HYDROLYSIS AND ISOMERIZATION OF CHLOROTOLUENES TO *m*-CRESOL

R. Norris Shreve
and Charles J. Marsel[1]
PURDUE UNIVERSITY, LAFAYETTE, IND.

The simultaneous hydrolysis and isomerization of orthochlorotoluene and parachlorotoluene have been investigated. The optimum operating conditions are 350° C., 2.5 moles of sodium hydroxide per mole of chlorotoluene, and 2-hour reaction time. Cresol mixtures of 60% of *m*-cresol content are obtained.

FOR a considerable part of the war period the supply of *m*- and *p*-cresols was insufficient to meet requirements for the manufacture of phenolic-type resins, plasticizers, etc. For most purposes a 50–60% *m*-cresol content appears necessary. Chlorination of toluene, however, forms little or no *m*-chlorotoluene. Purdue University therefore started in December, 1942, with War Production Board encouragement, a study of the simultaneous hydrolysis and isomerization of *o*- and *p*-chlorotoluenes to give *m*-cresol.

Theoretically it is possible that such a process might produce a mixture having less than the desired ratio of *m*- to *p*-cresol. In this case the following separation processes might be helpful in obtaining a useful product.

o-Cresol (boiling point, 191.1° C.) may be separated from *m*-cresol (201° C.) and *p*-cresol (202.3° C.) by fractional distillation in a good column. Several standard methods of separating the cresols employ as a common first step the sulfonation of the cresol mixture. From that point on, differences in the properties of the isomeric sulfonic acids and their salts, such as differences in solubility and ease of decomposition, may be utilized in the separation procedure (*8, 10, 22, 23, 27*).

Perhaps the most important method of separating *m*-cresol from mixtures of *m*- and *p*-cresol is the formation of selective addition compounds with such substances as sodium acetate (*5*), sodium nitrite (*9*), oxalic acid (*6*), urea (*25*), and phenol (*4*). One of the more important industrial processes for separating *m*-cresol from *p*-cresol involves phenol and may be considered representative of the entire class of compounds. *m*-Cresol forms a solid addition product with phenol even in the presence of *p*-cresol. This addition compound may be separated from the residual liquid *p*-cresol. The addition product is easily separated into its individual chemicals by simple rectification.

DETERMINATION OF *m*-CRESOL

Since we were interested not only in the amount of cresol produced in an individual run, but also in the proportion of meta isomer in the mixture, the method of analyzing for *m*-cresol was of fundamental importance. The mixture contained *o*-, *m*-, and *p*-cresols and some phenol.

These methods of analysis were available: bromate-bromide, infrared analysis, and Raschig nitration. The bromate-bromide method, taking advantage of the fact that *m*-cresol will brominate in the 2,4,6-position whereas *o*-cresol will brominate 4,6- and *p*-cresol will brominate 2,6-, is applicable only to phenol-free mixtures of *o*- and *m*-cresols or *p*- and *m*-cresols if all three isomers are to be determined. Infrared analysis too is applicable only to phenol-free mixtures. Unfortunately this instrument was not available for use. The Raschig nitration method can be used for analysis of *m*-cresol in mixtures containing less than 10% phenol, and accordingly a modified Raschig procedure was used. The other two methods could be used if phenol were removed. The Raschig method (*24*) involves transformation of the cresol to trinitro-*m*-cresol and determination of this compound. It consists essentially of sulfonating the cresol mixture with concentrated sulfuric acid and then nitrating with concentrated nitric acid, during which procedure only the trinitro-*m*-cresol survives. During the process, according to Raschig, the *o*- and *p*-cresols are oxidized to oxalic acid. Trinitro-*m*-cresol may then be determined gravimetrically, since it is relatively insoluble in water.

This method is applicable to cresol solutions containing phenol up to 10%. If the phenol content is higher, the picric acid formed is no longer soluble in water but precipitates along with trinitro-*m*-cresol. Since trinitro-*m*-cresol is a relatively strong acid, it can be determined volumetrically by ordinary titration with sodium hydroxide, using phenolphthalein as indicator (*26*).

Careful study indicated that a modified gravimetric method is better for determination of trinitro-*m*-cresol than a titrimetric method. First, a relatively tedious technique is necessary to crush and wash trinitro-*m*-cresol, in order to prevent occlusion of nitric and sulfuric acids, which would interfere in the titration. Second, since the alcoholic solution of trinitro-*m*-cresol is a deep orange-yellow in color, it is not easy to determine the end point accurately by a colorimetric method. It might be noted that in a study of various indicators possible for this method, thymol blue gave a somewhat sharper end point than phenolphthalein.

MODIFIED RASCHIG GRAVIMETRIC METHOD. The sample must be relatively pure and moisture-free. A sample with a phenol content of over 10% should have the excess removed by distillation. The fraction boiling from 180° to 210° C. was used for the test. The sample should contain not less than 45% and not more than 80% *m*-cresol; sufficient *m*-cresol or *o*- and *p*-cresol, respectively, should be added to the sample to bring the percentage of *m*-cresol within the prescribed limits, because an empirical factor is used in calculating the results. This factor corrects for such things as incompleteness of reaction and solubility losses of trinitro-*m*-cresol. This factor is obviously more inaccurate with very large or very small amounts of *m*-cresol in the sample.

A 10-gram sample of cresol is accurately weighed into a 600-ml. beaker[2], and 15 ml. of concentrated sulfuric acid are added. The beaker is swirled several times to mix the components thoroughly, and the mixture placed in an oven at 103–105° C. for one hour. The beaker is allowed to cool to room temperature, and operations are continued in a hood. Ninety milliliters of concentrated

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[1] Present address, Colgate-Palmolive-Peet Company, Jersey City, N. J.

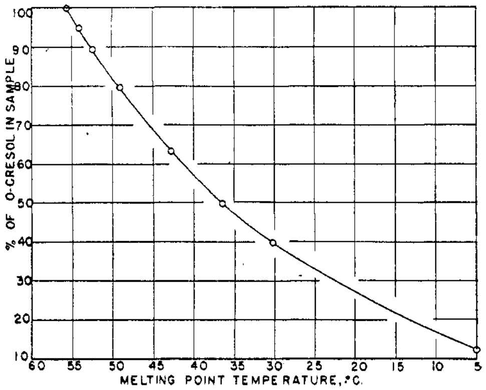

Figure 1. Determination of *o*-Cresol in Mixtures with *m*- and *p*-Cresols *(21)*

(63%) nitric acid are added to the beaker, which is shaken slightly. After a few moments NO_2 is evolved, slowly at first, but then more rapidly until the evolution is quite violent. After about 5 minutes the evolution of dense fumes of nitrogen oxides is complete, and at this point stirring is commenced slowly with a Hershberg stirrer (*15*). This causes the oily trinitro-*m*-cresol to separate as finely divided crystals. (After several runs the amount of precipitate which adheres to a new stirrer is negligible. The stirrer must be of some acid-resistant wire such as tantalum.) Stirring is continued for 15 minutes, after which time the trinitrocresol has completely crystallized. Eighty milliliters of water are added, and stirring is continued for 5 minutes. The solution is then allowed to stand for one hour, and the supernatant liquid is decanted off through a previously weighed sintered-glass Gooch crucible. Any small lumps should be crushed in the beaker. The precipitate is then transferred to the crucible. The precipitate remaining in the beaker is washed into the crucible with some of the wash water, of which 100 ml. are used in separate 20-ml. portions.

The crucible and precipitate are dried in an oven at 105° C. (trinitro-*m*-cresol melts at 150° C.) for 2 hours, allowed to cool to room temperature in the desiccator, and weighed:

$$\%\ m\text{-cresol} = \frac{\text{wt. trinitro-}m\text{-cresol}}{1.74 \times \text{wt. sample}} \times 100$$

The product obtained from very high-temperature runs contained larger amounts of phenol than ordinary runs and was consequently more difficult to analyze.

On known samples of 49.9, 60.2, and 10.0% *m*-cresol, analysis by this method gave 49.3, 59.6, and 9.1% *m*-cresol. In general, the method is certain to be accurate to ± 1% if pure cresols are used; with a product from a high-temperature run the accuracy may drop to ±5%.

DETERMINATION OF *o*-CRESOL

Once the *m*-cresol content of a mixture has been ascertained, it is possible to determine the *o*- and *p*-cresol constituents from the freezing points of various mixtures. However, the calculations involved are rather tedious. The preferred determination of *o*-cresol is that used by the Reilly Tar and Chemical Corporation and described by Potter and Williams (*21*); *o*-cresol reacts with cineole in molecular proportions, the freezing point of the mixture depending on the percentage of *o*-cresol in the sample.

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The sample should be water-free; however, if the water content is not over 0.5%, a correction may be made by adding 0.17° C. to the freezing point for each 0.1% of water in the sample. The method is applicable for mixtures containing 30–100% *o*-cresol; but if the sample contains less than 30% *o*-cresol, a sufficient amount of pure *o*-cresol may be added to bring the composition within the prescribed limits.

The freezing point of the sample can be determined in the ordinary physicochemical way (*17*, *19*). Potter and Williams (*21*) have outlined a fairly simple procedure. It is helpful to seed the mixture with a sample of the cineole-*o*-cresol compound, and thus prevent excessive supercooling. The kickback in temperature on initial crystallization should only be a few tenths of a degree. Figure 1 illustrates the relation between the melting point of the cineole-*o*-cresol compound and the percentage of *o*-cresol in the sample.

The *p*-cresol content in each case was determined by difference.

DETERMINATION OF CHLOROTOLUENES

Analysis of the isomeric composition of the chlorotoluenes was made by determining the freezing point of the mixture, and then referring to the eutectic freezing point diagram for the system ortho-para-monochlorotoluenes (Figure 2). Known mixtures of 95, 75, and 80.2% of *o*-chlorotoluene analyzed 94.5, 75.0, and 80.5% *o*-chlorotoluene, respectively.

DEVELOPMENT OF HYDROLYSIS AND ISOMERIZATION

There is ample evidence to show that a halogen attached to the ring is capable of rearrangement. Copisarow (*7*) carried out the reaction:

$$2\ C_6H_5Br \rightleftarrows C_6H_6 + C_6H_4Br_2 \qquad (1)$$

Certain *p*-halogen-substituted phenols behave peculiarly on nitration, in that the halogen atom is replaced by the NO_2 group and migrates to the ortho position (*11*). When fused with alkali, both *o*- and *p*-chlorobenzenesulfonic acids yield some resorcinol (*29*). Dibromonaphthalene is capable of rearrangement under the influence of aluminum chloride, using carbon disulfide as solvent (*16*). The 1,2-dibromonaphthalene yielded 1,4-, 1,5-, and 2,6-dibromonaphthalenes on rearrangement.

Norris and Turner (*20*) indicate that chlorotoluene, upon treatment with aluminum chloride and hydrogen chloride at 100° C., undergoes two reactions, rearrangement and disproportionation. Rearrangement in each case is to the other two isomeric chlorotoluenes. The *p*-chlorotoluene undergoes the maximum and *o*-chlorotoluene, the least rearrangement. In fact, under similar conditions approximately three times as much of the para isomer undergoes rearrangement as of the ortho isomer.

Despite the work of Copisarow indicating movement of halogen atom during disproportionation of bromobenzene, Norris and Turner believe that, by the use of milder conditions, the disproportionation of chlorotoluenes involves the methyl radical and not the chlorine atom. This evidence was based upon identification of certain of the disproportionation products; chlorobenzene was positively identified, and the remainder identified as probably being chloroxylenes with no apparent evidence of any dichlorotoluenes.

The hydrolysis of chlorobenzene to produce phenol is a well known industrial process (*12*, *13*, *14*). The production of cresol from chlorotoluene resembles in processing detail the similar process of making phenol. Britton's work first revealed rearrangement of chlorinated aromatics upon hydrolysis (*2*); among the examples cited is the production of *m*-cresol from *o*-chlorotoluene. Reaction at 350–360° C. for one

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[2] The authors believe this is preferable to the common practice of putting the sample into a 125-ml. Erlenmeyer flask, sulfonating, and then removing the contents of the flask into a beaker for nitration. The beaker can easily be weighed on a triple beam laboratory balance to ±0.05 gram; this is satisfactory since the method is accurate to only ±1%. In addition, the probable error resulting from the transfer of the viscous cresolsulfonic acid to the beaker is avoided.

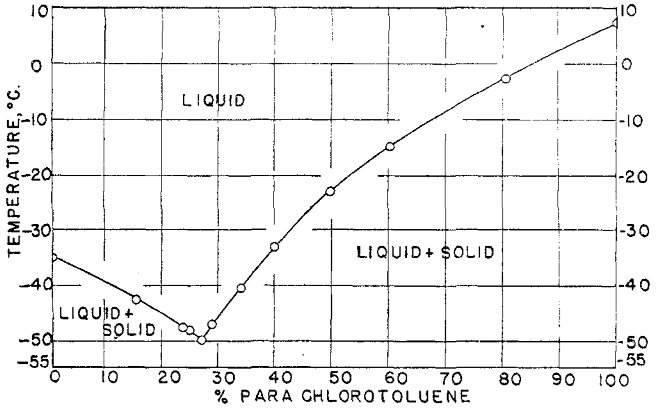


Figure 2. Freezing Point Diagram for the System o-, p-Chlorotoluene (*28*)

hour yielded 77% of cresols with 59% of *m*-cresol. The process may be carried out in the vapor phase as well as the liquid (*3*).

Meharg and Allen (*18*) also report the rearrangement of chlorotoluenes during alkali hydrolysis. They describe several runs whereby *o*- and *p*-chlorotoluene, when heated at 315–320° C. with alkali and copper catalyst, yield a mixture of products containing *m*-cresol. For example, *o*-chlorotoluene gave 55.4% of pure mixed cresols of which 25.3% was *m*-cresol; *p*-chlorotoluene gave 55.5% phenolic products, of which 38.2% was *m*-cresol.

INVESTIGATION OF *m*-CRESOL PRODUCTION

CHEMICALS. The chlorotoluenes, with the exception of the meta isomer, were purchased from the Heyden Chemical Corporation. After purification the *o*-chlorotoluene gave an analysis of 94% purity, the *p*-chlorotoluene was 99.4% pure, and the technical mixed chlorotoluenes consisted of 55% para and 45% ortho (by the method described). The *m*-chlorotoluene was purchased from the Eastman Kodak Company.

APPARATUS. Reaction was carried out in a 12-ml. standard steel autoclave purchased from the American Instrument Company; heating was provided by an electrical jacket. The agitator was a standard cradle-rocking mechanism.

PROCEDURE. From 1.5 to 2 hours were required for the autoclave to heat up to the desired temperature, agitation being continued during this period. The reaction was then allowed to run the desired time, and the autoclave cooled. The contents were removed, and the autoclave was carefully washed with ether and then water. The washings were added to the reaction products, and the whole was extracted with ether to remove all caustic-insoluble products, consisting for the most part of tolyl ethers formed during the run and any unreacted chlorotoluene. The ether extract was distilled, and any chlorotoluene present was easily separated from the tolyl ether since the difference in boiling points was more than 100° C. The weights of chlorotoluene and tolyl ether were recorded.

The alkali solution was neutralized with hydrochloric acid, and cresolic products were thus freed. These were extracted with benzene, and the benzene extract was distilled. The cresols were separated from the higher-boiling residues and analyzed as explained previously. Figure 3 depicts the operating pressure of the hydrolysis mixture as a function of temperature. The autoclave described was found to be satisfactory for these pressures.

FLOWSHEET. Figure 4 is a proposed flowsheet of an industrial process for *m*-cresol. The chlorotoluene is first used to extract the tolyl ether from the reaction mixture and then passed through a preheater after addition of caustic solution. The reaction tubes or coils, which may be of heavy copper or steel, are heated only to start the continuous system. After reaction, the hot hydrolyzed mixture is passed through the preheater and then through a cooler from whence it is run to the tolyl ether extractor and to a neutralizing tank. It is then fed to a separating tank, where the cresol is separated as the upper layer upon acidification. The aqueous layer is extracted with benzene to remove dissolved cresol, and the benzene solution together with the upper cresol layer is passed to a distillation column. The mixture of benzene, phenol, and *o*-cresol coming from the tower is reworked; the *m*-*p*-cresol mix proceeds to a reaction tank where a material such as phenol or urea is added to cause a solid addition product (with *m*-cresol) to separate. After centrifuging, this is placed in a column where the pure *m*-cresol is taken from the bottom. The phenol is recycled.

REACTIONS IN HYDROLYSIS OF CHLOROTOLUENE

It is difficult to understand the mechanism whereby the hydrolysis of *o*- or *p*-chlorotoluene can yield *m*-cresol. There are four obvious possibilities: (1) The chlorotoluene may undergo rearrangement before hydrolysis, (2) the rearrangement may take place during the hydrolysis, (3) the cresol formed may isomerize, or (4) a combination of these reactions may occur. There is ample evidence that all these reactions can occur.

There is apparently 48–49% *m*-chlorotoluene in an equilibrium mixture of the chlorotoluenes (*20*), and in most cases the amount of *m*-cresol in our mixtures was 40% or lower. Also, the *p*-chlorotoluene rearranged more easily than the *o*-chlorotoluene (*20*), and *p*-chlorotoluene gave a cresol of higher meta content than *o*-chlorotoluene. However, analysis of the unreacted chlorotoluenes recovered from the hydrolysis mixture revealed no appreciable rearrangement. This either refutes the theory or indicates that rearranged chlorotoluene hydrolyzes immediately.

The more plausible of the theories involves the formation of *m*-cresol during actual hydrolysis. No isomerization reagents were present in most of the runs, and when copper was present, it did not materially affect the percentage of *m*-cresol formed. Also, analysis of cresol obtained from *p*-chlorotoluene revealed no *o*-cresol, which would not be likely assuming mechanism 1 or 3.

The isomerization of cresol seems to be carried out only under strenuous conditions and under the influence of powerful isomerization reagents such as aluminum chloride.

In all reactions involving cresol, *m*-cresol is present as well as *o*- or *p*-cresols and, hence, can react to form isomers of the compounds in question. The main reactions, then, are:

$$C_6H_4(CH_3)Cl + 2NaOH \longrightarrow C_6H_4(CH_3)ONa + NaCl + H_2O \qquad (2)$$

$$C_6H_4(CH_3)Cl + C_6H_4(CH_3)ONa \longrightarrow C_6H_4(CH_3)OC_6H_4(CH_3) + NaCl \qquad (3)$$

$$2C_6H_4(CH_3)OH \rightleftharpoons C_6H_4(CH_3)OC_6H_4(CH_3) + H_2O \qquad (4)$$

$$2C_6H_4(CH_3)Cl \rightleftharpoons C_6H_4(CH_3)C_6H_3(CH_3)Cl + HCl \qquad (5)$$

$$C_6H_4(CH_3)C_6H_3(CH_3)Cl + NaOH \longrightarrow C_6H_4(CH_3)C_6H_3(CH_3)OH + NaCl \qquad (6)$$

$$C_6H_4(CH_3)OH \rightleftharpoons (CH_3)H_2C_6H_3{:}O \qquad (7)$$

$$C_6H_4(CH_3)Cl + (CH_3)H_2C_6H_3{:}O \rightleftharpoons (CH_3)C_6H_4{\cdot}C_6H_3(CH_3)OH + HCl \qquad (8$$

$$2C_6H_4(CH_3)Cl + Fe \longrightarrow C_6H_4(CH_3)C_6H_4(CH_3) + FeCl_2 \qquad (9$$

These reactions are very similar to those occurring during the hydrolysis of chlorobenzene to phenol (*12*).

MATERIAL BALANCE

Material balances were made on many runs. In an average run, decomposition during reaction plus handling losses did not amount to more than 10%. A sample material balance follows:

Product	Yield, %
Cresol	62.0
Tolyl ethers	20.7
Tolylcresols	10.2
	92.9
Decomposition and handling	7.1

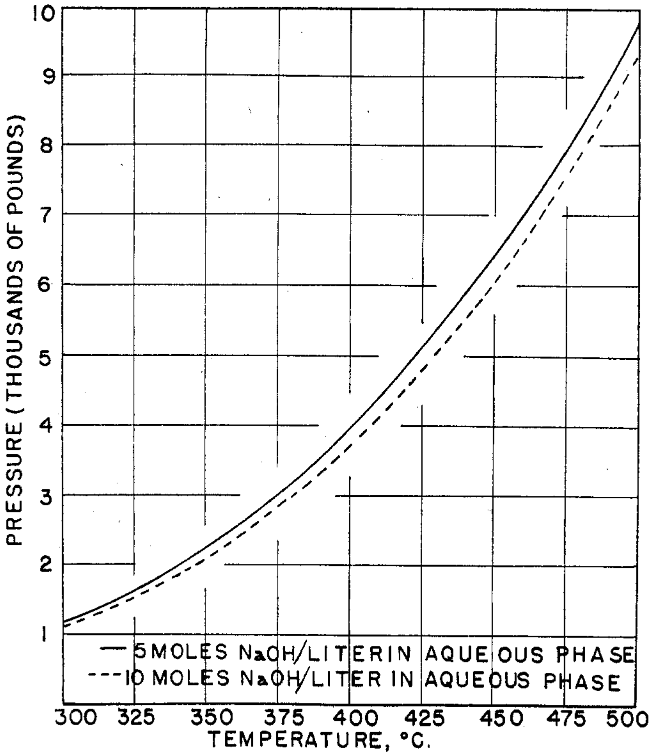


Figure 3. Operating Pressure for Chlorotoluene Hydrolysis Mixture

The products were separated by distillation. The ranges over which they were collected are as follows:

Caustic-soluble fraction	
Cresols and phenol	180–220° C.
Tolylcresols	220–300° C.
High-boiling fraction	300° C.
Caustic-insoluble fraction	
Chlorotoluenes	145–220° C.
Tolyl ethers	220–300° C.
High-boiling fraction	300° C.

Results are reported both as per cent conversion and per cent yield of products. The conversion to cresol may be defined as the moles of cresol produced divided by the moles of cresol theoretically obtainable, assuming 100% reaction; the yield of cresol, as the moles of cresol obtained divided by the moles of cresol theoretically produced from reacted chlorotoluene (moles of original chlorotoluene minus moles of chlorotoluene recovered).

VARIABLES AFFECTING HYDROLYSIS

TIME. Figures 5 and 6 show the effect of time upon the hydrolysis of chlorotoluene. Runs were made at a constant temperature of 325° C. and constant pressure of 1600 pounds per square inch, with 2.5 moles of sodium hydroxide per mole of chlorotoluene; the time varied from 0.5 to 20 hours.

Since the hydrolysis of chlorobenzene was reported to be a unimolecular reaction (*12*), the results obtained in this work were scrutinized carefully; no such conclusion was warranted from the results obtained. It was difficult to determine the time of reaction accurately because the period of heating to temperature was relatively long and there was undoubtedly some reaction during this time. Unfortunately also the main reaction was complicated by several side reactions between cresolates and chlorotoluenes to produce tolyl ethers and tolylcresols. It was difficult, therefore, to calculate the amount of cresol which would be present if the side reactions had not occurred, since in some cases the mechanism of the side reactions was not known. The data obtained are believed to have good precision since many of the runs were repeated several times until check values were obtained. Substitution in the formula for a unimolecular reaction yielded no constant:

$$K = \frac{1}{t} \ln \frac{A}{A - x}$$

where t = time, minutes
A = original amount of chlorotoluene present
x = amount of cresol formed after time t

For example, for 0.5, 1.0, and 2.0 hours, $K = 1.29$, 0.937, and 0.562×10^{-2}. Even by adding to the actual cresol obtained the amount of cresol which presumably had been used to form tolyl ether alone, or the amount used to form both tolyl ether and tolylcresol, no constants were obtained.

Several conclusions may be drawn from a study of the time variable. In the case of both *o*- and *p*-chlorotoluene over 90% of the material had reacted after 2 hours of agitation at 325° C. (plus heating time). The extent of isomerization, as measured by the *m*-cresol content of the total cresol, was not appreciably affected by variation of time. This may be explained by assuming that the *m*-cresol was formed during the actual hydrolysis and the amount present would be independent of time. Once the cresols had formed, there was not much possibility of further isomerization. In other words, the amount of *m*-cresol was determined by the fact that tests on the cresols themselves revealed that they did not isomerize readily. The values for conversion to cresol were what had been expected, with this interesting difference: The amount of cresol produced after a 20-hour run was slightly less than the cresol obtained after a 10-hour run. This is quite different from the case of phenol, where prolonged heating of the hydrolysis mixture gave high phenol yields due to the hydrolysis of diphenyl ether by sodium phenolate. One must therefore conclude that ditolyl ether was much more resistant to hydrolysis, and subsequent experiments validated this idea. The amount of by-product changed only slowly during the initial stages of the reaction, and reached a fairly constant level after 5 hours, which is proof of the stability of these compounds. A higher amount of by-products was formed during the hydrolysis of *p*-chlorotoluene, which accounted for the lower yields of cresol from this raw material as compared to *o*-chlorotoluene.

CONCENTRATION OF ALKALI. The concentration of sodium hydroxide was one of the most important variables. A study was made of the effect of changing not only the mole ratio of caustic to chlorotoluene but also the aqueous volume of the solution (and hence the concentration of sodium hydroxide), keeping the mole ratio of alkali to chlorotoluene constant. Figures 7 and 8 show the results at 325° C. and 1600 pounds per square inch for one-hour reaction time. First consideration might lead to the conclusion that this hydrolysis was a heterogeneous reaction involving, as it does, reaction between two immiscible phases. A similar case (*1*) was the oxidation of *o*-benzoyltoluidine to benzoylanthranilic acid by permanganate in neutral solution, where reaction proceeded by the permanganate ions striking an adsorbed surface layer of toluidine molecules (on the aqueous surface). For a relatively slow reaction rate, such as the cases being considered, the reaction velocity is independent of the rate of stirring and, therefore, not dependent on the rate of diffusion of either reactant toward the interface. Instead it depends simply on the rate at which the molecules react on the surface.

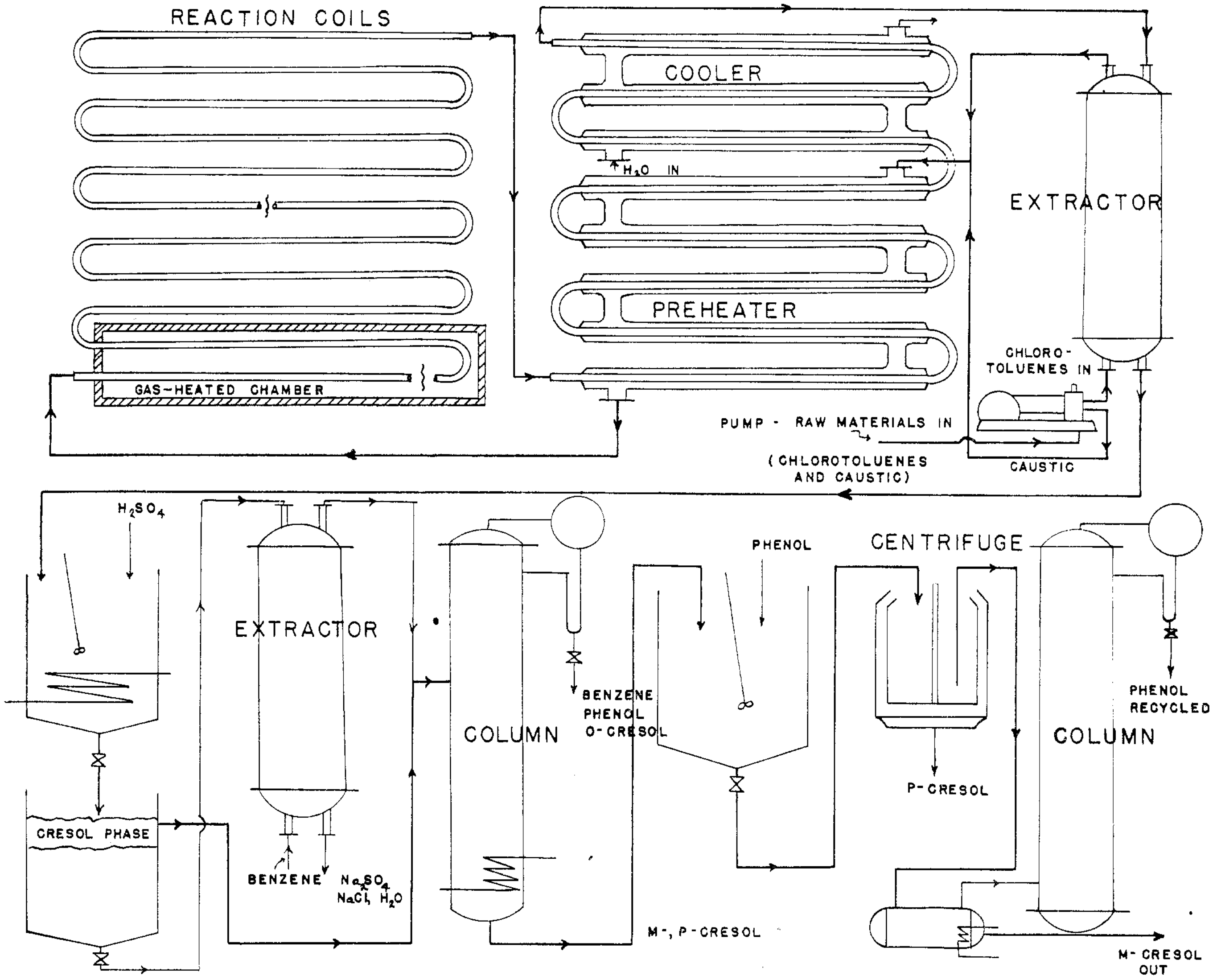


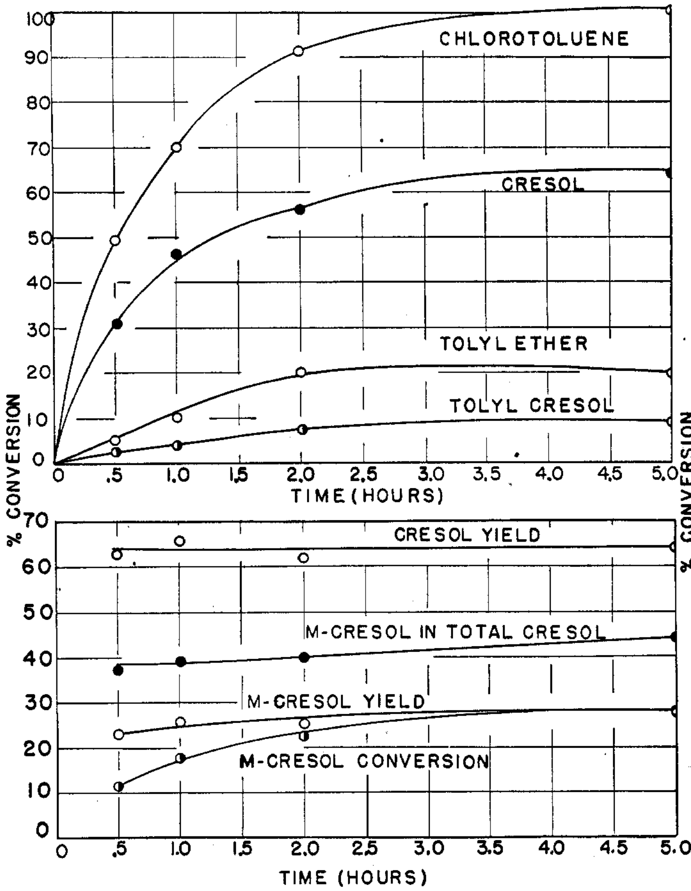
Figure 4. Proposed Flowsheet for *m*-Cresol Production

However, several considerations pointed away from the conception of a simple heterogeneous reaction in the hydrolysis of chlorotoluene. Even though the reaction was carried out below the critical temperature of both reactants, the temperature was sufficiently high (325° C.) so that chlorotoluene was appreciably soluble in the alkali solution. Also important is the fact that caustic is a particularly good emulsifying agent in some cases, and there is no doubt that an intimate emulsion was present at these high temperatures.

Therefore, the reaction may be considered primarily as homogeneous. Proof is provided by either Figure 7 or 8 where, upon increased concentration of caustic, the conversion of chlorotoluene to cresol is materially decreased. This seems to indicate that the reaction is not taking place on the surface of the aqueous phase. In other words, with increased concentration of caustic the solubility of chlorotoluene in the aqueous phase is decreased, and hence the conversion to cresol is decreased. This would not be true if the reaction took place on the aqueous surface, since in each case the aqueous volume was constant.

In addition, the following conclusions can be drawn: The percentage of *m*-cresol in the total cresol recovered increased with increased amount of base. It was not clear why this should be so and, doubtless, is tied in with the reaction mechanism. The conversion of chlorotoluene to cresol was slightly higher for the *o*- than for *p*-chlorotoluene, owing to increased by-product formation from the para isomer, and also to the apparently greater solubility of *o*-chlorotoluene in concentrated base. The amount of tolyl ether recovered decreased sharply with increased caustic concentration; it decreased several hundred per cent in the case of *p*-chlorotoluene when the base concentration was changed from 1 to 5 moles. This simply indicated the greater splitting of the ether in more concentrated caustic solution. However, commercially it would seem impractical to use such a large excess of caustic, since there would be no way of recycling the used material. A maximum yield of cresol was obtained when using approximately 3 moles of caustic per mole of chlorotoluene.

A study was also made of the result of changing the sodium hydroxide concentration (by changing aqueous volume) while keeping the ratio of caustic to chlorotoluene constant at 2.5 moles. Figure 9 shows the results at 325° C. and 1600 pounds per square inch; they are quite consistent with those noted earlier for high concentrations of base. There was a slight but consistent increase in *m*-cresol content with increased sodium hydroxide concentration, even though the mole ratio was constant. This would seem to indicate that the increase of *m*-cresol content previously noted was due to the higher concentration of base rather than the increase in mole ratio of base to reactant. Comparison of Figures 7 and 9 shows that, at equal concentrations of base (moles/liter), the values for chlorotoluene reacted and cresol obtained were much greater for the greater aqueous volume.



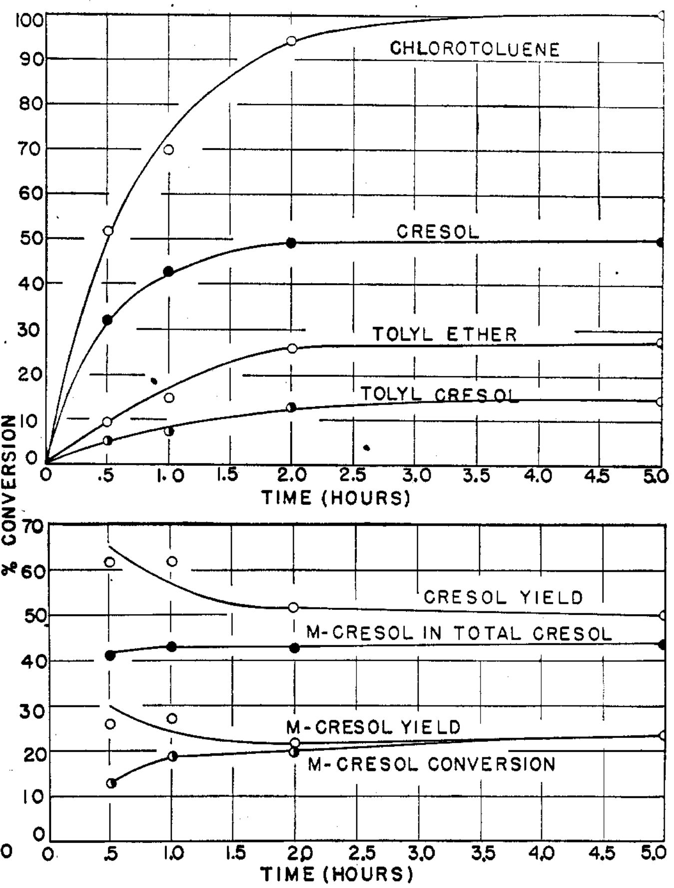


Figure 5. Effect of Reaction Time on Hydrolysis of *o*-Chlorotoluene

Figure 6. Effect of Reaction Time on Hydrolysis of *p*-Chlorotoluene

This indicated that probably both the increased aqueous reacting volume and the increased ratio of caustic to chlorotoluene favored the hydrolysis (Table I).

These three effects of caustic concentration are therefore: (*a*) influence of hydroxyl ion strength (as applied to ratio of OH^- to chlorotoluene) on the rate of hydrolysis and isomerization (and also on the hydrolysis of the ether formed); (*b*) effect of OH^- strength on the solubility of chlorotoluene in the aqueous phase; (*c*) effect of change in volume of the aqueous phase (the more volume, the more reaction).

TABLE I. EFFECT OF CAUSTIC CONCENTRATION AND VOLUME ON HYDROLYSIS OF *o*-CHLOROTOLUENE

NaOH Concn., Moles/Liter		Mole Ratio of NaOH to Chlorotoluene		Aqueous Phase Vol., Ml.		Chlorotoluene Reacted, %		Cresol Conversion, %	
A	B	A	B	A	B	A	B[a]	A	B[a]
6.3	6.3	2.5	3.2	400	500	78	81	51	55
8.3	8.3	2.5	4.2	300	500	57	83	35	56

[a] Interpolated values.

TEMPERATURE. Apparently 350–390° C. is the optimum temperature range for the hydrolysis of both *p*- and *o*-chlorotoluene (Table II). The following conclusions can be drawn: Over the range 350–390° C. slightly higher yields of cresol were obtained from *o*-chlorotoluene. Between 340° and 350° C., with 2.5 moles of caustic per mole of chlorotoluene, all the chlorotoluene reacted after one hour at the temperature in question. At higher temperatures the analysis for *m*-cresol became more complicated because of the higher amounts of phenol present as a decomposition product, as mentioned previously. As soon as the temperature rose above 390° C. (the approximate critical temperature of chlorotoluene), the conversion of cresol was materially decreased; the formation of the by-products tolyl ether and tolylcresol was also lessened. After the hydrolysis reaction there was always a slight residual pressure in the autoclave upon cooling, an indication of certain gaseous decomposition products. Above 390° C. this decomposition took place at a much greater rate, as evidenced by residual autoclave pressure of as much as 1000 pounds per square inch after cooling, in comparison with a normal residual pressure of about 100 pounds. The gas was not analyzed but probably was mostly methane. The *m*-cresol content of the mixture increased with increase in temperature up to a certain point.

EMULSIFYING AGENTS. It was believed that intimate mixing would hasten completion of the reaction, mostly by providing intimate contact between the two phases so that maximum solubility of chlorotoluene in the aqueous phase would be maintained; therefore the effect of emulsifying agents on the reaction was studied. The emulsifying agents did not particularly aid the reaction, principally because it was believed the agents were unstable in strong caustic at the elevated temperature encountered, and perhaps at these temperatures the reaction mixture approached a single phase. Even Tergitol 08, often used in strong caustic, did not increase conversion to cresol.

CATALYSTS. Copper is known to be a catalyst for the hydrolysis of aryl halides, and this was confirmed in the reaction being studied; however, the copper did not appear to affect the amount of *m*-cresol formed. One explanation, according to Britton (*1A*), is that to obtain the catalytic effect of copper it is necessary to have copper surfaces or copper electrolytically in-

Table II. Effect of Temperature on Hydrolysis and Isomerization of Chlorotoluenes

(Reaction time, 1 hour; 2.5 moles NaOH per mole chlorotoluene; volume, 500 ml.)

Run No.	Temp., ° C.	Chlorotoluene Reacted, %	*m*-Cresol in Total Cresol, %	Total Cresol, %		*m*-Cresol in Total Cresol, %		Tolyl Ether, %		Tolylcresol, %	
				Conv.	Yield	Conv.	Yield	Conv.	Yield	Conv.	Yield
				o-Chlorotoluene							
60R	312	53	44	31	59	13	26	3	5	5	9
57	325	70	39	46	66	18	26	10	15	4	6
65	350	100	41	61	61	25	25	15	15	7	7
109	362	100	46	60	60	28	28	16	16	8	8
66	370	100	39	62	62	24	24	12	12	10	10
110	380	100	52	58	58	30	30	11	11	13	13
67	390	100	44	62	62	27	27	14	14	6	6
67AR	406	100	55	51	51	28	28	13	13	5	5
111	430	100	44	15	15	6	6	17	17	3	3
				p-Chlorotoluene							
63R	325	70	43	43	62	19	27	15	21	7	10
73	330	92	42	47	51	20	21	18	20	13	14
74	350	100	45	49	49	22	22	16	10	15	15
74A	364	100	47	55	55	27	27	15	15	11	11
75	369	100	49	54	26	26	26	13	13	11	11
75A	383	100	42	57	57	24	24	15	15	12	12
76R	390	100	45	51	51	26	26	14	14	10	10
76A	410	100	32	50	50	16	16	5	5	10	10

sulated from the iron walls of the vessel. For comparison, data from two typical runs follow:

	% Conversion to Cresol	% *m*-Cresol
No catalyst	42.2	43
10 grams Cu catalyst	53.0	43

By-Products. The two main by-products formed were tolyl ether and tolylcresol. As a result of the isomerization accompanying hydrolysis, many isomeric compounds were formed, and the separation and identification of the individual isomers would be a time-consuming process. For example, six isomeric tolyl ethers are possible.

In line with the commercial process of recycling enough phenyl ether so that the ether hydrolyzed balanced new ether formation, an investigation was conducted on the effect of recycling the by-product tolyl ether. By adding at the beginning of the run an amount of this ether equal to the amount which would have formed, the ether obtained amounted to 57% of that otherwise expected. By adding a 100% excess, the subsequent yield of ether was cut to 30% of the amount expected; in the latter case it amounted to approximately 6% of the total reaction products (Table III). The formation of tolylcresol seemed to be independent of caustic concentration (Figure 9), an indication of its stability toward alkali.

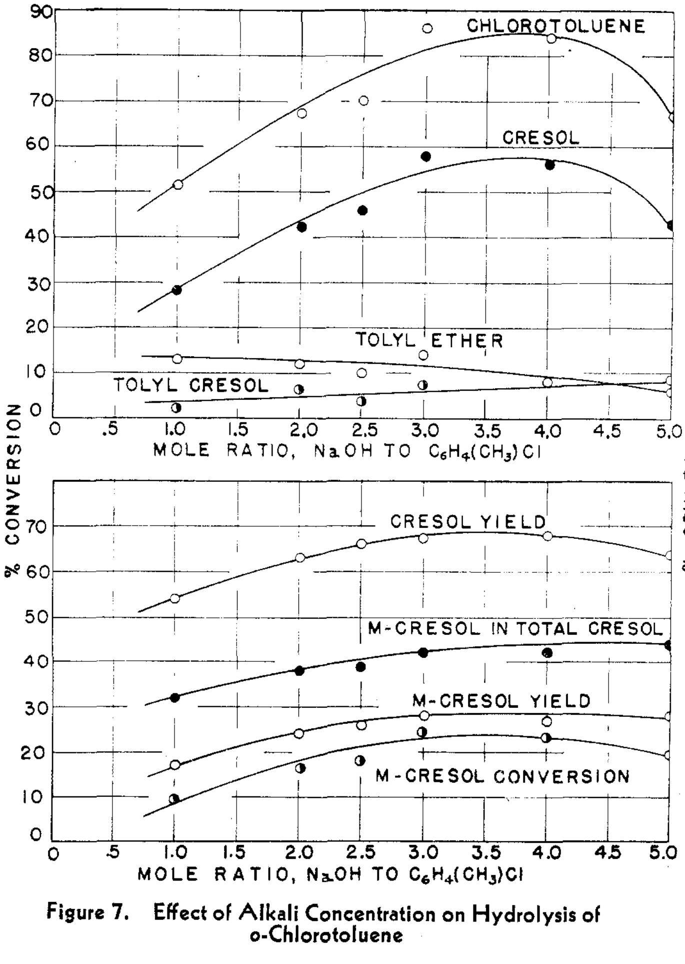


Figure 7. Effect of Alkali Concentration on Hydrolysis of o-Chlorotoluene

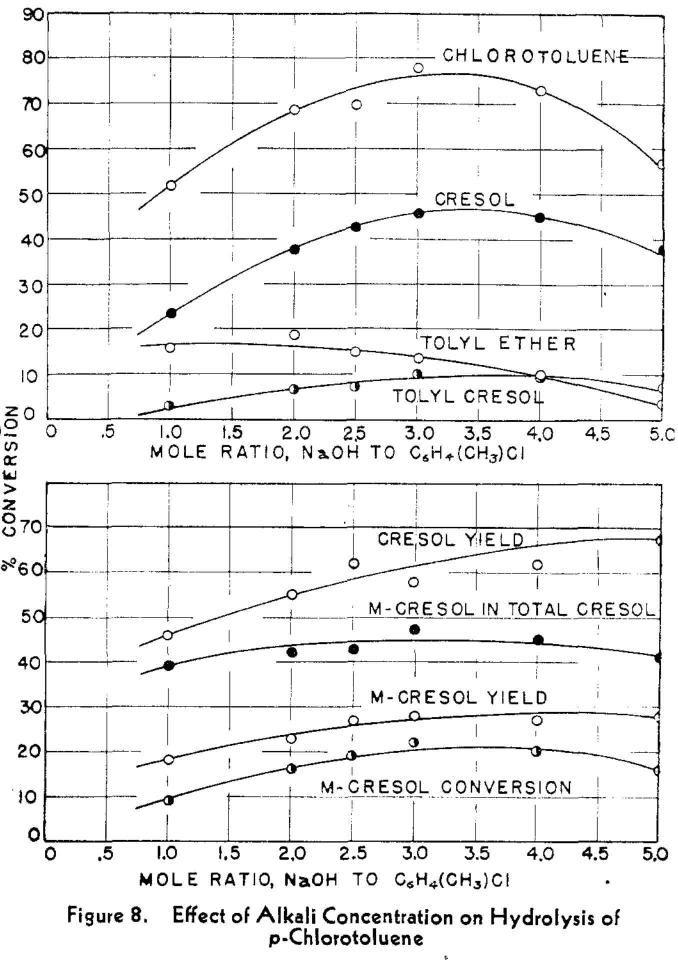


Figure 8. Effect of Alkali Concentration on Hydrolysis of p-Chlorotoluene

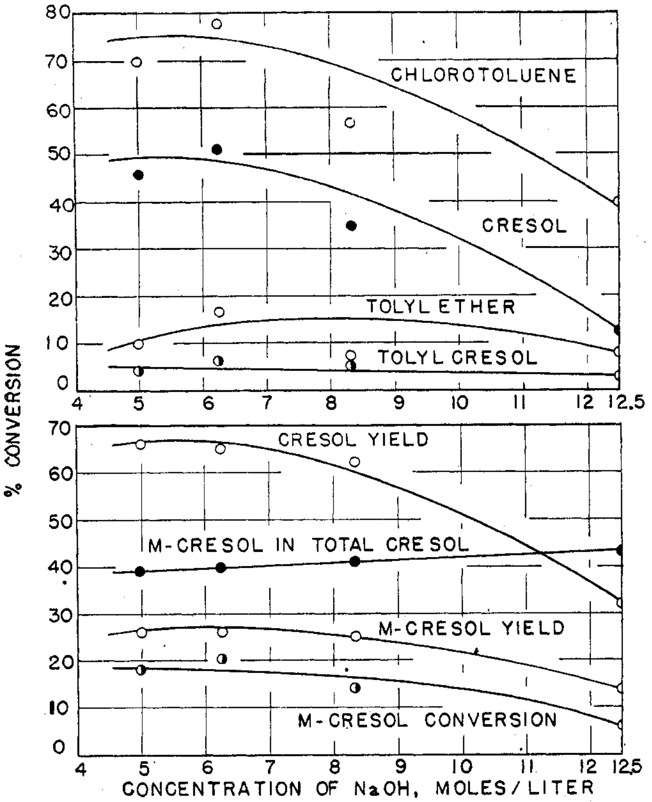


Figure 9. Effect of Aqueous Volume on Hydrolysis of o-Chlorotoluene

Table III. Effect of Recycling *p*-Tolyl Ether

(Reaction time, 1 hour at 330° C.; 2.5 moles NaOH per mole *p*-chlorotoluene; volume, 500 ml.)

Run No.	Tolyl Ether Added, % Excess	Tolyl Ether after Hydrolysis, % of Amount Ordinarily Obtained
113	100	57
114	200	30

MISCELLANEOUS REACTIONS

A reaction was run with 1 mole of *m*-chlorotoluene at 325° C. with 2.5 moles caustic and no catalyst. Analysis of the resulting cresol mixture gave: 66% *m*-cresol, 21% *o*-cresol, and 13% *p*-cresol (by difference). This is probably not an equilibrium mixture of the cresol isomers.

A run was made with a technical mixture of chlorotoluene (Heyden Chemical Corporation), 55% para and 45% ortho, and the usual caustic concentration. The expected yields were obtained—i.e., results consistent with an average of the yields obtained from the pure products.

In an attempt to combine the optimum operating conditions, 1 mole of *p*-chlorotoluene was hydrolyzed with 5 moles of sodium hydroxide (concentration, 10 moles per liter), one-hour reaction time at 360° C., and no catalyst. A total cresol yield of 63% and a *m*-cresol content of 62% were obtained.

CONCLUSIONS

Results of a quantitative study of the hydrolysis of *o*- and *p*-chlorotoluenes indicate that this reaction could probably be adapted to the commercial production of *m*-cresol. The following conclusions were reached:

1. Ninety per cent of the *o*- and *p*-chlorotoluene had reacted after 2 hours of agitation at 325° C. (plus heating time of 2 hours). The isomerization of the chlorotoluenes (as measured by the *m*-cresol content of the total cresol) was not appreciably affected by time. Tolyl ether is much more resistant to hydrolysis than its homolog, phenyl ether.
2. The influence of caustic was considerable: (*a*) The percentage of *m*-cresol in the total cresol increased with increased mole ratio of caustic to chlorotoluene. (*b*) The amount of tolyl ether recovered decreased sharply with increase in caustic concentration, as a result of hydrolysis. (*c*) At high concentrations of caustic the conversion to cresol decreased, apparently as a result of decreased solubility of chlorotoluene in the aqueous phase.
3. At higher temperatures slightly higher yields of cresols were obtained. Reactions carried out in the critical state reveal decreased yields of cresol and increased decomposition to phenol.
4. Emulsifying agents had no apparent effect on the reaction rate, an indication of the possibility of a homogeneous liquid-phase reaction.
5. A maximum cresol yield of 63% (*m*-cresol 62%) was obtained from *p*-chlorotoluene (no recycle of tolyl ether).

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UNIT PROCESSES