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AZEOTROPIC SULFONATION OF CHLOROBENZENE

BY

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ABSTRACT

A series of experiments were conducted to determine the efficiency of the sulfonation of chlorobenzene by equimolar proportions of sulfuric acid in various organic media under azeotropic conditions. The efficiency of the system was shown to be time dependent, and based upon the conditions used, yields of 20% were obtained.

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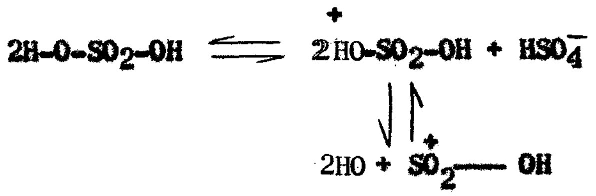
I. INTRODUCTION

Sulfonic acids are primarily of value for their use in the preparation of intermediates for dyestuffs. In such application the sulfo group enhances dyestuff coating and wetting properties because of its property of increasing the water solubility of a compound. The free acids are of about the same acidic strength as sulfuric acid; with p-chlorobenzene sulfonic acid being a low melting hygroscopic solid with a melting point of approximately 68°C.

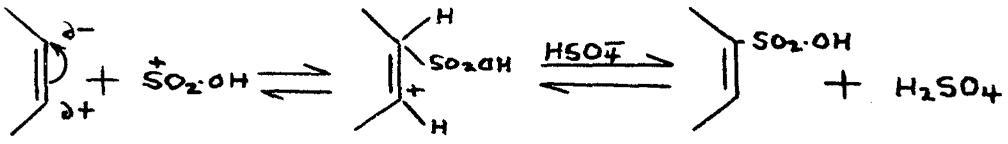
It is usually difficult to isolate the sulphonic acids due to their great solubility in water and their relative non-volatility. For practical usage, the isolation of the acids is not attempted, since the salts undergo the desired synthetic reactions usually obtainable with the free acid.

Aromatic sulfonation is most commonly accomplished by treatment of the aromatic by concentrated sulfuric acid or oleum. It is assumed that ionization of sulfuric acid occurs and reacts as follows:[1]



$$\begin{array}{ccc} 2H\text{-}O\text{-}SO_2\text{-}OH & \rightleftharpoons & 2\overset{+}{H}O\text{-}SO_2\text{-}OH + HSO_4^- \\ & & \downarrow\uparrow \\ & & 2HO + \overset{+}{SO_2}\text{—}OH \end{array}$$

The positive ion $\overset{+}{SO_2}\text{-}OH$ is the active electrophilic agent which attacks the aromatic nucleus at the position of highest electron density during the reaction.



In general, there is a marked decrease in the activity of a chlorine atom adjacent to an aromatic nucleus. The explanation involves resonance and is more descriptively explained in terms of π bonds. Since a π bond leads to a considerable attraction between the bonded atoms, a carbon-carbon double bond is stronger than a carbon-carbon single bond. However, a π bond is weaker than a σ bond, therefore, a carbon-carbon double is less than twice as strong as a carbon-carbon single bond. On this basis, it is easier to break the π component of a double bond (which is thereby converted into a single bond) than it is to break a single bond of the σ type. The strong permanent inductive effect of electron attraction exerted by the chlorine atom on the benzene nucleus by reducing the electron density of the entire benzene nucleus, causes a partial loss of the π bond influence. This lessening of π bond effect and greater dependence upon the σ bonds renders chlorobenzene more resistant than benzene to the electrophilic attack of sulfonation. Electron diffraction studies of chlorobenzenes indicate a shortening of the usual aliphatic C-Cl bond about 0.06 A, corresponding to about a 15% double bond[2].

While the electron density of the entire aromatic nucleus is low making an attack by an electrophilic reagent difficult, the references para position is deactivated the least, resulting in the preferential formation of para-chlorobenzene sulfonic acid.[3]

In standard laboratory preparations chlorobenzene is sulfonated slowly with concentrated sulfuric acid at 100°C, [4] and with oleum[5] of various concentrations at faster rates and reduced temperatures. The preferred conditions are: enough 10% oleum to contain one mole of sulfur trioxide per mole of chlorobenzene and at a temperature of 60°C.[6]

Chlorobenzene when heated with 20% oleum at 300°C gives chiefly the 3,5 disulfonic acid.[7] On a commercial basis monochlorobenzene vapor is continuously passed into the bottom of a column containing a flow of hot (262°C) 95% sulfuric acid (approximately four moles of acid per mole of chlorobenzene) yielding a mixed product of monosulfonic acid and sulfone.[8] Calculations indicate the yield of p-chlorobenzene sulfonic acid based on chlorobenzene to be approximately 55-58%, and based on sulfuric acid the yield is approximately 14-15%.

The sulfonation of chlorobenzene by sulfur trioxide in nitrobenzene is second order at 25° to 100°C with respect to sulfur trioxide. Sulfuric acid retarted the reaction at lower temperatures but not appreciably at higher temperatures. The reaction was retarded by compound formation between sulfur trioxide and the sulfonic acid.[9]

It is noted that from the form of the equations on page 1 that sulfonation is different from ordinary substitution reactions due to the reversibility of the reaction.

The easiest and most economical method of controlling the equilibrium and forcing the reaction to completion is to remove one of the products. In the case of high boiling reactants, this can be accomplished by simply allowing the water to distill out as it is formed. When either reactant is volatile, however, the distillation problem is more complex. Advantage may be taken of the fact that carbon tetrachloride, chloroform, etc. form ternary constant boiling mixtures with water and chlorobenzene, whereas they do not form binary constant boiling mixtures with dry chlorobenzene. The phase containing carbon tetrachloride and chlorobenzene is continuously returned to the reaction mixture from an automatic separator as shown in Figure 1.

If the chlorobenzene is itself used as the azeotropic agent then the reaction should be accompanied by excess sulfone formation, a process which is favored by an excess of the hydrocarbon.

Previous work on sulfonation of chlorobenzene indicated that the control of the reaction at approximately 60°C produced p-chlorobenzene sulfonic acid concurrent with the reduced formation of 4-4' dichloro diphenyl sulfone.[10] This temperature along with consideration of previously mentioned azeotropic conditions suggested the use of carbon tetrachloride, chloroform, and carbon disulfide respectively as reaction media.

The use of equimolar quantities of sulfuric acid and chlorobenzene serves two purposes. First, this lessens use of sulfuric acid, and consequently is expected to increase the economy of the reaction. Secondly the use of excess sulfuric acid is undesirable since it promotes polysubstitution.[3]

II. OBJECTIVE

The objective of this work is to ascertain whether any advantage is gained by the use of azeotrope conditions in the preparation of p-chlorobenzene sulfonic acid when equimolar proportions of chlorobenzene and sulfuric acid are used. This is not an attempt to realize the highest yield but rather a study of the efficiency of the method.

III. EQUIPMENT AND MATERIALS

The equipment was set as per Figure 1. Heat was supplied with a powerstat controlled electric heating which was set at a constant setting for each group of particular experiments. The flask was a four-neck 500 cc. flask equipped with a teflon blade stirrer, thermometer, and dropping funnel inlet, and a reflux or azeotrope outlet. The cooling water in the condensor was set at a rate fast enough to force condensation in the lower quarter of the condensor so as to minimize loss of vapor.

The materials used were:

A. Chlorobenzene - Fisher Scientific Company. This material was redistilled and the fraction boiling at 131-132°C was collected and used in the experiments.

B. Sulfuric acid - J. T. Baker Chemical Co. Assay 97.1% H_2SO_4. Used as received.

C. Carbon tetrachloride - J. T. Baker Chemical Company. Technical grade. Used as received.

D. Chloroform - J. T. Baker Chemical Co. Technical grade.
Used as received.

E. Carbon disulfide - NM grade Fisher Scientific Company.
Used as received.

IV. EXPERIMENTAL

An experiment typical of the manner in which all were conducted is described as follows: With the equipment set up as per Figure 1, 350 cc. of carbon tetrachloride diluent was added to flask A. The stirrer B and electric heating mantle H was set in operation. When the carbon tetrachloride reached reflux temperature, as evidenced by condensate collecting in trap G, 51 cc (0.5 mole) chlorobenzene in E and 27 cc (0.5 mole) sulfuric acid in D were added simultaneously over a five minute period. The condenser cooling water was adjusted so that the vapors condensed in the lower quarter of the condenser. The condensate dropped into trap G where the water and carbon tetrachloride separated and the heavy carbon tetrachloride flow continuously back into flask A. The temperature was read from readings of thermometer C and recorded.

When the desired reaction time was complete the electric heating mantle power was shut off and the stirrer continued for another five minutes to allow for cooling below the reflux temperature. The reaction mixture was slowly stirred into 500 cc water to dilute the acid and wash traces of sulfonic acid out of the warm carbon tetrachloride.

The water and carbon tetrachloride layers are separated by the use of a separatory funnel and the organic layer washed twice with 50 cc water. The water layer and washes are combined and treated with a slurry of technical calcium hydroxide until the mixture is permanently basic to litmus paper. The slurry, containing a precipitate of calcium sulphate and undissolved calcium products from the technical calcium hydroxide slurry, is filtered and the filter cake washed with two 100 cc water washes. The filtrate contains excess dissolved calcium hydroxide and is treated with an excess of carbon dioxide to form calcium bicarbonate. The solution is heated and the volume reduced to 600 cc. At this point all soluble calcium bicarbonate has been converted to relatively insoluble calcium carbonate and the solution is filtered leaving a water solution of the soluble calcium salt of p-chlorobenzene sulfonic acid.

The filtrate is divided into three portions and evaporated slowly to dryness. Care must be taken to evaporate very slowly in the final stages to prevent bumping or spattering of the salt. The yield is calculated on the basis of $(Cl-C_6H_4-SO_3)_2Ca$. The water of crystallization is lost in drying when the evaporation is carried out with care.

Various samples of the calcium salt isolated were placed in capillary tubes and heated in a Vanderkamp "Melt-Pointer". It was observed that samples previously dried carefully at 150° - 200°C showed no signs of water vapor condensation in the cooler upper portions of the capillary tubes upon heating. However, samples dried at temperatures up to 100°C under reduced pressure showed signs of water vapor condensation in the capillary tubes.

Examination of the carbon tetrachloride layer by distillation and evaporation showed unreacted, chlorobenzene, traces of p-chlorobenzene sulfonyl chloride, traces of benzene sulfonyl chloride, and less than 2% 4,4' dichlorophenyl sulfone. The sulfonyl chlorides were only found in instances where carbon tetrachloride was used as the organic diluent and a slight odor of phosgene detected. The formation of phosgene and the sulfonyl chlorides may be explained by the following equations:

1. $Cl\text{-}C_6H_5 + H_2SO_4 \longrightarrow C_6H_6 + ClSO_3H$
2. $C_6H_6 + ClSO_3H + CCl_4 \longrightarrow C_6H_5SO_2Cl + COCl_2 + HCl$
3. $Cl\text{-}C_6H_5 + ClSO_3H + CCl_4 \longrightarrow Cl\text{-}C_6H_4SO_2Cl + COCl_2 + HCl$

Variations were used in the mode of addition of the reactants, and the results are shown in Table II.

In order to ascertain how much of the yield could be attributed to the effect of azeotroping, a series of experiments were conducted whereby the reaction mixture was merely refluxed with no attempt being made to trap the water out of the vapor or condensate. To determine whether heat played the major part rather than azeotroping, runs were conducted with the same reactants and contact time but at room temperature. Comparison of the yields is shown in Table III.

V. CONCLUSIONS

A comparison of data indicates that Azeotrope conditions favor increased yields of p-chlorobenzene sulfonic acid when chlorobenzene is treated with equimolar quantities of sulfuric acid. The yields do not approach theoretical, but it is felt that the azeotroping-time conditions are not strong enough to remove enough water to swing the equilibrium beyond the point reached in these experiments. If the azeotroping-time conditions are strengthened, by better azeotrope agents and increased time, it may be assumed that larger yields of p-chlorobenzene sulfonic acid would be attained. Conditions may also be shifted to favor increased formation of 4-4' dichlorophenylsulfone and subsequent reduction to the desired sulfonic acid upon continued removal of water from the sulfuric acid mixtures.

The efficiency of the system as used appears to produce yields of approximately 20%.

TABLE I

EXPERIMENTAL CONDITIONS OF SULFONATION OF CHLOROBENZENE

Exp No.	M C_6H_5Cl	M H_2SO_4	Media	Temp. °C	Time hrs.	Wt. Ca Salt Grams.	% Yield
C-1	0.5	0.5	A	79-82	0.5	6.2	2.9
C-2	0.5	0.5	A	79-82	2.0	14.0	6.6
C-3	0.5	0.5	A	79-83	6.0	23.0	10.9
C-4	0.5	0.5	A	79-83	10.0	31.8	15.0
C-7	0.5	0.5	A	79-83	12.0	41.0	19.4
C-8	0.25	0.25	A	79-83	12.0	43.0	20.1
C-9	1.0	1.0	A	79-83	12.0	39.1	18.5
C-10	0.5	0.5	A	79-82	0.5	9.8	4.6
C-11	0.5	0.5	A	79-82	1.0	10.0	4.7
C-12	0.5	0.5	A	79-82	2.0	14.4	6.8
C-13	0.5	0.5	A	79-82	3.0	16.4	7.7
C-14	0.5	0.5	A	79-83	5.0	17.2	8.1
C-16	0.5	0.5	A	79-83	5.0	20.1	9.5
C-17	0.5	0.5	A	79-83	8.0	24.2	11.4
C-18	0.5	0.5	A	79-83	13.0	42.4	20.0
D-1	0.5	0.5	B	60-66	0.5	4.0	1.9
D-2	0.5	0.5	B	60-66	1.0	5.8	2.7
D-3	0.5	0.5	B	60-66	3.0	9.8	4.6

TABLE I (Cont'd)

Exp No.	M C_6H_5Cl	M H_2SO_4	Media	Temp. °C	Time hrs.	Wt. Ca Salt Grams.	% Yield
D-4	0.5	0.5	B	60-66	6.0	17.2	8.1
D-5	0.5	0.5	B	60-66	12.0	30.3	14.3
E-1	0.5	0.5	C	48-50	1.0	0.5	0.2
E-2	0.5	0.5	C	48-50	3.0	2.9	1.4
E-3	0.5	0.5	C	48-50	6.0	3.8	1.8
E-4	0.5	0.5	C	48-50	12.0	7.1	3.4

A = carbon tetrachloride
B = chloroform
C = carbon disulfide

TABLE II

MODE OF REACTANT ADDITION

Exp. No.	Time of H_2SO_4 (min)	Time of C_6H_5Cl (min)	Time of Run (hr)	Yield of Calcium Salt	Yield %
C-2	5	5	2.0	14.0	6.6
C-3	5	5	6.0	23.0	10.9
G-1	5	30	2.0	11.8	5.6
G-2	5	30	6.0	23.8	11.2
G-3	30	5	2.0	14.1	6.7
G-4	30	5	2.0	22.2	10.5

$$\left.\begin{array}{ll} 0.5 \text{ mole} & H_2SO_4 \\ 0.5 \text{ mole} & C_6H_5Cl \\ 350 \text{ cc} & CCl_4 \end{array}\right\} \text{Constant Conditions}$$

TABLE III

COMPARISON OF AZEOTROPE WITH NON-AZEOTROPE EXPERIMENTS

Exp. No.	Time of run (hrs)	Temp. °C.	Wt. of Calcium Salt	Yield %	Remarks
F-1	12.0	20-25	8.7	4.1	
F-2	12.0	20-25	6.8	3.2	
F-3	1.0	20-25	1.2	0.6	
F-4	6.0	20-25	4.3	2.0	
F-5	12.0	79-82	29.2	13.8	Refluxed, no water trap
F-6	1.0	79-82	8.1	3.8	Refluxed, no water trap
F-7	6.0	79-82	17.9	8.4	Refluxed, no water trap
C-7	12.0	79-83	41.0	19.4	Azeotroped w/water trap
C-11	1.0	79-82	10.0	4.7	Azeotroped w/water trap
C-3	6.0	79-83	23.0	10.9	Azeotroped w/water trap

$$\left.\begin{array}{ll} 0.5 & H_2SO_4 \\ 0.5 & C_6H_5Cl \\ 350 & CCl_4 \end{array}\right\} \text{Constant Conditions}$$

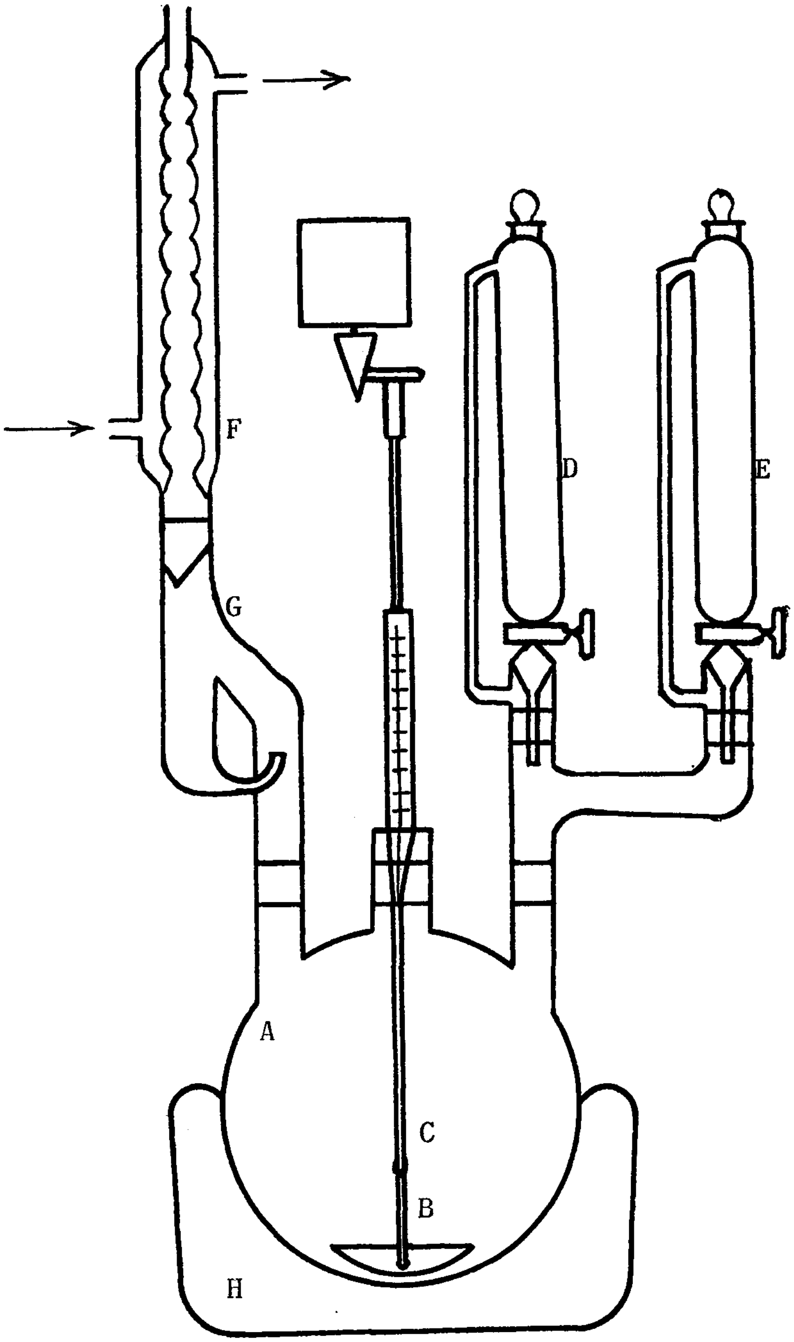


Fig. 1. EQUIPMENT SET-UP

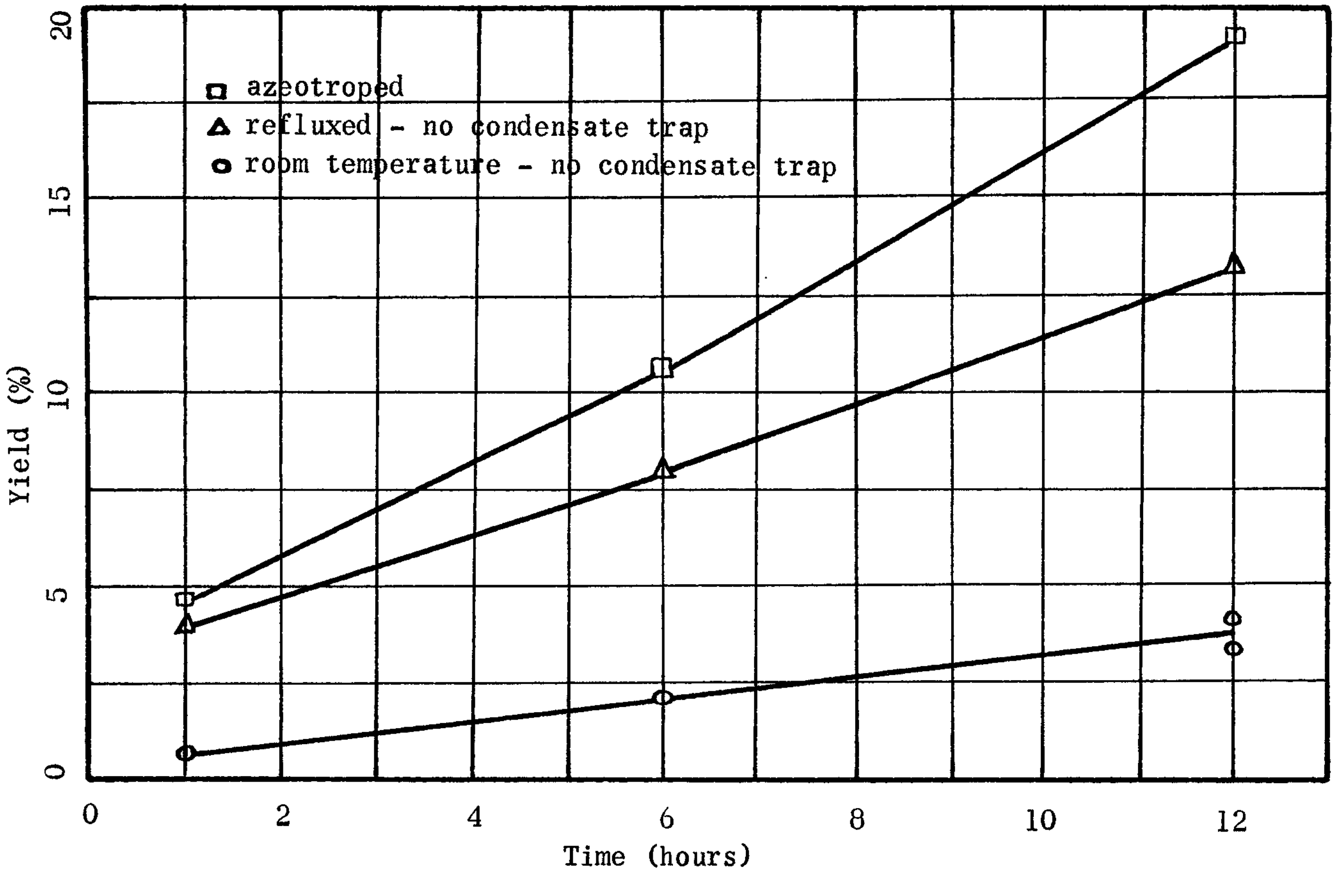


Fig. 2. COMPARISON OF AZEOTROPE EFFECT WITH NON-AZEOTROPE EFFECT:

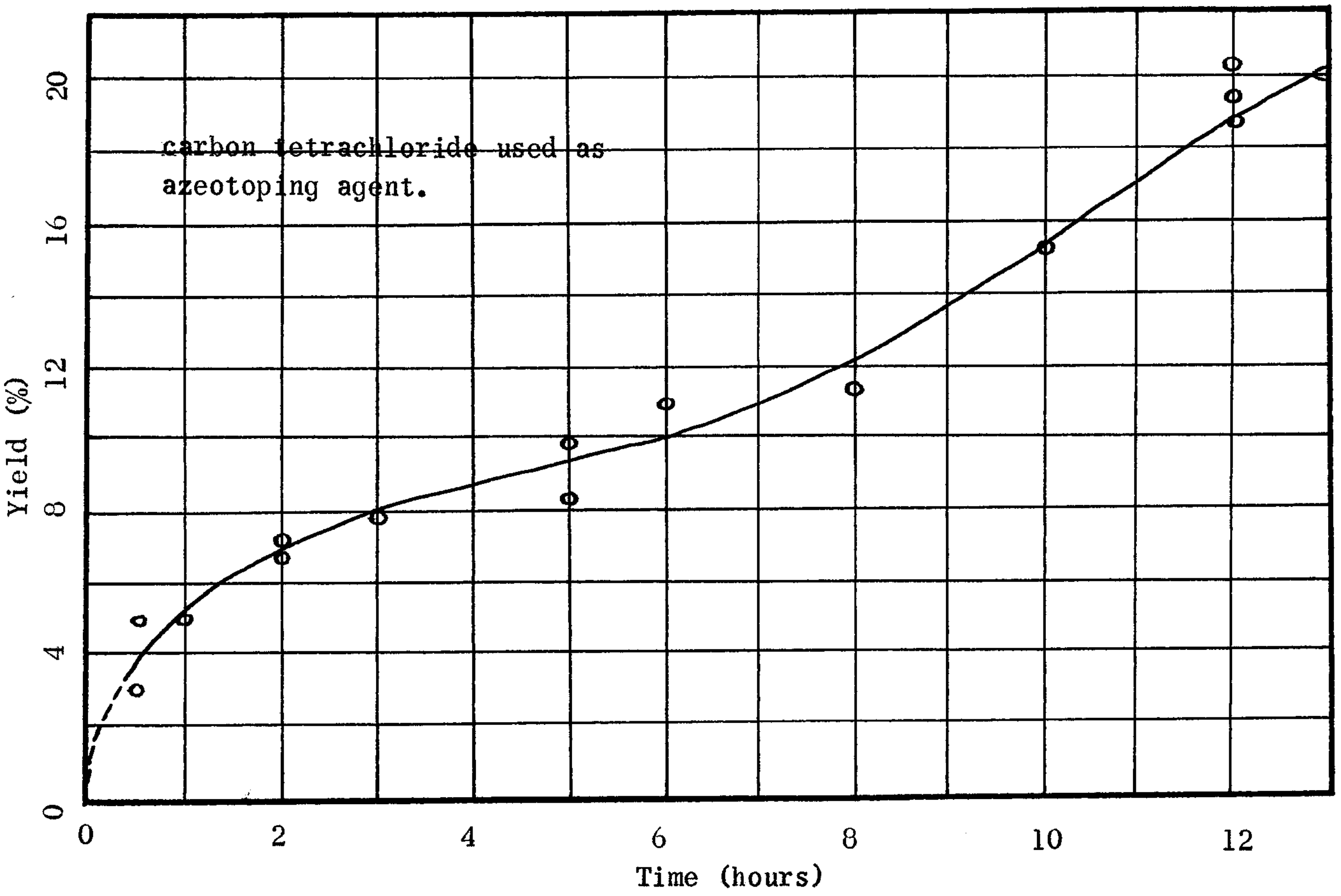


Fig. 3. YIELD AS A FUNCTION OF TIME.

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