representing an example of a Lewis acid-catalyzed alkylation reaction. Some peak assignments were made via spiking experiments using three pure model compounds prepared by classical synthetic techniques. Others were made through mass spectrometric data and presumptive evidence based on the known behavior of straight chain alkylbenzene isomers on similar GLC columns. The model compounds were 2(*o*-hydroxyphenyl)-, 5(*o*-hydroxyphenyl)- and 5(*p*-hydroxyphenyl) nonane. For the sake of simplicity, compounds in which the phenolic moiety is attached at the 1- or 2-carbon atom of the side chain are henceforth called "near end-attached," all others being designated "internally attached" isomers.

Catalytic Aklylation

Table I presents product composition data for a series of reactions carried out under the influence of a variety of typical Lewis acid-type catalysts. The 2-attached isomer content varies considerably (no 1-attached alkylphenols were detected). As can be seen, a number of the catalysts screened led to the formation of large quantities of alkylphenyl ethers as well as the aklylphenols. Figure 3 shows a GLC trace of such a product mixture. Peak assignments for the ether were based on IR and mass spectrometric data obtained on small samples isolated via GLC separation. Most of the analytical results were obtained only on products isolated after a reaction time of 3 hr. With the HF and $SnCl_4$ systems, however, additional samples were analyzed. We discovered that at short reaction time, the product contained large quantities of the 2-ether, but then when allowed to stand, only aklylphenol was found, indicating that the intermediate ether had undergone rearrangement. The presence of such a rearrangement, at either considerably faster or slower rate than was the case for $SnCl_4$ or HF, cannot be ruled out for the other catalyst systems studied. Indeed, we found that some catalysts, e.g., $FeCl_3$ would rearrange the 2-ether to the aklylphenol, but the resulting product contained a large amount of internally attached isomers.

Olefin conversion was in general very high except for a few of the weak catalyst systems, e.g., $SbCl_5$, $CuCl_2$, $H_5P_3O_{10}$, where conversion was low. For these, the 2-*ortho* and 2-*para* isomer content was also low and the 2-ether content high. If additional reaction time had been allowed, 2-ether might have rearranged giving rise to a moderate increase in the amount of near end-attached alkylphenols present. Apparently there was no parallel between the Lewis acid catalyst strength and product distribution. For example, the strong catalyst $AlCl_3$ gives excellent conversion, low near end-attached isomer and high ether content. On the other hand, weaker systems such as $FeCl_3$ and $BF_3 \cdot Et_2O$, while still showing excellent conversion, give relatively high near end-attached isomer content and no alkylphenyl ether. These results may be explainable on the basis of widely varying isomerization rates (ether to aklylphenol) of these catalyst systems, but further conclusions cannot be drawn from our data.

Thermal Alkylation

Since catalytic alkylations did not show the desired selectivity, i.e., $<90\%$ near end-attachment, with respect to product distribution, another reaction system was sought.

TABLE I

Catalytic Alkylations[a]

Catalyst	2-*Ortho*, %	2-*Para*, %	2-Ether, %	Other, %	Olefin conversion
$BF_3 \cdot H_3PO_4$	55	11	---	34	80
$BF_3\cdot$ØOH	54	14	---	32	99
$BF_3 \cdot Et_2O$	55	11	---	34	99
$H_5P_3O_{10}$	27	5	54	14	45
H_2SO_4	52	14	---	34	99
$FeCl_3$	55	17	---	28	98
$AlCl_3$	35	3	58	4	96
$Al\ (OO)_3$	23	3	69	5	96
$SbCl_5$	26	7	60	7	50
$CuCl_2$	21	15	60	4	30
$SnCl_4$	31[b]	5	50	14	80
	55[c]	16	---	29	99
HF	34[b]	3	47	16	98
	51[d]	11	---	38	99

[a] Reaction conditions: 10:1 phenol-olefin w/w; 20 mole % catalyst (based on olefin); 65 C, 3 hr reaction time.

[b] Sampled immediately after olefin addition.

[c] Sampled 1 hr after olefin addition.

[d] Sampled after standing overnight.

TABLE II

Thermal Alkylation of Phenol With α-Olefins
Glass Capillary Tube Data[a]

Temp., C	Time, hr	Olefin conv., %	1-Attached, %	2-*Ortho*, %	2-*Para*, %	Other, %
325	1	40	---	68	4	28
	3	45	4	73	3	20
	5	55	4	70	5	21
350	1	35	2	78	3	17
	3	75	7	76	4	13
	5	80	7	74	4	15
370	1	35	3	85	6	6
	3	75	7	82	4	7
	5	90	10	75	3	12
400	1	60	10	78	5	7
	2	90	12	66	3	19
	3	90	9	77	3	11
450	1	90	13	49	2	36
	2	95	4	5	---	91

[a] Phenol-1-Nonene, 5:1 w/w).

TABLE III

Thermal Alkylation of Phenol in Continuous Reactor[a]

Olefin[b]	Temp., C	Pressure, psig	Time, hr	Olefin conv., Mole %	MAP[c] Yield, Mole %	Near end-attached Isomers, %
C_9-C_{10}[d]	370	600	0.3	21	71	92
C_9-C_{10}[d]	370	600	1.2	55	60	95
C_9-C_{10}[e]	370	600	0.3	19	64	96
C_9-C_{10}	325	350	1.4	34	86	96
C_9	295	350	1.5	23	80	93
C_9	315	750	1.5	39	71	92
C_9	370	600	0.3	48	58	93
C_9	370	750	0.3	41	69	92
C_9	370	600	1.25	65	79	84
C_9	370	600	1.8	85	60	81
C_9	400	850	0.4	52	74	87
C_9	400	850	1.1	77		
C_{10}	370	750	0.3	31	86	95

[a] Phenol-olefin 5:1 w/w, unless otherwise indicated.

[b] Chevron Alpha Olefins except last entry, which was 1-decene from Humphrey Chemical Co.

[c] MAP, monoalkylphenol.

[d] Phenol-olefin 1:1.

[e] Phenol-olefin 2:1.

TABLE IV

Comparison of Vapor and Condensed Reactions

Phase	Conversion, %	Temp., C	ϕOH/olefin	Near end-attached isomers, %
Vapor	17	370	2:1	85
Condensed	17	370	2:1	>94
Vapor	69	370	2:1	66
Condensed	69	370	2:1	80
Vapor	10	370	1:1	85
Condensed	10	370	1:1	>95
Vapor	69	370	1:1	71
Condensed	69	370	1:1	90

A series of reactions was attempted at high temperature in which the catalyst was omitted completely. Certain aspects of the thermal alkylation of phenol have been described in the literature (13,14) but complete structure analyses are lacking.

The first indication that the desired product distribution could be made by thermal, noncatalytic alkylation of phenol was obtained from a number of experiments carried out in sealed glass capillary tubes (Table II). Under optimum conditions (370 C, 3 hr), a significant improvement in 2-attached alkylphenol over that found earlier in Lewis acid-catalyzed reactions was obtained. In many cases, a substantial amount of 1-attachment was detected. As a result of these encouraging batch results, the study of the thermal reaction was pursued in a continuoue reactor. Analytical data on the continuous runs are summarized in Table III. High near end-attached isomer content (96%) and yield (86%) were obtained at 325 C, 1.4 hr residence time, and 350 psig. Similar results were obtained at lower temperature (295 C) and longer reaction time (1.5 hr).

The value of the work using the continuous unit was that (a) a product whose near end-attached content was slightly higher (96%) than that obtained in capillary glass tubes could be produced and (b) the residence time for the reactants could be shortened considerably.

Vapor Phase Reaction

Data obtained from the continuous reactor indicated that the product alkylphenols were the result of alkylation occurring predominantly in the condensed phase. Evidence for this was obtained from the observed "pressure plateau." As the reactants were initially pumped into the hot reaction zone, they immediately vaporized causing the pressure to increase steadily. The pressure increased to a certain point (approximately 300 lb. for a 5:1 weight ratio of phenol-olefin at 157 C), where it remained constant for a time, then rapidly increased again after the reactor coil was filled with condensed phase. This pressure plateau must be interpreted as the point at which a proportionate amount of vapor is converted into some kind of condensed phase when the system pressure is increased by external means, e.g., a pump. The existence of a condensed phase must be concluded even though in some runs the reaction temperature was above the critical temperature of each reactant.

It was, therefore, of interest to see what would happen when the reactants were maintained completely in the gas phase. A simple experiment was carried out in which a very small amount of phenol and olefin was heated in a vessel of relatively large volume. The vapor phase reaction was found to be much slower. A comparison of the liquid phase vs. vapor phase reaction at 370 C and equal conversions (Table IV) shows that the vapor phase reaction afforded a product significantly richer in internally attached isomers. For example, at a 2:1 phenol-olefin ratio and an olefin conversion of only 17%, the near end-attached component of the vapor phase product (85%) was much lower than the corresponding condensed phase product (>94%).

To obtain more data per unit time, smaller scale batch experiments were resumed but with several modifications. This work was done using 8 mm i.d., 15 cm long, 316 stainless steel tubes. The larger tubes provided greater mobility for the contents than could be obtained in

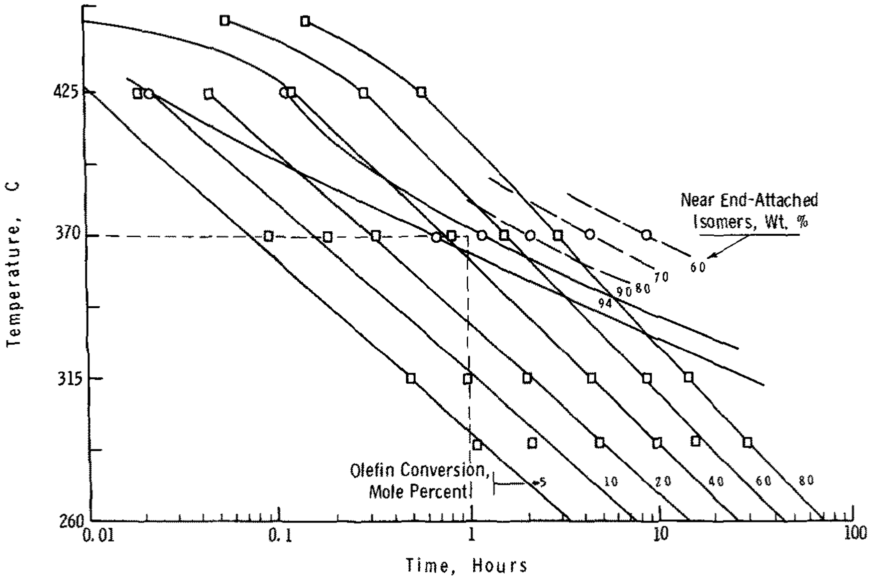


FIG. 4. Stainless steel tube data. Effect of time and temperature on conversion and near end-attached isomer content of linear alkylphenols. Phenol-1-nonene, 2:1 w/w.

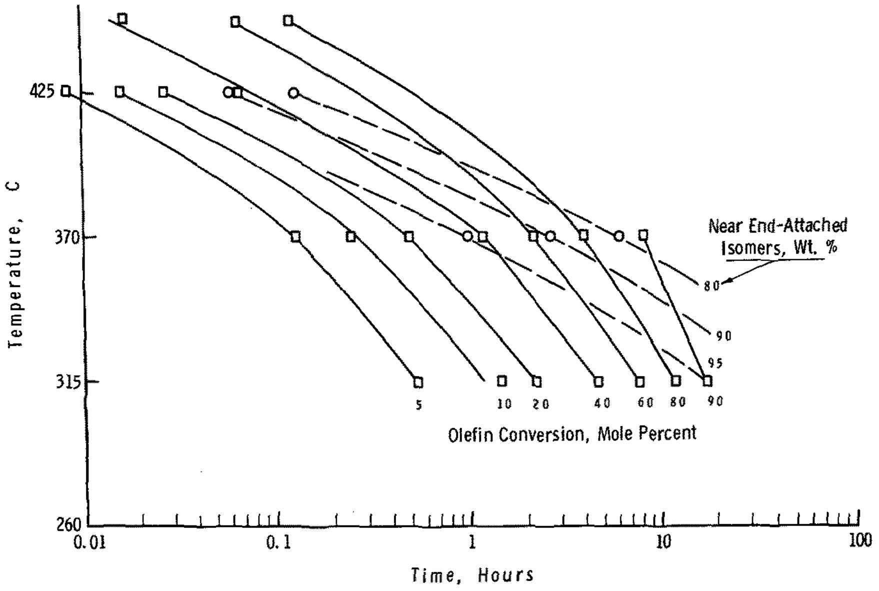


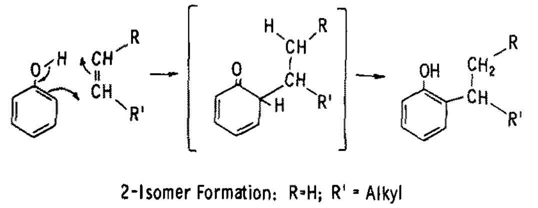
FIG. 5. Stainless steel tube data. Effect of time and temperature on conversion and near end-attached isomer content of linear alkylphenols. Phenol-1-nonene, 1:1 w/w.

capillary glass tubing used previously. Figures 4 and 5 summarize the results from all stainless steel tube reactions. In general, three variables were examined: temperature, time and phenol-olefin weight ratio. Conversion and near end-attached component are given as functions of temperature and time. For example, at 370 C and 1 hr (2:1 phenol-olefin ratio), olefin conversion is 45% and product near end-attachment is about 92%. At a given time and temperature, reactions in which the phenol-olefin ratio was 2:1 gave slightly higher conversion than the 1:1 case (at 370 C, 2 hr: 70% vs. 60%), the near end-attached isomer content was higher for 1:1 than 2:1 (370 C, 2 hr: 93% vs. 82%). However, the 1:1 ratio gave significantly more yield loss (presumably by dialkylation) than the 2:1 case.

Thermal Stability of Monoalkylphenols and Dialkylphenols in the Presence of Excess Phenol

A sample of dialkylphenol obtained from distillation of the bottoms from a thermal alkylation run was heated to 370 C with a fourfold excess of phenol. Gas chromatographic analysis showed that with time, peaks attributed to dialkylphenol steadily decreased and monoalkylphenol peaks increased. After 5 hr, dialkylphenol had almost disappeared. The internally attached isomer content of the newly formed monoalkylphenol was very large. This observation suggests a method for making monoalkylphenols of high internally-attached content.

In a similar manner, we determined that *ortho*-(2-alkyl) phenol shows some thermal instability in the presence of phenol. The internally attached components increased significantly when a monoalkylphenol consisting mainly of *ortho*-(2-nonyl)phenol was heated for 2 hr at 370 C with a 100% weight excess of phenol.



2-Isomer Formation: R=H; R' = Alkyl

1-Isomer Formation: R = Alkyl; R' = H

FIG. 6. Probable mechanism.

These stability data show very convincingly that if products of high near end-attachment are required, long reaction times are not desirable in thermal alkylations. One must strike a balance between reaction times long enough to give reasonable conversions and short enough to assure good product quality.

Thermal Reaction Mechanism

The most likely mechanism for the thermal alkylation of phenol is a concerted one involving a six-membered transition state. This type of mechanism (Fig. 6) seems necessary to account for the highly predominant formation of both 2-attached and 1-attached isomers with *ortho* orientation.

Structure Versus Biodegradability

Control of the isomer distribution of products resulting from the alkylation of phenol with straight chain olefins was tried in order to improve the biodegradability of surfactants derived from these products. It is well known in the case of alkylbenzene sulfonates that altering the side chain from a highly branched structure (ABS) to a straight chain (LAS) results in great improvement in the biodegradability of the product. The position of attachment of the aromatic group to the side chain is relatively unimportant. In the case of alkylphenol-derived surfactants, however, a

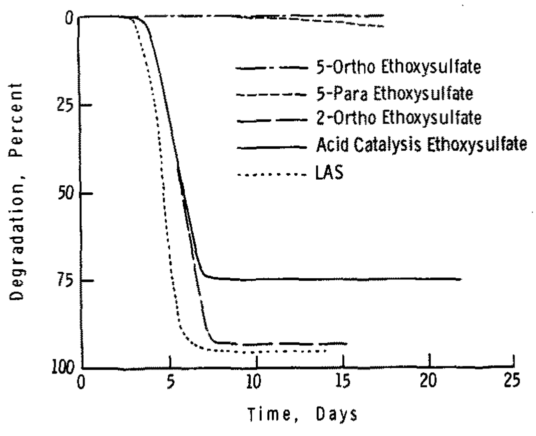


FIG. 7. Mild die-away test.

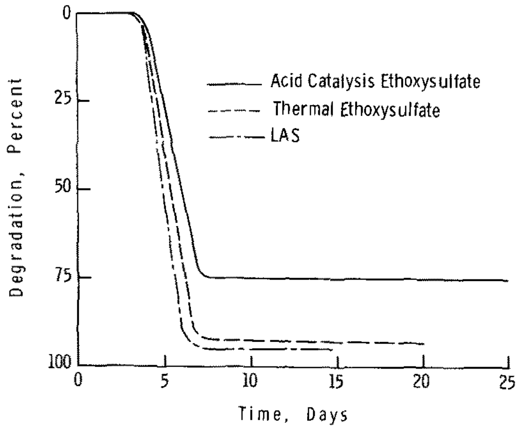


FIG. 8. Mild die-away test.

simple straightening of the side chain improves biodegradability significantly; but the product made via normally employed acid catalysis routes does not nearly match LAS in this regard.

The two most probable explanations for the relatively poor degradability of the typical acid catalyst-derived linear alkylphenol surfactants were considered: (a) the effect of the position of attachment of the aromatic group to the side chain and (b) the effect of *ortho* vs. *para* structure. To evaluate these points, the three pure isomeric nonylphenols discussed earlier were ethoxylated, sulfated and tested in a typical mild die-away test (relatively inactive bacterial system). The results (Fig. 7 and with LAS) indicated that the 2-*ortho* isomer was highly biodegradable. The unbiodegraded residue, although low, may be due to side reactions occurring during the ethoxylation and sulfation steps. The 5-*ortho* and 5-*para* isomers showed no degradation at all. Even in a more active bacterial system, the 5-*para* isomer was shown to be only slightly degraded and the 5-*ortho* isomer not at all. By inference, therefore, the 2-*para* isomer is also biodegradable.

From these data, it is concluded that *ortho* attachment has only a slight deleterious effect on biodegradability; and the most important consideration is the position of aromatic attachment to the side chain.

It was soon shown that not only the 2-*ortho* isomer but all the near end-attached isomers are highly biodegradable. Remarkably good agreement was obtained between the near end-attached isomer content (as measured by GLC) and the experimentally measured biodegradability of a product. For example, the near end-attached isomer content of a typical acid-catalyzed type product was shown to be about 71%. Its biodegradability was 70-75%.

Further support for the above statement and an indication of the improvement in biodegradability brought about by the switch from catalytic to thermal alkylation, are that the product from the last run in Table III was distilled into 38 equal cuts plus a bottoms product equal in weight to about two cuts. Cuts 2-36 (88% of the total) were blended together and converted to the corresponding ethoxysulfate. Die-away results (Fig. 8) showed this material to be about 95% biodegradable compared to only 65-75% for an acid-catalyzed type alkylphenol ethoxysulfate.

This biodegradability discussion treats only alkylphenol ethoxamer sulfate anionic surfactants. Nonionic alkylphenol ethoxamers also play an important role in the detergent industry. Smithson (15) has discussed the performance of such nonionics made via our thermal alkylation process. Since, however, all presently known methods (16; also, T.E. Brenner, written communication, August 1965) for measuring biodegradability of this type of surfactant have serious shortcomings, no reliable data have been obtained.

ACKNOWLEDGMENT

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