

QUANTITATIVE COMPARISONS OF METALLIC  
CHLORIDE CATALYSTS IN THE FRIEDEL-CRAFTS KETONE  
SYNTHESIS

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By

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Bachelor of Science

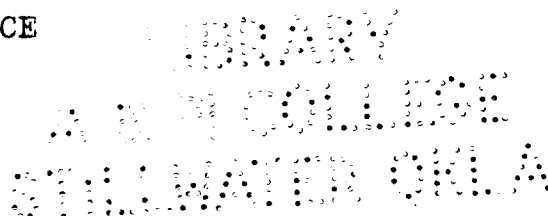
Panhandle A. and M. College

Goodwell, Oklahoma

1936

Submitted to the Department of Chemistry  
Oklahoma Agricultural and Mechanical College  
In Partial Fulfillment of the Requirements  
For the degree of  
MASTER OF SCIENCE

1940



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## ACKNOWLEDGEMENT

The author wishes to express his heartfelt appreciation to Dr. O. C. Dermer under whose direction and guidance this work has been accomplished. He wishes to acknowledge the valuable assistance of Dr. H. M. Trimble and Everett L. Adams in preparing the apparatus and supplying the chemicals.

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## INTRODUCTION

According to Calloway (5) "there are, perhaps, no reactions which have been so widely studied and still are so poorly understood as the Friedel-Crafts reactions. It is difficult to find other reactions which have been so widely applied to industry and in the laboratory as the Friedel-Crafts reactions".

This work is a continuation of Wilson's study (44) of catalysts for the Friedel-Crafts ketone synthesis. It is its purpose to establish the best ratio of various metallic chlorides to a given acid chloride and to ascertain the optimum time of reaction so that maximum yields may be obtained. Some of the catalysts studied are generally known to be effective; others had not hitherto been tested.

## HISTORICAL

The catalyst first employed in the reaction known by the name of its discoverers, Friedel and Crafts, was originally thought to be aluminum, but subsequent investigation by Friedel and Crafts showed that the active substance was aluminum chloride, formed by the union of the chlorine from the alkyl chloride and aluminum (6). Since this discovery many investigations have been made of this famous reaction using catalysts other than aluminum chloride. Although the latter is the one usually chosen for the Friedel-Crafts ketone synthesis, occasional use is made of ferric chloride, stannic chloride, and zinc chloride (5, 26).

Other chlorides known to have value as catalysts are antimony trichloride (11, 31), antimony pentachloride (11), titanium tetrachloride (1, 5, 21, 26, 40), zirconium tetrachloride (27), gallium trichloride (43), thallium trichloride (23), tungsten hexachloride (24), uranium tetrachloride (24, 28), molybdenum pentachloride (24), beryllium chloride (3), bismuth trichloride, tellurium dichloride, and tellurium tetrachloride (44). A catalyst that does not fit into the metallic halide group, but worthy of mention because of recent investigations, is hydrogen fluoride. In certain Friedel-Crafts reactions it has been found to be effective (14, 41). Only a few chlorides besides those studied by Wilson have been reported completely inactive: cuprous chloride (16), chromic chloride (16, 10), calcium chloride (5), silicon tetrachloride (5), and lead

tetrachloride (9), and lead dichloride (5).

Although the relative efficiency of these catalysts is somewhat different in different reactions, the most common order of decreasing activity is given as aluminum chloride, ferric chloride, zinc chloride, stannic chloride, titanium tetrachloride, and zirconium tetrachloride (5). The only work dealing specifically with quantitative comparisons, however, has been confined to examining mixed catalysts (15, 18, 19, 36).

If the Friedel-Crafts ketone synthesis were uncomplicated by side reactions and consecutive reactions, a comparison of catalysts could only mean a comparison of rates of reaction, such as has been made for both the hydrocarbon and the ketone synthesis (29, 43). Since in practice the maximum yields obtainable with different catalysts vary widely, these measures of the extent of the reaction constitute the usual basis of comparison. In the work here reported, the yields of p-methylacetophenone from acetyl chloride, toluene and various catalysts were measured. Both concentration of catalysts and time of reaction were separately varied until optimum conditions, as indicated by maximum yield, were obtained for each catalyst.

After considering the results of Wilson's investigations (44), a hydroxylamine hydrochloride method of measuring yield was chosen and used. The actual isolation of the desired product (36, 18, 19), is impractical and inexact when used in small-scale runs necessitated by expensive catalysts; and the



amount of hydrogen chloride evolved (15, 29) is not necessarily a measure of the rate or extent of the desired reaction (7, 8, 39). However, Wilson reported (44) the end point of the acidimetric titration to be so exceedingly blurred by pyridine, which Bryant and Smith (4) added to complete oxime formation, that the older procedure of Bennett and Cocking (2) was chosen. In this procedure the hydrochloric acid liberated from hydroxylamine hydrochloride as indicated by the following equation:



was titrated with standard sodium methoxide solution at intervals until a permanent end point was reached. The principal modification in this method was the use of absolute methanol instead of 95% ethanol as reaction medium.

## EXPERIMENTAL

## Materials Used

Friedel-Crafts Reagents.

C. P. toluene was used without further purification. The C. P. acetyl chloride was distilled and stored in small glass-stoppered bottles in a desiccator.

Analytical Reagents.

The hydroxylamine hydrochloride solution was prepared according to a modification of the method given by Bryant and Smith (4). The approximately 0.5 normal solution was made by dissolving 35-40 grams of C. P. hydroxylamine hydrochloride in a minimum quantity of absolute methanol and diluting to 1000 ml. with the same solvent.

The indicator used was an alcoholic solution of a recrystallized student preparation of butter yellow (p-dimethylamino-azo-benzene).

Standardized sodium methoxide was prepared by dissolving the approximate quantity of sodium required to give a 0.5 normal solution in the required amount of methanol. It was then standardized against an alcoholic solution of a known amount of benzoic acid or potassium acid phthalate. Several solutions were made up during the course of this experiment and in each instance the solution was accurately standardized.

Catalysts.

Three different samples of aluminum chloride were used in this study. One was prepared by the writer as directed by

Gattermann (17). Aluminum turnings were washed free from oil and grease by the use of alcohol and then dried for one hour in the open furnace. These turnings were placed in a combustion tube, which was provided with asbestos connections to a source of hydrogen chloride and to a condenser. The combustion tube and contents were then heated to a temperature of about 300°, at which temperature hydrogen chloride gas, previously dried, was passed over the aluminum. The aluminum chloride vapors were condensed in an Erlenmeyer flask with side arm attachment to remove excess hydrogen chloride and to permit its free flow. The yield was fair and was largely in powdered form. The aluminum chloride thus prepared was re-sublimed. The side arm of the condenser used in the original preparation was stoppered and a test tube with side arm attachment was fitted, by the use of asbestos packing, snugly into the mouth of said condenser. The flask was then heated until the aluminum chloride was revolatilized. The vapors then were condensed in the test tube while volatile impurities escaped through the side arm.

The C. P. anhydrous aluminum chloride was a special iron-free grade purchased from Mallinckrodt Chemical Company.

The commercial aluminum chloride was obtained from the stock room supply.

The anhydrous ferric chloride was prepared by placing iron filings in a combustion tube, one end of which was attached to a cylinder of chlorine and the other to a side arm condenser flask. Chlorine gas was passed through the tube

and condenser to sweep out air and water vapor. The combustion tube and contents were then gently heated while the current of chlorine was maintained. The ferric chloride crystals formed condensed and were then resublimed in an apparatus similar to that used for aluminum chloride.

C. P. antimony pentachloride was redistilled to remove chlorine resulting from decomposition.

Anhydrous tellurium tetrachloride was made by passing an excess of dry chlorine over molten tellurium (30). It was purified by distillation: b. p.  $380^{\circ}$ .

Anhydrous tellurium dichloride was made by refluxing tellurium tetrachloride with free tellurium (38) and then distilling out the product: b. p.  $324^{\circ}$ .

Anhydrous thorium tetrachloride was purchased from Eimer and Amend.

Anhydrous molybdenum pentachloride was a student preparation in Chemistry 610.

Anhydrous stannous chloride was obtained by fusing and distilling C. P. stannous chloride. The distillation apparatus was composed of two pyrex tubes sealed together to form an inverted Y tube. The ends of each leg of the Y were then sealed off so that the partially hydrated stannous chloride could be placed in one leg. On the application of heat the water vapor first escaped through the open stem; the salt then volatilized and condensed in the other leg. The distilled stannous chloride was then fused in order to pour it into a dry mortar. It was next powdered by placing a rubber diaphragm, into which

the pestle fits snugly, over the mortar and then grinding. The diaphragm helped prevent the stannous chloride from taking up moisture.

Anhydrous zinc chloride was obtained by fusing and distilling C. P. zinc chloride obtained from the stock room. The same apparatus as was used for the stannous chloride was used for the distillation and powdering process.

Lead tetrachloride was obtained by adding C. P. concentrated sulfuric acid to pyridinium hexachloroplumbate. The following reaction occurred:



The oily  $\text{PbCl}_4$  formed settled to the bottom of the container. The excess reagents and by-products of the reaction were decanted and more C. P. sulfuric acid was added and the mixture then stirred. This washing process was twice repeated. The  $\text{PbCl}_4$  obtained was kept submerged in concentrated sulfuric acid.

Germanium tetrachloride was loaned by Dr. Warren Johnson of the University of Chicago.

## PROCEDURE

Toluene was chosen for the aromatic compound, because it is cheap, does not react in the absence of a catalyst and gives comparatively large yields in most instances.

In studying a particular catalyst the amount was kept constant while the heating time was varied until the optimum was found; then runs were made to determine the effect of varying the amount of catalyst at this optimum reaction time.

In the course of this research, each catalyst was prepared and studied separately, but the same technique and procedure was followed throughout. An excess of toluene was used in each instance and each reagent was assigned a pipette of appropriate size, which was used for that reagent alone throughout the research.

The ratio of catalyst to acetyl chloride, where determination of optimum heating time was the aim, was .011 moles catalyst/.0137 moles acetyl chloride.

After optimum heating time was determined the amount of catalyst was varied to find out the quantity of catalyst required for maximum yield. The quantity of toluene and acetyl chloride remained constant. The ratio of catalyst to acetyl chloride was increased by increasing the quantity of catalyst used in each consecutive test. This increase was either .011 or .0065 moles.

All refluxing and distillation apparatus was provided with ground glass joints and all containers used were provided

with ground glass stoppers. These provisions eliminated the possibility of loss of ketone or acetyl chloride by absorption, which is likely to occur when rubber or cork stoppers or connections are used. The apparatus was thoroughly cleaned after each use. The flasks were washed with acid and pumice and then placed in a drying oven until all moisture was completely expelled. The condensers were flushed with hydrochloric acid, then steam or water. The reflux condensers were given from 12 to 24 hours to dry. In instances where the condensers were needed before they were perfectly dry, a stream of air was passed through until dryness was complete.

In the standard procedure 10 ml. of toluene was pipetted into a dry 250 ml. flask, which could be fitted to either a reflux condenser or a distillation condenser by an interchangeable ground glass joint. Exactly 1 ml. of acetyl chloride was added by means of a pipette calibrated by weighing its delivery of acetyl chloride. The selected amount of catalyst, having been weighed while enclosed in an air tight container, was then added all at once. Timing was begun from the first visible sign of reaction, usually bubbling; this might or might not require preliminary heating. During the reaction a further 5 ml. of toluene was dropped down through a loose plug of glass wool midway in the reflux condenser, to scrub acetyl chloride vapor from the escaping hydrogen chloride.

After whatever reaction time chosen was complete, the flask was quickly cooled and its contents hydrolyzed by adding cold water through the condenser. The hydrolysis

stopped the reaction immediately<sup>1</sup>. The glass wool plug was then forced down into the flask. The reaction mixture was made just alkaline to phenolphthalein. The alkali neutralized any acid which might be present and eliminated the possibility of its being distilled along with excess toluene and ketone. After being made alkaline the mixture was diluted to about 150 ml. Pieces of porcelain and a drop of oil were added. The porcelain along with the glass wool plug which was introduced earlier prevented bumping while the oil functioned to help prevent foaming. The flask and contents were then connected to a condenser (ground glass joint) and the ketone which had been prepared, along with excess toluene, was steam distilled. At least 75 ml. of distillate was collected in a separatory funnel. The possibility of drops of ketone adhering to the walls of the condenser and thus being lost was eliminated by disconnecting the condenser jacket and permitting the water to drain therefrom. When distillation was then continued the steam moving along the condenser tube swept the remaining drops of ketone into the separatory funnel. Plugs of glass wool in the neck of the flask prevented spray from being carried over into the condenser and thence to the receiving separatory funnel. This precaution was taken because the spray contained alkali and other metallic hydroxides which, if carried over into the separatory funnel and then to the

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1. If the reaction mixture had not been sufficiently cooled the addition of the water, in some instances, produced such a violent reaction that the mixture was forced out the top of the reflux condenser.



hydroxylamine hydrochloride treatment, might cause erroneous results.

Fifteen grams of C. P. sodium nitrate were powdered and dissolved in the distillate by shaking, for its salting out effect. The toluene layer was then separated and the salt solution washed with two 5 ml. portions of benzene to rinse out all ketone. These rinsings were then added to the toluene. The accumulated solution was then properly stoppered and set aside. When about six samples had accumulated each was treated with 20 ml. of an approximately 0.5N solution of hydroxylamine hydrochloride in methanol; this solution must be neutral to obtain accurate results. This neutrality was maintained by adding from time to time (whenever necessary) a drop of butter yellow and sufficient of the standard sodium methoxide to change the red (acid) color to peach. The solution after the above addition was allowed to stand, properly stoppered, for a period of approximately twenty-four hours. The hydrochloric acid liberated by the reaction between the ketone and the hydroxylamine hydrochloride was then roughly titrated with the standard solution of sodium methoxide in methanol using butter yellow as indicator. There was no necessity for accurate titration during the first titration, as the reaction is a gradual one and slight excess of the standard base would soon be used up. A large excess of alkali, however, would cause gradual and erratic decomposition of the hydroxylamine which it liberated. The titration was renewed at intervals of twenty-four hours, until a permanent end point was reached. The permanent end

point is determined by comparison to a standard, the color of which is a yellow to peach.

The entire process of isolating and determining the ketone was tested by the use of known amounts of acetophenone. Blanks were also run from time to time omitting only the acetyl chloride, particularly where there was suspicion that a catalyst was somehow producing spurious evidence of yield.

The above procedure was altered in several instances to follow the Perrier (33) method, recommended by Sorge (42). This alteration consisted of combining the catalyst and the acetyl chloride before adding the toluene. Since a molecular complex was usually formed, with evolution of heat, initial cooling in an ice bath was necessary to prevent loss of acetyl chloride.

## RESULTS

Table I

## Variation of Yield with Reaction Time

(Moles catalyst/moles  $\text{CH}_3\text{COCl}$  = 0.8 in every case)

Catalyst	Time on water bath (min.)	Reflux time (min.)	Yield (%)	Remarks
$\text{AlCl}_3$ (prepared with HCl)	10	0	64	
	15	0	63	
	20	0	62	
	20	30	53	
	20	60	44	
$\text{AlCl}_3$ (C. P., purchased)	5	0	34	
	10	0	43	
	25	0	43	
	25	30	50	
	25	60	50	
	25	120	54	
	16 hrs. at room temperature			56
$\text{AlCl}_3$ (partially hydrated, stock room supply)	5	0	3	
$\text{SbCl}_5$	10	0	66	(All runs by Perrier method)
	15	0	61	
	25	0	49, 50	
	25	30	33	
	25	60	30	

Table I  
continued

Catalyst	Time on water bath (min.)	Reflux time (min.)	Yield (%)	Remarks
FeCl <sub>3</sub>	10	0	45	
	15	0	40	
	20	0	36	
	20	30	25	
MoCl <sub>5</sub>	10	0	25	
	20	0	30	
	20	30	31	
TeCl <sub>4</sub>	20	0	18	
	20	30	28	
	20	60	23	
TeCl <sub>2</sub>	10	0	10	
	20	0	16, 17	
	20	30	21	
	20	60	20	
	20	0	6	(lump catalyst used instead of powder)
ZnCl <sub>2</sub>	20	0	3	
	20	30	7	
	20	60	13	(fused catalyst)
	20	60	13	(distilled catalyst)
	20	120	10	

Table I  
continued

Catalyst	Time on water bath (min.)	Reflux time (min.)	Yield (%)	Remarks
PbCl <sub>4</sub>	20	0	1.6	
	30	0	1.5	

Table II

## Variation in Yield with Amount of Catalyst

Catalyst	Moles catalyst/ moles $\text{CH}_3\text{COCl}$	Yield (%)	Reaction time
$\text{AlCl}_3$ (prepared with $\text{HCl}$ )	0.8	62	10 min. on water bath
	1.2	70	
	1.6	69	
$\text{AlCl}_3$ (C.P., purchased)	0.8	55	20 min. on water + 2 hrs. reflux.
	1.2	63	
	1.6	71	
	2.4	71	
	0.8	43	10 min. on water bath.
	1.6	57	
	2.4	56	
$\text{SbCl}_5$	0.8	66, 66	10 min. on water bath; all runs by Perrier method
	1.2	70	
	1.6	68	
	2.4	45	
$\text{FeCl}_3$	0.8	45, 46	10 min. on water bath.
	1.2	58	
	1.6	57	

Table II  
continued

Catalyst	Moles catalyst/ moles $\text{CH}_3\text{COCl}$	Yield (%)	Reaction time
$\text{TeCl}_2$	0.8	22	20 min. on water + 30 min. reflux
	1.2	26	
	1.6	36	
	2.4	32	
$\text{TeCl}_4$	0.8	28	20 min. on water bath + 30 min. reflux
	1.2	27	
	1.6	13	
$\text{ZnCl}_2$	0.8	13, 13	20 min. on water bath + 1 hr. reflux
	1.2	6	
	1.6	6	

The following chlorides were found to give no ketone:  
thorium tetrachloride, germanium tetrachloride, and stannous  
chloride.

Table III

Influence of Perrier Method  
(When moles catalyst/mole  $\text{CH}_3\text{COCl} = 0.8$ )

Catalyst	Reaction time (min.)	Ordinary yield (%)	Perrier yield (%)
$\text{AlCl}_3$ , C.P.	50	50	65
$\text{SbCl}_5$	10	30*	66
$\text{FeCl}_3$	10	45	60
$\text{MoCl}_5$	10	25	35
$\text{ZnCl}_2$	80	13	12

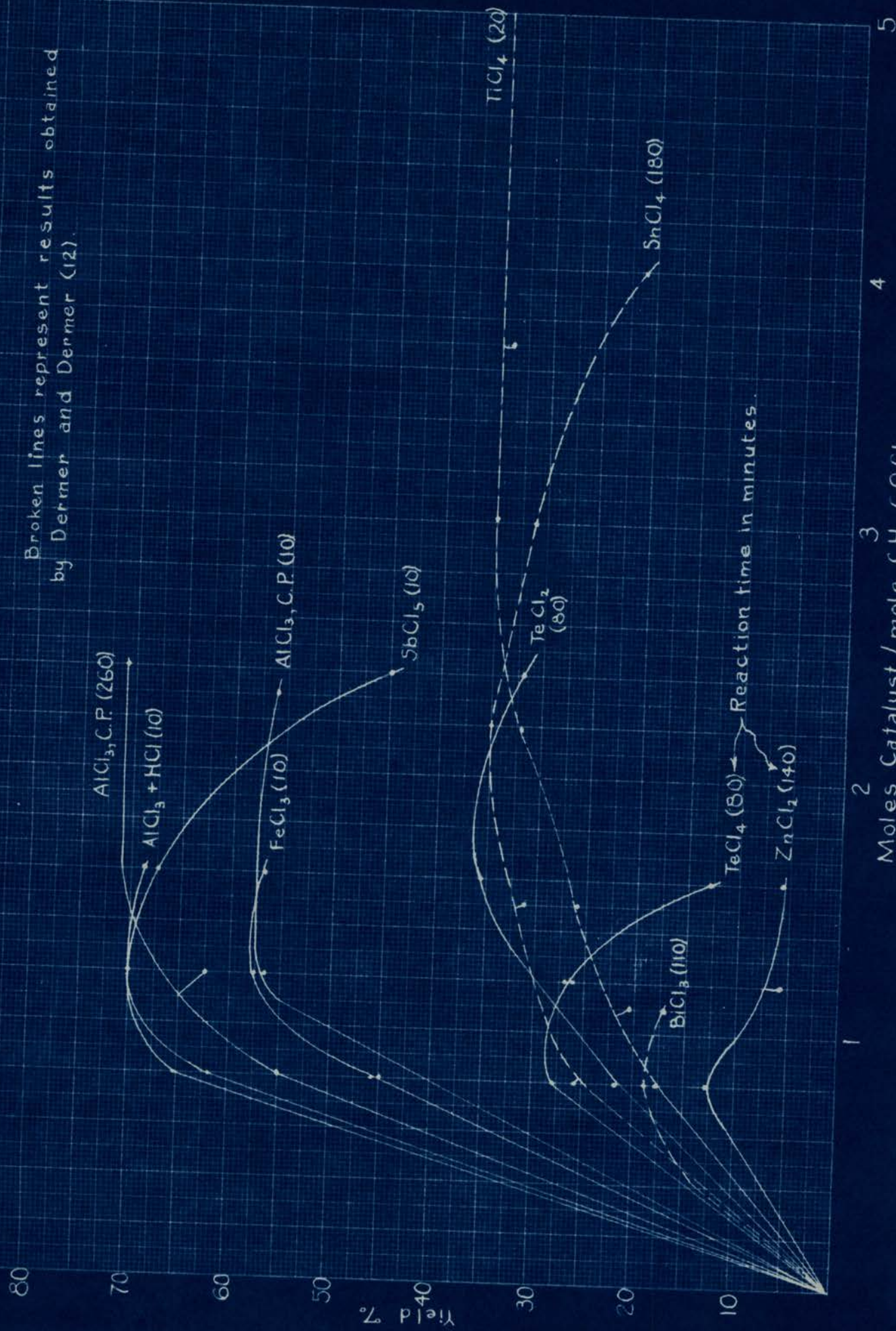
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\* Information supplied by Dermer and Dermer (12).





Broken lines represent results obtained by Dermer and Dermer (12).

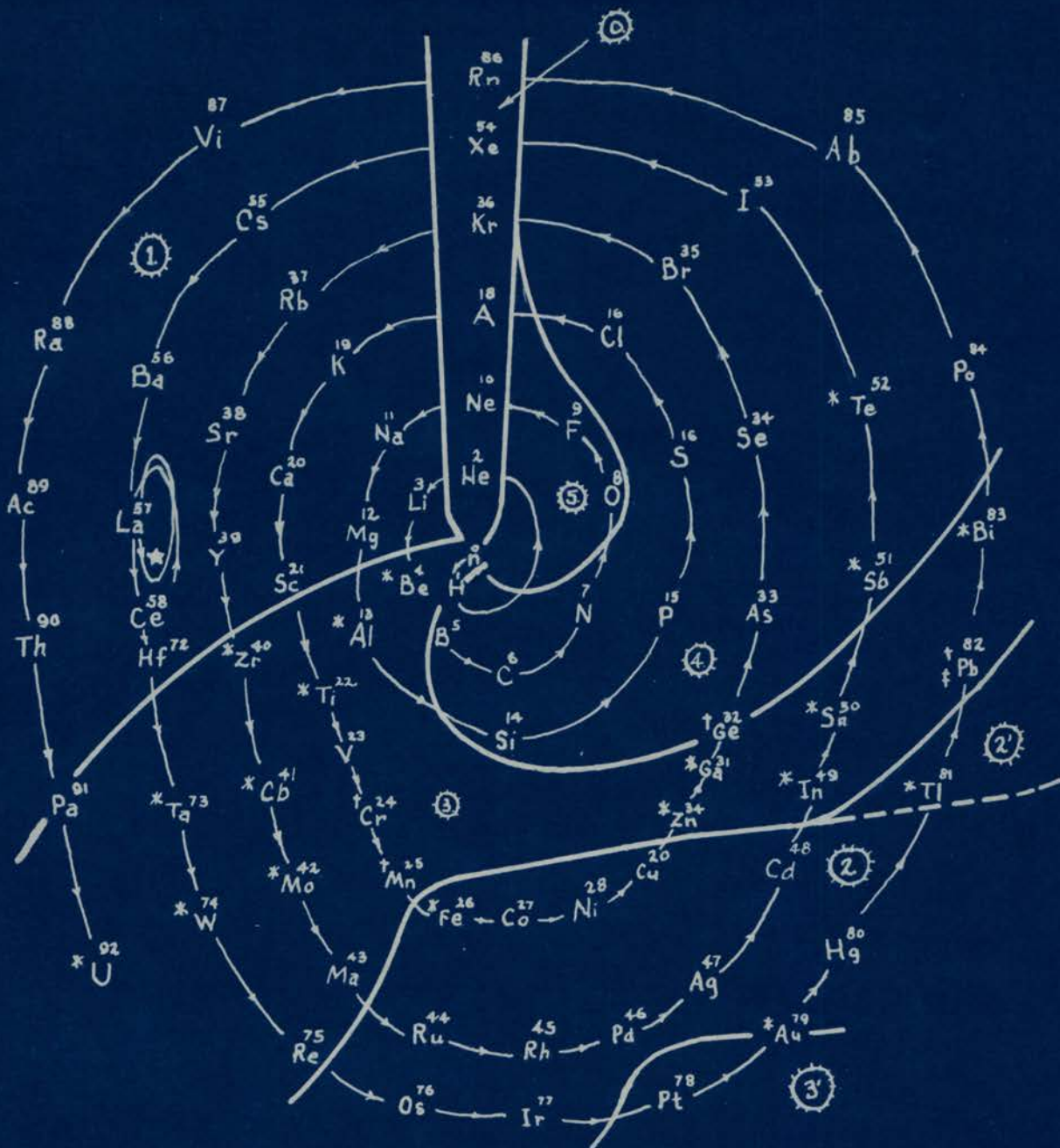


Moles Catalyst / mole C<sub>4</sub>H<sub>6</sub>

1 2 3 4 5

Yield %

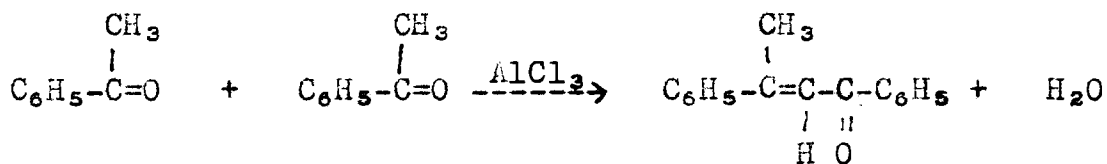
Reaction time in minutes



★ 13 Rare Earth Elements Omitted.

## RESULTS AND THEIR INTERPRETATION

The fallacy in refluxing Friedel-Crafts reaction mixtures as long as hydrogen chloride is evolved has been pointed out (8), but there seems to be no literature record of marked decrease in yield with increased reaction time. This effect is shown by reaction involving  $\text{AlCl}_3$  activated by  $\text{HCl}$ ,  $\text{SbCl}_5$ , and  $\text{FeCl}_3$ . Its cause is probably the self-condensation of the ketone demonstrated by Calloway (8). The equation for this condensation is as follows:



$\text{TeCl}_4$ ,  $\text{TeCl}_2$ , and  $\text{ZnCl}_2$  produce apparent decreases, which however are much smaller and may be within the range of experimental error of analysis.

The proportionality of yield to the ratio moles of catalyst/moles of acid chloride for values of the ratio up to and including one has been demonstrated too often to need confirmation, at least for  $\text{AlCl}_3$ . However, Riddell and Noller (26) say of  $\text{AlCl}_3$  and  $\text{FeCl}_3$ : "A point that does not seem to be previously recorded is that the yield rapidly falls off when more than these optimum amounts (1:1) are used." This is not substantiated by data reported by Groggins (20) nor by the data here given. Only the data obtained by the study of  $\text{AlCl}_3$  activated with  $\text{HCl}$ ,  $\text{SbCl}_5$  and  $\text{FeCl}_3$  could be considered as upholding the above contention, and even then marked decrease is

noted only when a considerable excess of each catalyst has been added. The yield of ketone using  $\text{SbCl}_5$  and  $\text{FeCl}_3$  as catalysts drops considerably when the ratio of moles catalyst/moles acetyl chloride becomes as high as 2.4. When aluminum chloride activated by  $\text{HCl}$  was used a slight drop was observed when the ratio of moles catalyst/moles acetyl chloride reached 1.6; a higher concentration of this catalyst was not tested. Excess  $\text{ZnCl}_2$  seems to also have a small deleterious effect. In the use of  $\text{TeCl}_2$  a ratio of 2 moles catalyst/1 mole  $\text{CH}_3\text{COCl}$  shows a marked increase in yield over that given by the usual ratio (1:1). Except when  $\text{TeCl}_4$  or  $\text{ZnCl}_2$  is used a slight excess of catalyst is advantageous. It is probably no coincidence that the catalysts which show marked decrease in yield with increase in heating time also show a decrease with increased amounts of catalyst. Catalysts which dissolve incompletely or with difficulty, such as  $\text{ZnCl}_2$  and  $\text{TeCl}_2$ , must be powdered for maximum efficiency. All catalysts must be protected from moisture.

Only when there is pronounced reaction between toluene and catalyst ( $\text{SbCl}_5$ ,  $\text{PbCl}_4$ ) does it matter whether the acetyl chloride or the catalyst is first added to the toluene. However, it is evident from Table III that the Perrier method of combining reagents is usually better than the common one.

The  $\text{AlCl}_3$  prepared by use of  $\text{HCl}$  was probably activated by absorbed hydrogen chloride or other impurity, and so the results obtained by its use are not representative of the behavior of pure  $\text{AlCl}_3$ . Yet it is altogether possible that

others among the solid catalysts used-- $\text{FeCl}_3$  and  $\text{MoCl}_5$  particularly--were similarly contaminated and probably activated by absorbed hydrogen chloride or chlorine; such impurities are notoriously difficult to remove except by repeated resublimation.

The  $\text{AlCl}_3$  obtained from the stock room was partially hydrated and hence relatively ineffective as a catalyst.

The yields obtained using  $\text{SbCl}_5$  as the catalyst were so very much higher than anticipated that several steps were taken to check the procedure used in this case and also to duplicate yields obtained. Blanks were run where one of the reactants had been omitted (acetyl chloride) and no evidence of yield was obtained by the analytical procedure used. Runs were repeated in several instances and each time the agreement of results was well within experimental error.

$\text{PbCl}_4$  in several trials gave evidence of a small but perceptible reactivity, but the apparent yield of ketone may be due to some side reaction in the analytical method, especially in view of Calloway's report that this chloride is inactive.

$\text{SnCl}_2$  has been reported as a non-catalyst (44), but it was retested in this instance to find out whether distillation of the catalyst might make it active.

$\text{GeCl}_4$  is here reported as a non-catalyst for the first time.

$\text{ThCl}_4$  has been previously reported as inactive as regards the hydrocarbon synthesis (45), but this is its first trial for the ketone synthesis.

The order of decreasing efficiency of catalysts as found in this work is  $\text{AlCl}_3$ ,  $\text{AlCl}_3$  activated with  $\text{HCl}$ ,  $\text{SbCl}_5$ ,  $\text{FeCl}_3$ ,  $(\text{SnCl}_4)$ ,  $(\text{UCl}_3)$ ,  $\text{TeCl}_2$ ,  $(\text{TiCl}_4)$ ,  $\text{TeCl}_4$ ,  $(\text{BiCl}_3)$ ,  $(\text{UCl}_4)$ ,  $\text{ZnCl}_2$ . The data for determining the location of those catalysts placed in parenthesis were obtained from Dermer and Dermer (12). The order given above differs from that given by Calloway (5) in that  $\text{SbCl}_5$ ,  $\text{UCl}_3$ ,  $\text{UCl}_4$ ,  $\text{TeCl}_2$ , and  $\text{TeCl}_4$  do not appear in his list and the position of the  $\text{ZnCl}_2$  has been changed. The superiority of  $\text{TeCl}_2$  over  $\text{TeCl}_4$  is surprising, for the lower chloride of a metal is generally too much more salt-like to be active (cf. chlorides of iron, tin, antimony and probably titanium).

The yields obtained in most instances of this study are considerably higher than those reported by Wilson (44). This is explained by the fact that it was the express purpose of this research to determine proper heating time and proper quantity of catalyst to obtain the maximum yield. The extreme variation between yields obtained using  $\text{SbCl}_5$  is explained by the use in this instance of the Perrier method of reagent addition.

The explanation for the variation in yield produced by the Perrier method of addition of reagents is indeed difficult. Perrier showed the formation of complexes (34) and isolated a number of them. Kohler found (25) from boiling point and freezing point determinations that the Perrier compounds invariably are composed of two molecules of the carbonyl compound and one (double) molecule of aluminum halide:  $\text{Al}_2\text{Cl}_6 \cdot 2\text{RCOCl}$  and  $\text{Al}_2\text{X}_6 \cdot 2\text{R}_2\text{CO}$ . Pfeiffer and Haack (35) confirmed the work of Kohler.

Olivier (32) claims these complexes hinder the reaction particularly the double compound of the ketone formed in the condensation. The explanation given is that the ketone binds the catalyst so firmly as to render it unavailable for catalysis, so that more catalyst is required. Fieser (13) agrees with the contention of Olivier. Nevertheless, the results using the Perrier method as reported here seem to contradict the above claims. Much better yields were obtained using the Perrier method under conditions identical with those used when the ordinary order of addition prevailed, so that the preliminary formation of the acetyl chloride-catalyst complex must be a marked aid to reaction.

It is difficult to correlate activity of catalysts with position of the metal in the ordinary form of the periodic table; the oxide periodicity pattern on the spiral table of Irwin (32), which has been reproduced in Figure 3, groups more Friedel-Crafts catalysts together than any other arrangement that has been found.

Only a few of the catalysts studied (chlorides of antimony, tellurium, gold, and iron) fall in groups other than 3 on the oxide periodicity chart. All of the elements on the chart that have been reported as yielding catalysts are indicated by use of an asterisk; those in Group 3 that are known to be ineffective have been indicated by use of a cross. Those where any doubt exists due to factors not wholly explained have been indicated by a two-bar cross.

Those elements which fall outside Group 3 and still have



catalytic properties, resemble in many respects the elements in that group, particularly in their amphoteric nature.

The chlorides of the elements within Group 3 which have been reported ineffective are salts of the metal in a lower valence state with the exception of chlorides of germanium, chromium and lead. The germanium is a border line case and resembles those elements whose oxides fall in Group 4. From the position of lead it would be expected that the tetrachloride should function effectively as a catalyst in this reaction. Although lead tetrachloride has been reported as non-effective there is some doubt as to that conclusion. A possible explanation of the apparent lack of effectiveness is that lead tetrachloride is a strong chlorinating agent, prepared by the use of concentrated sulfuric acid from which it can never be completely separated. When the lead tetrachloride along with this impurity is added to either toluene or acetyl chloride a violent reaction occurs and a white precipitate is formed, presumably lead dichloride or lead sulfate. Thus the tetrachloride is decomposed before it can serve as a catalyst; no doubt manganese tetrachloride would do the same thing.

It may be predicted that those elements in Group 3 whose higher chlorides have not yet been tested will prove to be catalysts.

A continuation of this problem might well entail a study of the reaction time factor where no heat is applied, since it is known that low temperatures minimize the condensation reactions, which lower the yield of ketone. In this work both re-

action times and amounts of catalyst were varied only until a new increment produced a decrease in yield and so indicated a maximum. It would be desirable to extend measurements beyond this point to determine the further shape of the curves. The Perrier method of combining reagents opens a field that has just been touched upon.

The number of catalysts that have possibilities for this particular reaction has not been exhausted. A number of compounds other than the halides might be tried.

## SUMMARY

Although  $\text{FeCl}_3$ ,  $\text{ZnCl}_2$ , and especially  $\text{AlCl}_3$  have been long known and much studied as catalysts for the Friedel-Crafts ketone synthesis, a number of other metallic chlorides have been mentioned in the literature. This problem consists of a study of metallic chloride catalysts to determine optimum heating time for maximum yield, and to determine the best ratio of catalyst to acetyl chloride that can be used during the optimum heating time to obtain the greatest possible yield. Toluene, acetyl chloride, and one of the catalysts, which were either commercial products or laboratory preparations, comprised the materials for each run. The whole procedure was a combination of several found in the literature, modified as a result of previous studies made at Oklahoma A. and M. College.

The Perrier method of reagent addition was found to give better yields in most instances. The order of decreasing effectiveness as determined by this study is:  $\text{AlCl}_3$ ,  $\text{AlCl}_3$  activated with  $\text{HCl}$ ,  $\text{SbCl}_5$ ,  $\text{FeCl}_3$ ,  $\text{TeCl}_2$ ,  $\text{TeCl}_4$ ,  $\text{ZnCl}_2$ .  $\text{PbCl}_4$  previously reported as a non-catalyst may possibly have some catalytic effect.  $\text{ThCl}_4$  and  $\text{GeCl}_4$  are here first reported as non-catalysts for the ketone synthesis.

The results indicate that best reaction conditions and most effective concentrations are not the same for all catalysts, and that even maximum yields vary widely according to the nature of the catalyst.

Extension of this problem to greater heating times, a greater variety of catalysts, and the use of the Perrier method would be desirable.

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## BIOGRAPHY

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He taught school at Dewar, Oklahoma during the school year of 1936-37 and enrolled in the graduate school of Oklahoma A. and M. College in the summer. The school years included between 1937-40 were spent in teaching at Cameron State Agricultural College, while the summers were devoted to study in the graduate school in which he enrolled in 1937.

Typed by:

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