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Preparation of *tert*-Alkylbenzoic Acids by Liquid Phase Catalytic Oxidation

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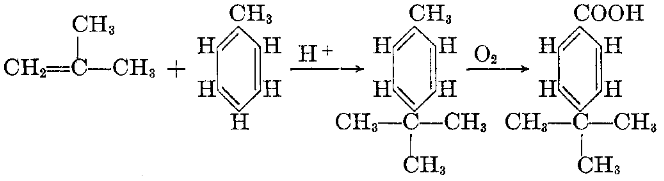
Although the technique for liquid phase oxidation of alkylaromatic hydrocarbons has been known for some time, its use has been restricted largely to the synthesis of benzoic acid itself or to benzoic acids, in which the only alkyl substitutents are methyl groups (toluic acids). One reason for this is that many of the larger alkyl groups are easily cleaved during the oxidation. The carbon-hydrogen bond most susceptible to attack in oxidation is the one adjacent to the benzene ring, and its reactivity is increased by replacing the other hydrogen atoms on this carbon by alkyl groups. Thus *p*-cymene forms toluic acid predominantly, with an accompanying loss of two carbon atoms (*7*). However, cumic acid has been claimed as a product when the oxidation is performed at relatively low temperatures (*6*). The only procedure by which many alkylbenzoic acids—e.g., *n*-hexylbenzoic acid—can be derived from hydrocarbon oxidation is to start with a dialkylaromatic containing two identical side chains. This results in a considerable loss of weight to undesirable oxidation products. Another alternative, the alkylation of benzoic acid, leaves much to be desired because the carboxyl group deactivates the aromatic ring toward alkylation.

The *tert*-alkylaromatic hydrocarbons stand in distinct contrast to the other alkylaromatics in that the side chains are much more stable toward oxidation. The carbon atom adjacent to the benzene ring is quaternary and the reactive carbon-hydrogen bond is absent. If both tertiary and nontertiary groups are present, oxidation proceeds at the latter with the formation of *tert*-alkylbenzoic acids. By varying the nature of the tertiary group, a family of *tert*-alkylbenzoic acids can be made available (*2*).

p-tert-Butylbenzoic acid, the simplest member of the series, is currently in commercial production by Shell Chemical Corp. at Martinez, Calif.



Tertiary alkyl groups are added as last step in synthesis

The hydrocarbons from which the *tert*-alkylbenzoic acids are derived have an aromatic nucleus joined to one or more tertiary and one or more nontertiary alkyl groups. In synthesizing these compounds it is desirable to add the tertiary alkyl groups as the last step. Relatively mild conditions are required for introducing these radicals (as compared to nontertiary groups), and the resulting alkylates are somewhat unstable toward isomerization and disproportionation. As the nontertiary alkyl component serves merely as a source for the carboxyl group, it is desirable to limit this to methyl or ethyl as in toluene or ethylbenzene. The former is preferred on the basis of cost and oxygen consumption. For the preparation of an aromatic acid containing both a tertiary and a nontertiary alkyl group, the appropriate xylene isomer can be substituted for toluene. The *tert*-alkyl groups are

Table I. Preparation of *tert*-Alkyl Toluenes

Compound	Starting Material		Catalyst	Yield on Aromatic, Wt. %	Analyses			B.P., ° C./ *P*, Mm. Hg
	Aromatic	Olefin			Br. No.	Mol. Wt. Calcd.	Mol. Wt. Found	
p-tert-Butyltoluene	Toluene	Isobutene	H_2SO_4	90	..	148	147	193/760
m-tert-Butyltoluene	Toluene	Isobutene	H_2SO_4	..	..	148	148	189/760
2-Methyl-4-*tert*-butyltoluene	*o*-Xylene	*tert*-Butyl alcohol	H_2SO_4	46	..	162		85/10
3-Methyl-5-*tert*-butyltoluene	*m*-Xylene	*tert*-Butyl chloride	$AlCl_3$	74	..	162		96/20
p-tert-Amyltoluene	Toluene	*tert*-Amyl alcohol	H_2SO_4	83	0.6	162	174	100/20
p-Hexyltoluene	Toluene	Propene dimer	H_2SO_4	88	0.5	176	178	60–1/2
3,5-Di-*tert*-butyltoluene	Toluene	*tert*-Butyl chloride	$AlCl_3$	83	..	204	202	103/10
p-tert-Octyltoluene	Toluene	Diisobutene	H_2SO_4	50	..	204	...	131/20
p-Nonyltoluene	Toluene	Propene trimer	H_2SO_4	58	..	218	225	70–82/0.3–1.0
p-Dodecyltoluene	Toluene	Propene tetramer	H_2SO_4	64	..	260	257	84–9/0.3
2-Methyl-4-dodecyltoluene	*o*-Xylene	Propene tetramer	H_2SO_4	92	0.75	274	252	126–39/0.4

Table II. Preparation of *tert*-Alkylbenzoic Acids

						Alkylbenzoic Acid Recovered					
Compound	Alkylate Oxidized	Oxidant	Temp., ° C.	Time, Hours	Catalyst, P.P.M. Co	Conv. of applied alkylate	Yield on consumed alkylate	Melting point obsd., ° C.	Equiv. Wt. of Acid Calcd.	Equiv. Wt. of Acid Found	Melting point, ° C. lit.
p-tert-Butylbenzoic acid	*p-tert*-Butyltoluene	O_2	118	24	157	43	87	165	178	177	165.0–165.6 (*8*)
m-tert-Butylbenzoic acid	*m-tert*-Butyltoluene	Air/70 lb./sq. inch gage	165	2	200	58	75	127	178	178	127.0–127.6 (*8*)
2-Methyl-4-*tert*-butylbenzoic acid	2-Methyl-4-*tert*-butyltoluene	Air/50 lb./sq. inch gage	140	2.5	40	44 (total acids)	....	138–143	192	197	140 (*1*)
3-Methyl-5-*tert*-butylbenzoic acid	3-Methyl-5-*tert*-butyltoluene	Air/50 lb./sq. inch gage	180	3.5	30	52 (total acids)	...	161	192	188	162 (*1*)
p-tert-Amylbenzoic acid	*p-tert*-Amyltoluene	O_2	110	15	60	59	85	105–7	192	193	158(*3*)
p-Hexylbenzoic acid	*p*-Hexyltoluene	O_2	110	24	60	36	62	Partly crystalline	206	253	
3,5-Di-*tert*-butylbenzoic acid	3,5-Di-*tert*-butyltoluene	O_2	140	20.5	48	55	..	171	234	232	
p-tert-Octylbenzoic acid	*p-tert*-Octyltoluene	Air/50 lb./sq. inch gage	135	4	30	50	..	158	234	233	
p-Nonylbenzoic acid	*p*-Nonyltoluene	O_2	120	21	157	27	64	Not crystalline	248	248	
p-Dodecylbenzoic acid	*p*-Dodecyltoluene	O_2	105	27.5	240	56 (total acids)	..	Not crystalline	290	308	
2-Methyl-4-dodecylbenzoic acid	2-Methyl-4-dodecyltoluene	O_2	118	24	157	50	69	Not crystalline	304	301	

easily introduced into toluene by alkylation with a tertiary alcohol, halide, or olefin.

The alkylations summarized in Table I were catalyzed by either sulfuric acid or aluminum chloride. When sulfuric acid was used, the mole ratio of aromatic to olefin to 93% acid was 4:1:8 with reaction at 0° for several hours. The aluminum chloride alkylations were also done at 0° with a mole ratio of aromatic to aluminum chloride of 1 to 0.15 with various ratios of aromatic hydrocarbon to olefin.

p-tert-Butyltoluene and *p-tert*-amyltoluene were synthesized by alkylating toluene with *tert*-butyl and *tert*-amyl alcohol, respectively, in the presence of sulfuric acid. The *p-tert*-butyltoluene contains about 5% of the meta isomer. As this was not removed prior to oxidation, it was necessary to separate the isomeric benzoic acids after oxidation. A sample of *m-tert*-butyltoluene was, however, isolated by careful fractionation in a 40-plate column and its behavior on oxidation observed. When *o*-xylene was substituted for toluene in the sulfuric acid–catalyzed alkylation with *tert*-butyl alcohol, the product was indicated to be 1,2-dimethyl-4-*tert*-butylbenzene. *p-tert*-Octyltoluene was prepared by sulfuric acid–catalyzed reaction between diisobutylene and toluene. This was accompanied by some *p-tert*-butyltoluene by cleavage of the olefin or the alkylate.

The *p*-hexyl-, nonyl-, and dodecyltoluenes were derived from the sulfuric acid–catalyzed alkylation of toluene with the C_6, C_9, and C_{12} fractions from the polymerization of propylene over a catalyst of phosphoric acid on silica gel. These fractions consist of a mixture of unsaturated branched-chain hydrocarbons containing a high proportion of tertiary olefins. The alkylate had a relatively wide boiling range, but the substituents were indicated by infrared analysis to be over 90% in the para position. The C_{12} fraction from propylene polymerization was also used to prepare an alkylate with *o*-xylene. This was indicated to have the structure of a 1,2-dimethyl-4-dodecylbenzene.

3,5-Di-*tert*-butyltoluene was prepared by alkylation of toluene with *tert*-butyl chloride catalyzed by aluminum chloride. It is a crystalline solid melting at 31.0–31.5° C. The symmetrical structure was proved by infrared analysis. 1,3-Dimethyl-5-*tert*-butylbenzene was synthesized from *m*-xylene, *tert*-butyl chloride, and aluminum chloride.

From the above it is seen that sulfuric acid serves to introduce the *tert*-alkyl group principally into the para position (with respect to the methyl group) with very little dialkylation. Aluminum chloride causes alkylation to take place in the meta position, with dialkylated products predominating. Very little alkylation takes place in the ortho positions with either catalyst, which may indicate steric hindrance at some intermediate stage in the reaction. *o-tert*-Alkyltoluenes have been synthesized by a Grignard reaction (*8*).

Aluminum chloride brings about an easy migration of the *tert*-alkyl group. Treatment of *p-tert*-butyltoluene with aluminum chloride converted it into a mixture of toluene, 3,5-di-*tert*-butyltoluene and, *m*- and *p-tert*-butyltoluene. Alkylation of *p-tert*-butyltoluene with *tert*-butyl chloride and aluminum chloride yielded principally 3,5-di-*tert*-butyltoluene.

Tertiary product is oxidized by air or oxygen in presence of cobalt catalyst

The *tert*-alkyltoluenes were oxidized by passing air or oxygen through them at 110° to 180° C. in the presence of a soluble cobalt catalyst. Cobalt naphthenate, acetylacetonate, and isovalerylacetonate were used interchangeably. The reactors were entirely of glass and consisted of either a stirred flask operating at atmospheric pressure or a tower-type vessel capable of usage at 50 pounds per square inch gage. The oxidant gas was introduced through a fritted-glass disperser. Gaseous products were withdrawn to a condenser equipped with a separating trap to remove the aqueous phase and return the hydrocarbon layer to the reactor. The apparatus was enclosed in a screen booth, because of hazards associated with the use of a glass reactor under pressure and the possibility of an explosive hydrocarbon-oxygen mixture in the vapor phase. The experiments are summarized in Table II.

The *tert*-alkylbenzoic acids were usually isolated from the reaction mixture by extraction with a slight excess of 10 weight % aqueous sodium hydroxide. The aqueous phase was separated and extracted with isopentane to remove impurities. The acids were sprung with concentrated hydrochloric acid. Crystalline, water-insoluble acids were separated from the aqueous phase by filtration, dried, and recrystallized from an alcohol-water mixture.

Three of the *tert*-alkylbenzoic acids shown in Table II contain a methyl substituent. The resistance of these methyl groups toward further oxidation is attributed to the deactivating influence of the carboxyl group. No dibasic acid was found in the oxidations leading to 2-methyl-4-*tert*-butylbenzoic acid and 2-methyl-4-dodecylbenzoic acid. This is in line with the stability of *o*-toluic acid toward further oxidation (*4*). A dibasic acid believed to be 5-*tert*-butylisophthalic acid was isolated in small amount from the oxidation leading to 3-methyl-5-*tert*-butylbenzoic acid. This was separated by its limited solubility in hot hydrocarbon. It had approximately the theoretical acid number and melted above 317° C. with sublimation. This characteristic of *tert*-butylisophthalic acid was also observed by earlier workers, who obtained a sealed tube melting point of 343° C. (*5*).

The oxidation was usually terminated when roughly 40 to 50% of the hydrocarbon had been converted to acid. It was observed that the oxidation rate often tended to decrease at about this conversion level and was not accelerated by the addition of more catalyst. In order to obtain complete oxidation of the alkylaromatic hydrocarbon, it was, therefore, necessary to remove the acidic oxidation products and recycle the remainder. In the case of high-melting crystalline acids, this can be done by crystallization as well as by alkaline extraction.

The crystallization-recycle system was employed for the oxidation of *p-tert*-butyltoluene in order to obtain information as to the ultimate yield of products. The hydrocarbon was treated with oxygen at atmospheric pressure in the stirred flask reactor for 18 hours at 135° C. in the presence of 0.25 weight % cobalt naphthenate. Six cycles were completed in which the crystalline acids were removed by filtration and washed with make-up *tert*-butyltoluene. The filtrate was recycled without adding more catalyst. The crystals were washed with petroleum ether and dried in vacuo. The *tert*-butylbenzoic acid prepared in this manner melted sharply at 164.5° C., but was found to contain a small amount of terephthalic acid (less than 0.5%). This could have been removed by filtration of the hot solution before crystallization of the major product. The acid was recovered from the final filtrate by alkaline extraction, which also saponified any ester present. This acid was recrystallized from isooctane.. Approximately 75% was recovered in the first crystallization and melted substantially at the melting point of *p-tert*-butylbenzoic acid. The balance melted considerably lower (110° and 89° C.) and was assumed to be a mixture of *m*- and *p-tert*-butylbenzoic acids.

This experiment showed that the yield of *p-tert*-butylbenzoic acid under these conditions was 86 mole %, while an additional 3% was indicated to be *m-tert*-butylbenzoic and 0.5% terephthalic acid. Other products present in small quantities were formaldehyde, formic acid, acetaldehyde, acetone, *tert*-butyl alcohol, and *p-tert*-butylbenzaldehyde.

tert-Alkylaromatic acids have many potential applications

A wide variety of *tert*-alkylaromatic acids can be made available by the techniques of alkylation followed by catalytic oxidation. *p-tert*-Butylbenzoic acid, which has been studied more intensively than the other members of the series, has established a place for itself in the field of plastics and resins. It is used as a modifier and regulator of air drying and baking alkyd resins, for the preparation of mono- and polyesters having properties ranging from liquids to brittle resinous solids, for the preparation of metal salts, and as a means of preparing derivatives previously not readily obtainable via the currently available commercial acids. In general, the derivatives of *p-tert*-butylbenzoic acid are characteristically higher in melting point, and have better hydrocarbon solubility and improved resin and oil compatibility, greater color stability, increased hardness, and less thermoplasticity as compared to derivatives of benzoic and rosin acids (*9*).

Acids containing a larger tertiary alkyl group or a tertiary alkyl group in the meta position form derivatives which are in general more soluble in hydrocarbons. The sodium salts of acids of higher molecular weight, such as dodecylbenzoic acid, have detergent properties similar to the aliphatic carboxylates, but these are subject to the same limitation as to calcium tolerance (*9*). Still another group of chemical intermediates may be made by aromatic ring reactions of *tert*-alkylbenzoic acids. The principal factors governing these reactions will be the deactivating effect of the carboxyl group and the steric hindrance of the tertiary alkyl group. Further potentialities of industrial application of *tert*-alkylbenzoic acids are still in the developmental stage.

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Split-Treatment Softening of Water

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THE split-treatment modification of lime-soda water softening offers very considerable advantages over conventional treatment. At Ann Arbor, Mich., split treatment is reported by McEntee (5) to have produced a satisfactory effluent using only 80% of the amount of lime required for conventional treatment and at Cedar Rapids, Iowa, Cherry (*2*) reports a saving of $14,000 annually. It is the author's belief that the general lack of appreciation of the benefits of split treatment stems, in part, from the absence in the literature of a mathematical analysis of the chemistry involved and, in part, from the fact that it is not applicable to all raw waters.

The following development of formulas for split treatment requires the selection of criteria for a satisfactory effluent. Larson (*4*) has stated that a good effluent should have an alkalinity of at least 50 p.p.m., a pH of from 8.2 to 8.5, and a slightly positive saturation index (*3*). For the purpose of this paper, this statement may be simplified to specify that the effluent should have a pH_s not exceeding 8.4. Split treatment automatically produces a water with a positive saturation index, and establishing an upper limit on pH_s ensures that the alkalinity will be reasonably high, for otherwise the calcium hardness will be excessive. Other values for pH_s may be required, depending upon the quality and temperature of the raw water (*4*). The following formulas are developed so that any pH_s value from 8.0 to 9.2 may be selected.

All concentrations and chemical dosages are expressed in terms of equivalent calcium carbonate in milligrams per liter (parts per million). The subscripts e, t, and r refer to the effluent, treated portion, and raw water, respectively, as indicated in the flowsheets (Figure 1). The fraction of raw water bypassed is designated by X, the fraction of the water bypassing zeolite is designated by Y, and the fraction of water treated with zeolite is designated by Z. A and B differentiate the calcium carbonate precipitated before and after mixing with the bypassed portion. Equilibrium constants are the same as those used by Caldwell and Lawrence (*1*), at 25° C. and an ionic strength of 0.01. For use at other temperatures and other values of ionic strength, the appropriate values should be substituted.