CHEMICAL PROCESSES

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# Mononitration of *p*-Cymene

## Information developed is also applicable to other easily oxidized hydrocarbons and should promote industrial use

THIS investigation is one in a series of studies of process variables in the mononitration of the alkyl benzenes. It is hoped that the results will promote the formulation of much-needed generalizations on the effects of the alkyl groups on product distribution, and the role of the mixed acid under various process conditions.

The unique features of *p*-cymene nitration are the susceptibility of the hydrocarbon to oxidation in the normal range of nitrating conditions, its dependence on reaction temperature and emulsification, and the simultaneous dealkylation to produce relatively large amounts of *p*-nitrotoluene. The information obtained for such a hydrocarbon should be useful when other easily oxidized compounds are nitrated. The main product, 2-nitro-*p*-cymene, is the important intermediate in synthesis of carvacrol from *p*-cymene. Relatively low yields in the nitration step, in the past, have kept this process and other processes based on the use of 2-nitro-*p*-cymene, from industrial use.

Early workers (*28, 29*) who nitrated *p*-cymene using nitric-sulfuric mixed acid found that large quantities of *p*-tolyl methyl ketone were formed; hence yields of nitro compounds were low. In 1918, Andrews (*2*) obtained yields as high as 85%. Much of the literature since then (Table I) has dealt with attempts to reproduce his results (*5, 10, 11, 14, 22, 27*).

## Equipment and Techniques

The reactor initially used was the 2-liter reactor described by Kobe and Mills (*19*), agitated by a Lightnin Model F laboratory mixer. Because of the relatively low power input per unit volume attainable with this apparatus, satisfactory emulsification was not attained. The second reactor was a modified Waring Blendor (Catalog No. 700, Waring Products Corp.). Agitation was produced by the 15,000-r.p.m. four-bladed impeller provided with the blender, plus the Lightnin mixer; both mixers were equipped with variable-speed motors. The Lightnin mixer was equipped with a three-bladed propeller type impeller 2 inches in diameter. The two agitators turned in opposite directions. An equal degree of agitation was maintained throughout the nitration by varying the relative positions and speeds of the two agitators, made necessary by variation in liquid level. The use of two agitators markedly improved mixing, as judged by appearance and the elimination of intermittent dark layers and streaks throughout the mixture. Cooling was obtained solely by addition of crushed solid carbon dioxide, kept free from frost crystals.

Table I. Previous Work

| Investigator | Temp., ° C. | $H_2SO_4$, G./G. Cymene | Initial $H_2SO_4$ Concn., % | $HNO_3$, % of Theory | Glacial $CH_3COOH$ Ml./Mole Cymene | Yield, % |
|---|---|---|---|---|---|---|
| **Andrews** (*2*) | 0 | 2.4 | 88 | 110 | 0 | 85 |
| **Phillips** (*27*) | 0 + 5 | 2.6 | 88 | 90 | 0 | 45–50 |
| **Demonbreun and Kremers** (*5*) | 0 + 3 | 2.6 | 85 | 112 | 0 | 65 |
| **Hixon and Cauwenberg** (*10*) | 0 + 3 | 2.6 | 85 | 112 | 0 | 55 |
| **Bert and Dorier** (*3*) | 0 + 10 | 2.5 | 88 | 114 | 20 | 50 |
| **Kuan** (*22*) | 0 | 2.5 | 88 | 110 | 0 | 60 |
| **LeFevre** (*23*) | −3 | 4.5 | 91 | 120 | 80 | 70 |
| **Inoue and Horiguchi** (*11*) | 0 | 2.5 | 88 | 110 | 0 | 81 |
| **Kimura** (*14*) | 0 | 2.4 | 88 | 110 | 0 | 46 |
| **Mann, Montonna, and Larian** (*26*) | 0 | 2.4 | 88 | 110 | 20 | 55–60 |
| **Kobe and Doumani** (*16, 17*) | −10 | 3.8 | 91 | 110 | 80 | 89 |

The *p*-cymene was purified from technical grade cymene by a mild oxidation (*8*), followed by fractionation in a 30-plate Oldershaw column. The acids were of reagent grade.

**Method.** One half of the sulfuric acid used was placed in the reactor, the stirrer turned on, and the total amount of cymene added slowly to emulsify it with the acid. The mixed acid, composed of the nitric acid plus the other half of the sulfuric acid, was then added at a constant rate calculated to produce the desired addition time. The temperature was maintained within 1° C. of the desired value by addition of solid carbon dioxide to the reaction mixture. In all runs except those in which a poor emulsion was intentionally maintained, agitation was maximum, but limited by excessive spattering or the power of the stirrer.

**Purification.** The equipment and technique employed in purification of the reaction products were essentially those of Kobe and Brennecke (*15*). The solution resulting from the quenching of the reaction mixture in a large beaker of crushed ice and water was poured directly into a 5-liter three-necked round-bottomed flask. The organic phase was steam-distilled from the flask, and the product was collected in the modified Dean and Stark moisture trap.

The possibility of attack on the organic compounds by the hot acid mixture during steam distillation was considered. Tests made by distilling known samples in acid mixtures showed no measurable effect.

**Analysis.** The variety of products formed causes difficulties in the analysis. These products include, under suitable conditions, 2-nitro-*p*-cymene, *p*-nitrotoluene, *p*-tolyl methyl ketone, dinitrated products, and degradation products or tar.

The complete analysis involves a combination of physical and chemical techniques.

1. The total organic product purified by steam distillation is weighed and its volume measured.

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Table II. Data and Results for Nitration of 125 Grams of p-Cymene

| Run No. | Temp., ° C. | $HNO_3$/ Cymene Mole Ratio | $H_2SO_4$/ Cymene Weight Ratio | Initial $H_2SO_4$ Concn., Wt. % | Reaction Time, Min. | Yield, % | Conversion, % | Mononitrated Products, % | Unreacted Cymene, % | Ketone, % | Dinitro, % | Tar, % | Nitrotoluene, % of Mononitrated Products |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 19 | 10 | 1.10 | 3.00 | 80.0 | 65 | 77.5 | 88.7 | 68.6 | 11.3 | 8.0 | 0.0 | 12.1 | 14.8 |
| 20 | 10 | 1.10 | 3.00 | 80.0 | 60 | 74.6 | 90.0 | 67.3 | 9.9 | 9.2 | 0.0 | 13.6 | 14.1 |
| 21 | 10 | 0.90 | 3.00 | 80.0 | 45 | 83.0 | 75.7 | 62.8 | 24.3 | 5.9 | 0.0 | 7.0 | 12.7 |
| 22 | 10 | 0.70 | 3.00 | 80.0 | 35 | 80.0 | 66.2 | 53.0 | 33.8 | 3.6 | 0.0 | 9.6 | 15.0 |
| 23 | 10 | 1.10 | 3.00 | 80.0 | 40 | 79.9 | 90.4 | 72.2 | 9.6 | 7.3 | 0.0 | 10.9 | 14.1 |
| 24 | 10 | 0.59 | 2.30 | 80.0 | 60 | 78.0 | 57.2 | 44.6 | 42.8 | 2.9 | 0.0 | 9.7 | 15.5 |
| 25 | 10 | 1.10 | 3.00 | 80.0 | 65 | 75.5 | 91.5 | 69.1 | 8.5 | 7.3 | 0.0 | 15.1 | 14.2 |
| 26 | 10 | 0.90 | 3.00 | 80.0 | 35 | 75.5 | 82.1 | 62.0 | 17.9 | 9.5 | 0.0 | 10.6 | 7.7 |
| 27 | 25 | 0.70 | 3.00 | 80.0 | 30 | 73.7 | 64.3 | 47.4 | 35.7 | 6.5 | 0.0 | 10.4 | 14.4 |
| 28 | 10 | 0.70 | 3.00 | 80.0 | 35 | 69.5 | 61.5 | 42.7 | 38.5 | 6.8 | 0.0 | 12.0 | 12.9 |
| 29 | 10 | 0.70 | 4.00 | 80.0 | 30 | 77.0 | 63.8 | 49.1 | 36.2 | 5.6 | 0.0 | 9.1 | 12.4 |
| 30 | 10 | 0.70 | 3.00 | 90.0 | 35 | 85.5 | 67.1 | 57.4 | 32.9 | 0.5 | 1.0 | 8.2 | 12.1 |
| 31 | 10 | 0.90 | 3.00 | 80.0 | 40 | 69.5 | 73.8 | 51.3 | 26.2 | 10.1 | 0.0 | 12.4 | 11.7 |
| 32 | 10 | 0.90 | 3.00 | 80.0 | 40 | 70.0 | 71.9 | 50.3 | 28.1 | 12.1 | 0.0 | 9.5 | 12.1 |
| 33 | 10 | 0.90 | 4.00 | 80.0 | 40 | 76.2 | 76.7 | 58.5 | 23.2 | 10.0 | 0.0 | 8.2 | 14.5 |
| 34 | 25 | 0.90 | 3.00 | 80.0 | 35 | 60.7 | 62.6 | 38.0 | 37.4 | 15.2 | 0.0 | 9.4 | 9.7 |
| 35 | 10 | 0.90 | 3.00 | 90.0 | 35 | 86.8 | 81.0 | 70.4 | 19.0 | 0.6 | 1.5 | 8.5 | 12.7 |
| 36 | 10 | 1.10 | 3.00 | 80.0 | 35 | 74.7 | 91.1 | 68.0 | 8.9 | 12.6 | 0.0 | 10.5 | 9.5 |
| 37 | 25 | 1.10 | 3.00 | 80.0 | 35 | 68.7 | 78.4 | 53.8 | 21.6 | 16.7 | 0.0 | 7.9 | 9.0 |
| 38 | 10 | 1.10 | 4.00 | 80.0 | 35 | 76.2 | 93.2 | 71.0 | 6.8 | 11.2 | 0.0 | 11.0 | 11.3 |
| 39 | 10 | 1.10 | 3.00 | 90.0 | 35 | 86.4 | 100.0 | 86.4 | 0.0 | 0.7 | 1.0 | 11.9 | 11.9 |
| 40 | 10 | 1.30 | 3.00 | 80.0 | 35 | 74.9 | 91.8 | 68.6 | 8.2 | 11.6 | 0.0 | 11.6 | 14.0 |
| 41 | 25 | 1.30 | 3.00 | 80.0 | 35 | 72.0 | 93.2 | 67.0 | 6.8 | 14.7 | 0.0 | 11.5 | 13.1 |
| 42 | 10 | 1.30 | 4.00 | 80.0 | 35 | 78.6 | 98.3 | 77.2 | 1.7 | 10.3 | 0.0 | 10.8 | 11.4 |
| 43 | 10 | 1.30 | 3.00 | 90.0 | 30 | 86.0 | 100.0 | 86.0 | 0.0 | 1.8 | 6.0 | 6.2 | 15.0 |
| 44[a] | 25 | 1.10 | 2.00 | 80.0 | 35 | 93.0 | 100.0 | 93.0 | 0.0 | .. | .. | .. | .. |
| 45[b] | −10 | 1.10 | 3.82 | 90.5 | 35 | 95.0 | 100.0 | 95.0 | 0.0 | 0.3 | 0.3 | 4.4 | 12.5 |
| 46 | 10 | 1.30 | 3.00 | 90.0 | 35 | 83.0 | 100.0 | 83.0 | 0.0 | 2.3 | 5.0 | 9.7 | 12.9 |
| 47 | 10 | 0.90 | 4.00 | 85.0 | 35 | 89.3 | 88.8 | 79.3 | 11.2 | 2.9 | 0.2 | 6.4 | 13.1 |
| 48 | 10 | 0.90 | 2.00 | 75.0 | 35 | 54.0 | 50.4 | 27.2 | 49.6 | 13.0 | 0.0 | 10.2 | 11.9 |
| 49 | 10 | 0.90 | 2.00 | 80.0 | 35 | 72.9 | 69.8 | 50.8 | 30.2 | 10.2 | 0.0 | 8.8 | 10.2 |
| 50 | 10 | 0.90 | 2.00 | 85.0 | 35 | 80.5 | 81.9 | 65.8 | 18.1 | 7.5 | 0.2 | 8.4 | 13.2 |
| 51 | 10 | 0.90 | 2.00 | 90.0 | 35 | 80.6 | 81.2 | 65.5 | 18.8 | 1.2 | 1.0 | 13.5 | 13.0 |
| 52 | 10 | 0.90 | 3.00 | 75.0 | 35 | 49.5 | 57.4 | 28.4 | 42.6 | 18.5 | 0.0 | 10.5 | 9.6 |
| 53 | 10 | 0.90 | 3.00 | 85.0 | 35 | 85.2 | 83.2 | 70.9 | 16.8 | 5.5 | 0.1 | 6.9 | 12.3 |
| 54 | 10 | 0.90 | 4.00 | 75.0 | 35 | 58.0 | 56.6 | 32.8 | 43.4 | 16.0 | 0.0 | 7.8 | 11.5 |
| 55 | 10 | 0.90 | 4.00 | 85.0 | 35 | 88.9 | 85.1 | 75.6 | 14.9 | 3.8 | 0.1 | 5.6 | 10.8 |
| 56 | 10 | 0.90 | 4.00 | 90.0 | 35 | 84.5 | 75.7 | 64.0 | 24.3 | 0.4 | 1.5 | 9.8 | 12.7 |
| 57 | 25 | 0.90 | 4.00 | 75.0 | 35 | 42.0 | 74.9 | 31.4 | 25.1 | 17.4 | 0.0 | 26.1 | 4.6 |
| 58 | 25 | 0.90 | 4.00 | 80.0 | 40 | 64.3 | 72.8 | 46.8 | 27.2 | 13.7 | 0.0 | 12.3 | 8.8 |
| 59 | 25 | 0.90 | 4.00 | 85.0 | 35 | 86.0 | 82.8 | 71.1 | 17.2 | 3.2 | 0.2 | 8.3 | 12.5 |
| 60 | 25 | 0.90 | 4.00 | 90.0 | 35 | 83.0 | 79.6 | 66.0 | 20.4 | 0.8 | 2.9 | 9.9 | 11.8 |
| 61 | −5 | 0.90 | 4.00 | 75.0 | 35 | 73.5 | 42.0 | 30.9 | 58.0 | 4.2 | 0.0 | 7.0 | 12.7 |
| 62 | −5 | 0.90 | 4.00 | 80.0 | 35 | 85.0 | 72.6 | 61.7 | 27.4 | 4.8 | 0.0 | 6.1 | 12.9 |
| 63 | 3 | 0.90 | 4.00 | 85.0 | 40 | 88.0 | 83.0 | 73.0 | 17.0 | 5.1 | 0.0 | 4.9 | 13.0 |
| 64 | 10 | 0.90 | 4.00 | 85.0 | 35 | 72.1 | 71.9 | 51.9 | 28.1 | 6.8 | 1.0 | 12.2 | 11.7 |
| 65 | 10 | 0.90 | 4.00 | 90.0 | 35 | 65.2 | 63.6 | 41.5 | 36.4 | 2.1 | 1.1 | 15.9 | 6.2 |
| 66 | 10 | 0.90 | 4.00 | 85.0 | 105 | 87.5 | 88.0 | 77.0 | 12.0 | 3.7 | 0.1 | 7.2 | 11.2 |
| 67 | 10 | 0.90 | 4.00 | 85.0 | 70 | 88.0 | 87.9 | 77.4 | 12.1 | 3.2 | 0.1 | 7.2 | 11.9 |
| 68 | 10 | 0.90 | 4.00 | 90.0 | 35 | 84.0 | 74.2 | 62.3 | 25.8 | 0.6 | 1.5 | 9.8 | 10.0 |

[a] *m*-Xylene nitrated.
[b] Conditions of Kobe and Doumani (*17*), includes 75 ml. of acetic acid.

2. Samples are analyzed for *p*-tolyl methyl ketone and dinitrated product.

3. A sample is also vacuum distilled in a 30-plate Oldershaw column, and volumes of the three cuts (unreacted cymene, *p*-tolyl methyl ketone plus *p*-nitrotoluene, and nitrocymene plus dinitrated product) are determined.

4. The results of step 2, combined with the known densities of the products, provide the data to convert volumes to weights. Thus the weights of all five components distilled can be computed.

5. These weights can be placed on the basis of original product weight determined in step 1, and then converted to a mole basis. Tar formation is evaluated as original moles less recovered moles of aromatics.

*p*-Tolyl methyl ketone was determined as proposed by Guenther (*7*). The reagent concentrations, sample size, reaction time, and technique were all followed explicitly.

The method for dinitrated product was developed from the qualitative method of Bost and Nicholson (*4*), and used by McKinley and White (*25*). When 10 ml. of acetone and 3 ml. of a 5% solution of sodium hydroxide are added to a small sample of the unknown, a purplish blue color develops upon shaking, if the unknown contains either 2,4-dinitrotoluene or 2,6-dinitrocymene. The dinitrated product formed contains about 30% of the former and 70% of the latter, according to Allenby and Nichols (*1*).

The quantitative procedure adopted consisted in colorimetric comparison of equal volumes of the unknown and of standard solutions made from pure 2,4-dinitrotoluene and nitrocymene in various molar strengths. All solutions were analyzed as indicated above. The assumption is that equal molarities of dinitrotoluene and dinitrocymene produce equal color intensities upon treatment. Although the absolute accuracy of this method is unknown, its utility for determining the relative amounts of dinitration is satisfactory. The color intensity produced increased regularly over the range of concentrations used, and results were reproducible. This method, after further development and refinement, should give a simple, rapid, and satisfactorily accurate analysis in the range 0 to 10% dinitrated product.

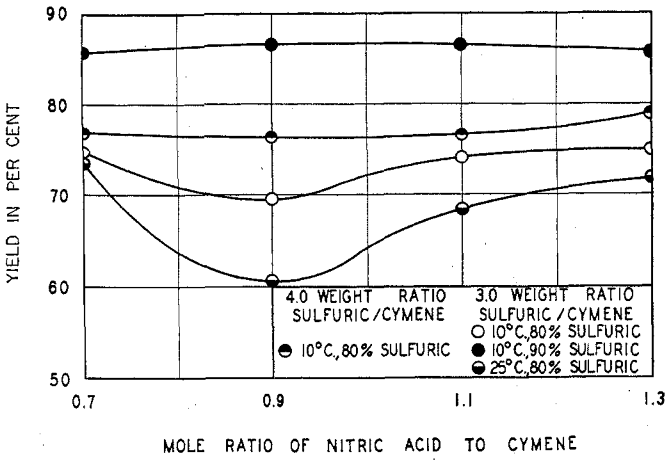

Figure 1. Effect of mole ratio of nitric acid to cymene on yield

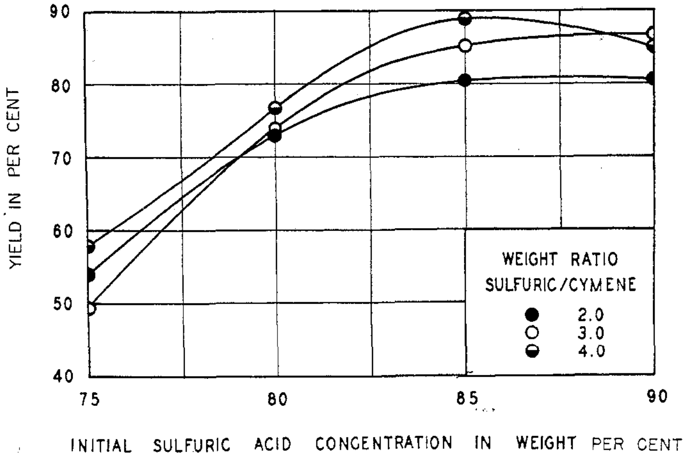

Figure 2. Effect of initial sulfuric acid concentration on yield

Temperature 10° C., reaction time 35 minutes, mole ratio of nitric acid to cymene 0.9

## Choice of Process Variables

The choice of process variables was based on those found important in previous work (*6*, *9*, *13*, *15–19*, *21*), as well as exploratory runs made with *p*-cymene. These initial nitrations indicated the practical limits of some variables and produced two important generalizations: Emulsification has an important effect on yield, and considerable amounts of by-products are produced.

The first observation led to the use of the Waring blender as the nitrator. The second indicated that less severe oxidizing conditions would result in higher yields. To obtain these, an excess of *p*-cymene over nitric acid was used, with the expectation that lower conversion would be accompanied by higher net yields. Conversion is defined as moles of *p*-cymene reacting divided by moles of *p*-cymene originally charged. Yield is defined as moles of mononitrated product formed divided by moles of *p*-cymene reacting.

It was decided to investigate systematically the mole ratio of nitric acid to cymene, weight ratio of sulfuric acid to cymene, initial concentration of sulfuric acid, temperature, reaction time, and emulsification. To reduce the total number of runs to a reasonable value, the following course of investigation was outlined:

Determine the optimum nitric acid–cymene ratio over a wide range of the other variables.

At the optimum ratio, and an average temperature, investigate the effects of initial sulfuric acid concentration and the weight ratio of sulfuric acid to cymene.

At optimum nitric acid–cymene and sulfuric acid–cymene ratios, investigate the effects of initial sulfuric acid concentration and temperature.

Investigate the emulsification properties of cymene, and their role in this reaction.

Determine the effect of reaction time at optimum nitrating conditions.

The data for the nitration experiments are given in Table II.

**Nitric Acid–Cymene Ratio.** In order to determine whether there is an optimum ratio of nitric acid to cymene, its effect on yield, from 70% of the stoichiometric amount of nitric acid to 30% excess, was studied. Standard values of the other variables were arbitrarily chosen on the basis of the preliminary runs as: 3.0 weight ratio of sulfuric acid to cymene, 10° C. reaction temperature, 80% initial sulfuric acid concentration, and 35-minute reaction time. The mole ratio of nitric acid to cymene was studied at these conditions initially, and then, to extend the range of investigation, the values were changed singly and the study was repeated (Figure 1).

The most striking feature of Figure 1 is the sensitivity of yield to the process conditions at a mole ratio of 0.9. Both the highest and the lowest yields over the range of conditions employed were obtained at this ratio. Although the conditions that produced the maximum yields, including the 90% initial sulfuric acid concentration, appeared to be relatively independent of the nitric acid–cymene ratio, this sensitivity at lower

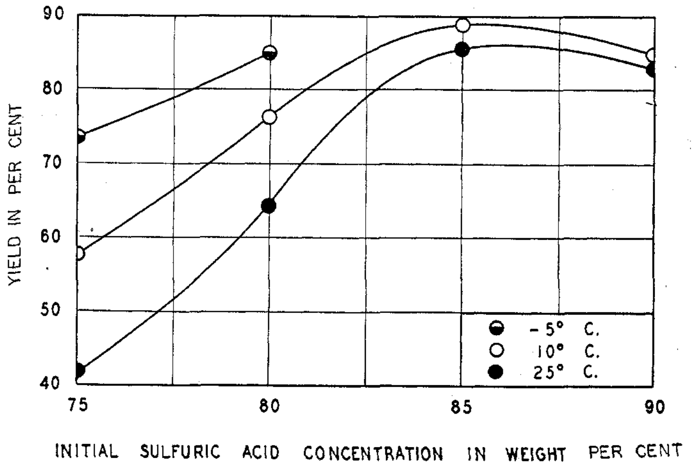

Figure 3. Effect of initial sulfuric acid concentration on yield

Reaction time 35 minutes, mole ratio of nitric acid to cymene 0.9, weight ratio of sulfuric acid to cymene 4.0

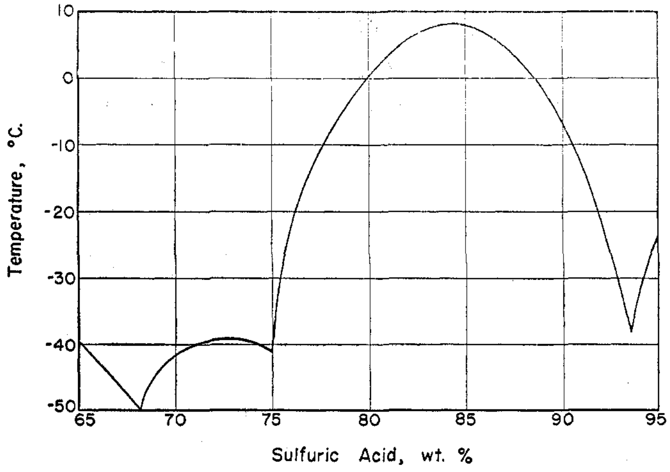

Figure 4. Freezing point diagram for sulfuric acid and water in nitration range

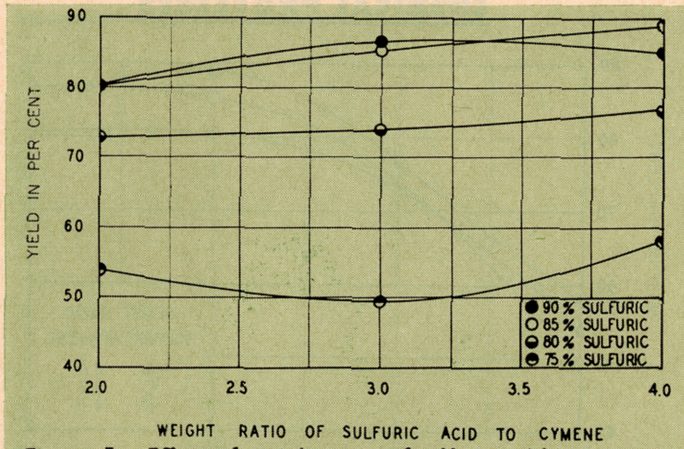

Figure 5. Effect of weight ratio of sulfuric acid to cymene on yield

Temperature 10° C., reaction time 35 minutes, mole ratio of nitric acid to cymene 0.9

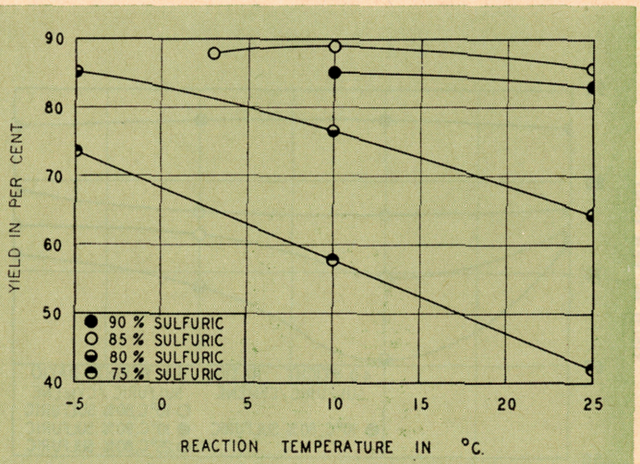

Figure 6. Effect of temperature on yield

Reaction time 35 minutes, mole ratio of nitric acid to cymene 0.9, weight ratio of sulfuric acid to cymene 4.0

concentrations was sufficient reason to establish this ratio as optimum.

Other generalizations involve the effect of some process variables on yield. Thus increase of the concentration of sulfuric acid from 80 to 90% resulted in a consistently large increase in yield. Increase of the weight ratio of sulfuric acid to cymene from 3.0 to 4.0 resulted in a smaller, yet consistent, increase in yield. Increase in temperature from 10° to 25° C. resulted in a relatively large decrease in yield.

**Initial Sulfuric Acid Concentration.** The effect of initial concentration of sulfuric acid on yield is shown in Figures 2 and 3. In Figure 2 the parameters are constant weight ratios of sulfuric acid to cymene. The initial sulfuric acid concentration has its greatest effect from 75 to 85%. Here the formation of *p*-tolyl methyl ketone is most pronounced, decreasing with increase in sulfuric acid concentration. The maximum in the 4.0 weight ratio curve is due to dinitration at higher concentrations, with increase in tar formation. The lack of a well-defined maximum for the curves of lower weight ratios is perhaps due to the increased diluent effect of the water of reaction with the resultant decrease in effective concentration, resulting in a lower tendency for dinitration.

In Figure 3 the parameters are constant reaction temperatures. The effect of initial sulfuric acid concentration is pronounced in the lower range, increasing with temperature. Well-defined maxima occur for both 25° and 10° C. isotherms.

The product distribution as a function of initial sulfuric acid concentration for the three temperature levels studied is shown in Figure 7. From this figure can be determined the product formation which affects the yield under various conditions. The two products that most seriously affect yield, ketone and tar, are formed in highest yields at high temperatures and low acid concentrations. Thus if reaction temperature is high, high concentrations of sulfuric must be used to obtain high yields. Choice of a low reaction temperature permits use of relatively low acid concentrations.

The limitation on concentration at temperatures below 10° C. is due to crystallization of the monohydrate of sulfuric acid in the range from 80 to 90% sulfuric acid. This phenomenon has been erroneously reported in the literature as crystallization of the products of nitration. A portion of the freezing point diagram of the sulfuric acid–water system (*12*) is shown in Figure 4.

**Sulfuric Acid–Cymene Weight Ratio.** The effect of the sulfuric acid–cymene ratio on yield under various conditions is shown in Figure 5. This variable has a much smaller effect on yield over the range investigated than does the sulfuric acid concentration. The maximum and minimum yields at a given acid concentration never differ by more than 10% over the range of 2.0 to 4.0 weight ratio. However, these runs were made under conditions of very intense agitation. The study of emulsification indicated that the phase ratio, which is a function of this weight ratio, is the most important variable affecting ease of emulsion. Thus, if a stirrer with low power had been employed, the effect of the weight ratio on yield probably would have been more pronounced.

**Reaction Temperature.** The effect of temperature on yield for various initial sulfuric acid concentrations is shown in Figure 6. The relatively great temperature dependence of low concentration reactions is immediately apparent. The effect of temperature on product distribution is seen in Figure 7.

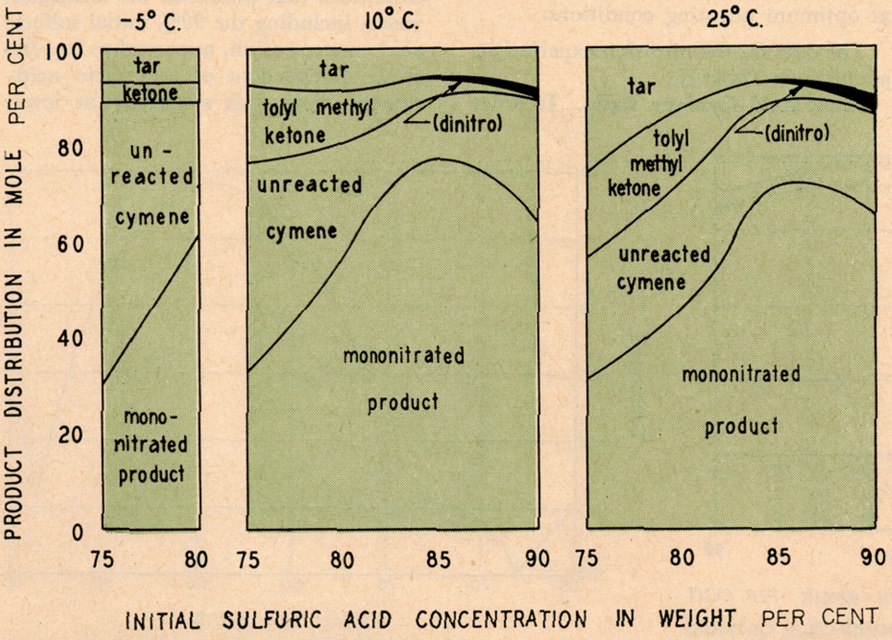

Figure 7. Effect of initial sulfuric acid concentration on product distribution at different temperatures

It is evident that operation at lower temperatures results in higher yields. Two practical limits are imposed on the lower range of temperature operation crystallization in the acid phase with high concentrations of acid (cf. Figure 4), and the relatively greater expense of low temperature operations.

**Reaction Time.** Mononitration of aromatics is generally considered to be a very fast, irreversible, and highly exothermic reaction. The limitation on reaction time in a batch reaction of this type is due to the heat transfer problem with the mass transfer problem of maintaining uniformity of concentrations throughout the solutions. Use of solid carbon dioxide to give cooling and maintenance of vigorous agitation circumvented these problems effectively, and permitted a reaction time of 35 minutes.

Thus it appeared that reaction time would not seriously affect yield, in view of the operation with excess cymene. To check this supposition, reaction time was varied under the conditions of optimum yield at 10° C., 0.9 mole ratio of nitric acid to cymene, 4.0 weight ratio of sulfuric acid to cymene, and 85% initial sulfuric acid concentration. Three reaction times were used: 35, 70, and 105 minutes. Results indicate that the yield is relatively insensitive to reaction time under these conditions.

| | Min. | % Yield |
|---|---|---|
| **Run 47** | **35** | **89.3** |
| **Run 55** | **35** | **88.9** |
| **Run 67** | **70** | **88.0** |
| **Run 66** | **105** | **87.5** |

**Agitation.** In an attempt to determine the qualitative effect of agitation on yield, two runs were made using one stirrer only, operated at a relatively low speed. This decrease in agitation decreased yield from about 89% (runs 47 and 55) to about 72% (run 64), and from about 84% (runs 56 and 68) to about 65% (run 65).

A composite nitrocymene sample was distilled at the high reflux ratio on a Podbielniak Series 3300 semiautomatic micro high temperature analyzer. This column is considered to have 100 theoretical plates. It was operated at an absolute pressure of 13.0 mm. of mercury, at which point the two isomers of nitrocymene differ in boiling point by about 10° C. (*20*). Under the conditions of operation, the presence of a few per cent of the 3-nitro-*p*-cymene in the sample would have been detected. However, no indication of the presence of this isomer was obtained.

Included in the routine analysis was determination of the nitrotoluene product. There appeared to be no correlation of the amount of this product formed with the process conditions. The percentage of *p*-nitrotoluene in the mononitrated product was averaged for the runs 19 through 68; about 12% of the mononitrated products formed consisted of *p*-nitrotoluene.

In two nitrations (runs 7 and 45) made under the conditions of Kobe and Doumani (*16, 17*) to check the reproducibility of the technique, yields of 95% were obtained in agreement with yields claimed by these investigators.

The conditions given as optimum by Kobe and Brennecke (*15*) for the nitration of *m*-xylene were duplicated in run 44. *m*-Xylene was nitrated with a yield of 93%, compared to an expected yield of 97 to 99%. The loss is attributed to the volatility of xylene, and can be accounted for by considering the amount of carbon dioxide generated in the reaction mixture by solid carbon dioxide used as a coolant. A consideration of the relative volatility of *m*-xylene and *p*-cymene indicates that the loss in yield caused by the volatility of cymene would be less than 1% under nearly all conditions employed in this investigation.

## Comparison of Nitration of Related Aromatics

Emulsification of the cymene was a factor of considerable importance. Kobe and Doumani (*16, 17*) indicated that technical grade *p*-cymene exhibited advantages in emulsion formation, over purified cymene, in agreement with Demonbreun and Kremers (*5*). The relative ease of nitration of other aromatics suggests either that they are more easily emulsified or that their reactions proceed smoothly regardless of the nature of the emulsion formed.

To clarify questions that had arisen, a brief study was made of the emulsification properties of cymene, benzene, and toluene. A procedure for study was developed along with criteria for evaluation of the emulsions formed.

**Apparatus.** The apparatus consisted of the Waring blender without the auxiliary stirrer. Two electrodes, placed in the reactor in position to be immersed in the emulsified mixture, provided a means of measuring the conductivity of the emulsion. The electrodes consisted of Nicrome wire sealed by fused polyethylene in small-diameter glass tubing, protected by insertion in a stainless steel tube. These electrodes were connected to an ohmmeter.

**Procedure.** A 100-ml. sample of the aromatic to be tested was placed in the reactor. Sulfuric acid of known composition was then added in 5-ml. increments, the stirrer being operated at a high speed for 3 minutes after each acid addition. This procedure was continued until the region of "stable" emulsion was reached. The criteria upon which emulsion stability was based include conductivity of emulsion, physical appearance of emulsion, and phase separation upon discontinuance of stirring.

**Discussion.** The use of conductivity as a criterion is based on the infinite resistance of the aromatic phase, and the relatively low resistance of the acid phase. Thus when the acid was completely emulsified in the continuous organic phase, the ohmmeter indicated infinite resistance. When the aromatic was completely emulsified in the continuous acid phase, the ohmmeter gave a steady reading equal to the resistance of the acid. The attainment of this steady reading for the latter case was defined as a condition necessary for a stable emulsion.

The presence or absence of a single continuous phase was also indicated by the physical appearance of the emulsion. This is particularly true in the case of cymene, for the color due to a slight reaction with sulfuric acid is more intense in the acid than in the organic phase. The addition of a slight amount of nitrotoluene brought out this effect in the case of toluene and benzene. Below the region of stable emulsions, the appearance of the emulsions was characterized by (1) intermittent dark layers and streaks throughout the mixture, and (2) frothing, splashing, and generally unstable conditions at the surface of the emulsion. In the stable region, the emulsions were of uniform color, and the surface was smooth and undisturbed.

The stirrer was turned off after 3 minutes of intense agitation upon addition of each 5 ml. of acid. Below the stable region, phase separation occurred within a few seconds, indicating incomplete emulsion. Within the stable region the phases did not separate for a minute or more.

The three criteria listed above were found to be mutually consistent, and the stable point, at which the aromatic was completely emulsified in the acid as the continuous phase, was relatively well defined and reproducible. Stable emulsions of acid in a continuous organic phase apparently existed only when the acid-organic volume ratio was very low.

The quantitative results given in Table III, plus the general observations of this study, led to the following conclusions:

Toluene and cymene are very similar in emulsifying properties.

Benzene is slightly more difficult to emulsify in sulfuric acid than cymene and toluene.

There exists a definite volume ratio of acid to aromatic phase at which emulsions become stable for a given acid concentration and a particular aromatic.

### Table III. Stability of Acid-Aromatic Emulsions

| Aromatic | Acid Concn., Wt. % $H_2SO_4$ | Stability Point, Vol. % Acid Phase |
|---|---|---|
| **Cymene (purified)** | 75 | 55 |
| | 85 | 52 |
| **Cymene (technical)** | 75 | 55 |
| | 85 | 52 |
| **Toluene (nitration grade)** | 75 | 55 |
| | 85 | 52 |
| **Benzene** | 75 | 58 |
| | 85 | 55 |

Below this ratio unstable emulsions exist.

Increase in acid concentration results in a decrease in the acid-aromatic volume ratio required for a stable emulsion.

There were no noticeable differences in the emulsifying properties of purified and technical grade cymene.

Lewis and Suen (*24*) reported that a stable benzene-acid emulsion occurred at about 50% by volume of the acid phase. McKinley and White (*25*) presented a curve of stirrer speed *vs.* rate of nitration, in which the rate is essentially zero until a given speed is reached, then increases rapidly to a relatively constant value. As these data were taken under conditions of very high acid volume, it is to be expected that stable emulsions would be easily formed. An examination of the data presented by these investigators reveals that practically all runs were made under conditions of stable emulsions. It would be of interest to investigate the effect of agitation under conditions of low acid–organic phase ratio.

The difficulties in studying the effects of emulsification in batch reactors should be emphasized. The phase ratio is perhaps the most important factor involved here. In batch reactions, however, this ratio is changing throughout the course of the reaction. Thus, to control this factor, use of the stirred tank reactor appears to be essential.

## Nitration of Similar Aromatics

The results of this study can be combined with those of previous investigators to compare a series of alkyl benzenes. The nitration conditions given in Table IV give the maximum yields. In order to indicate the sensitivity of yield to temperature and concentration, the ranges of these variables in which the yield remains within 2% of the maximum have been given.

The optimum temperatures for nitration of cymene and cumene are lower than those for the other compounds. The advantage gained by low temperature operation in the case of cymene has been shown to be a result of decreased formation of oxidation products. As the isopropyl group, which is susceptible to attack, is also present in cumene, the advantage of low reaction temperatures in the nitration of that compound is probably due to decreased oxidation.

The highest yields are obtained from hydrocarbons in which ortho and para positions are open for substitution.

## Conclusions

A systematic process variable study of the two-phase nitration of *p*-cymene using nitric-sulfuric mixed acid as the nitrating agent, shows that yield is a sensitive function of process conditions; the maximum yield of 89% is obtained under narrow conditions.

Temperature, 10° C.
Mole ratio, nitric acid–cymene, 0.9
Weight ratio, sulfuric acid–cymene, 4.0
Initial concentration of sulfuric acid, 85 wt. %
Intense agitation

*p*-Nitrotoluene is formed in this reaction along with 2-nitrocymene, and constitutes about 12% of the mononitrated product regardless of process conditions. No 3-nitrocymene could be found.

Dinitration occurred in trace quantities where 85% initial sulfuric acid concentration was used, and several per cent dinitrated product was formed with 90% acid.

Oxidation was the major side reaction which reduced the yield under normal nitrating conditions. It was found to be a function of temperature, emulsification, and acid concentration.

No significant differences were found in the emulsification properties of cymene, benzene, and toluene. It is evident that emulsification plays a much more important role in the nitration of cymene than in the other aromatics studied in this series.

### Table IV. Nitration of Alkyl Benzenes

| | Benzene | Toluene | *o*-Xylene | *m*-Xylene | *p*-Xylene | Cymene | *p*-Cymene |
|---|---|---|---|---|---|---|---|
| **Max. yield, %** | 98 | 99 | 90 | 98 | 92 | 94.5 | 89 |
| **Optimum temp., ° C.** | 60 | 30 | 25 | 30 | 30 | 15 | 10 |
| **Temp. range, ° C.** | 35–70 | 25–45 | 6–35 | 24–45 | 20–40 | 15–25 | 5–20 |
| **Optimum $H_2SO_4$ concn., wt. %** | 84 | 80 | 80 | 81 | 85 | 81 | 85 |
| **$H_2SO_4$ concn. range, wt. %** | 77–90 | 78–82 | 78–82 | 79–85 | 77–85 | 79–84 | 83–88 |
| **$H_2SO_4$/aromatic, wt. ratio** | 1.2 | 1.4 | 2.15 | 1.0 | 2.0 | 2.0 | 4.0 |
| **$HNO_3$/aromatic, mole ratio** | 1.0 | 0.56 | 1.16 | 1.10 | 1.05 | 1.2 | 0.9 |
| **Reaction time, min.** | 40 | 75 | 30 | 60 | 30 | 120 | 35 |

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