

UC
Thesis

THE ALKYLATION OF PHENOL

by

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A thesis presented to the Department of Chemistry of Union
College in partial fulfillment of the requirements for the
degree of Bachelor of Science with a Major in Chemistry.

By William R. Stine

Approved by Howard E. Sheffer

5/22/60

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Acknowledgment:

To Dr. Sheffer whose helpful advice aided
in making this research a success.

Gift of the author, October 20, 1960

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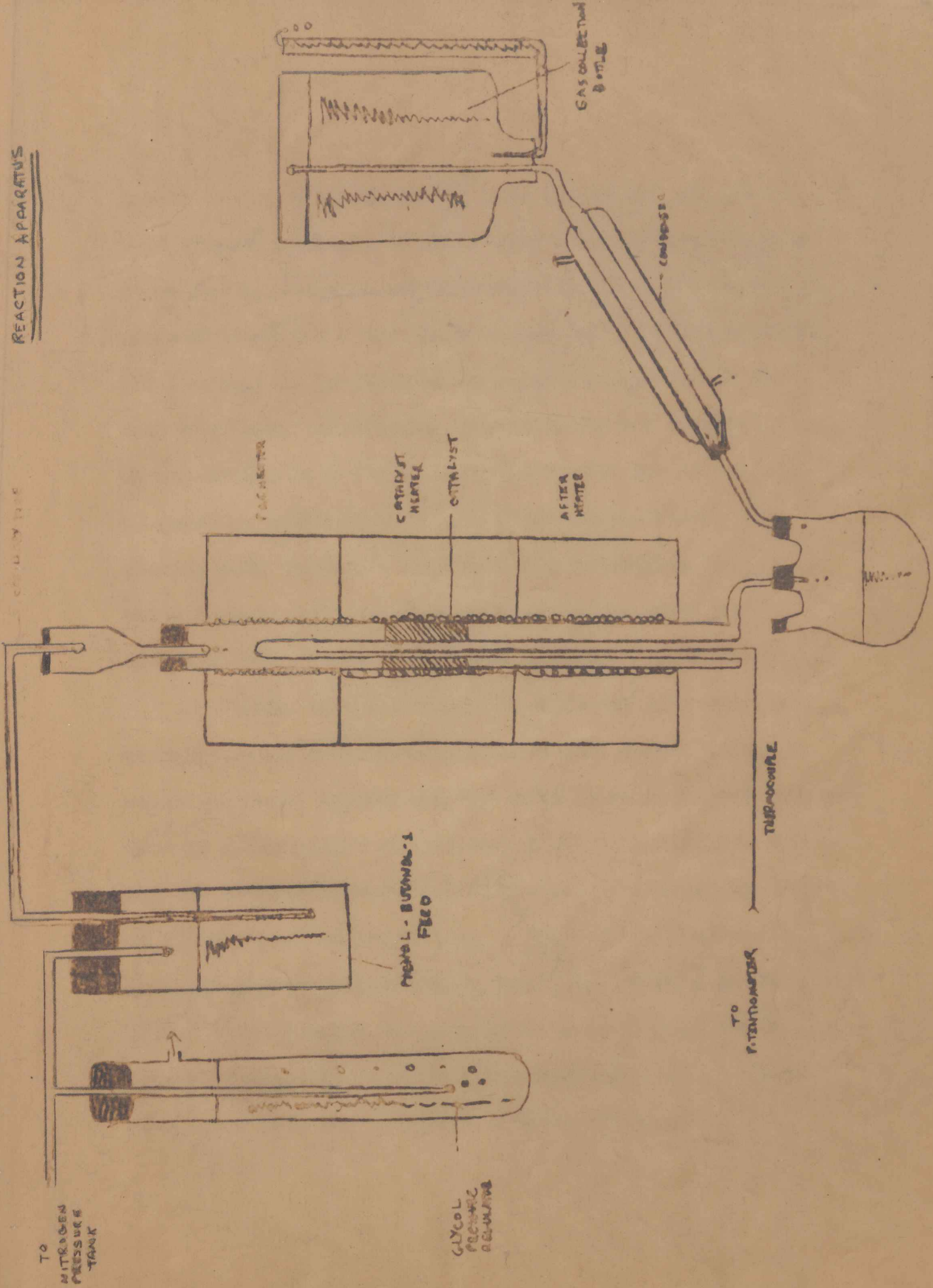
The Alkylation of Phenol

The reaction to be studied is the reaction between n-butyl alcohol and phenol using an activated alumina catalyst at a temperature around 350°C . I will refer to this reaction throughout as the alkylation. The actual alkylation was carried out about two years ago by Dr. Sheffer so that I can only describe here how it was carried out from the papers presented by students from other years. My task then was to take the products which were obtained and try to find out their structure.

First of all, I will indicate briefly how the alkylation was carried out. The more exact details such as temperature, time of contact with catalyst etc. are indicated in the chart on page 15. An approximately 1:1 molar solution of phenol and alcohol was prepared and placed in the apparatus as shown on page 2.

In the apparatus, with the feed (phenol-butanol) placed as shown, nitrogen gas is bubbled into the feed at a carefully controlled rate so that the feed is

REACTION APPARATUS

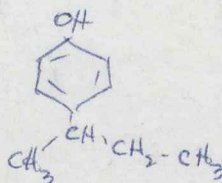
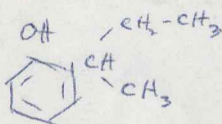
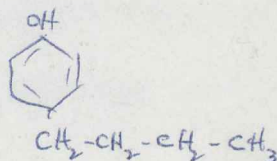
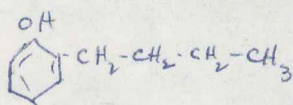


forced by the pressure of the nitrogen up and out of the feed chamber into the reaction chamber at a rate of 30-60 drops per minute. The reaction mixture is heated to the desired temperature and comes in contact with the catalyst. The temperature is measured by a thermocouple which is best seen from the diagram. The products are then collected at the bottom in a flask which has a neck for the escape of gases or volatile materials which are collected by passing them through a condenser and condensing the volatile materials and then collecting the gases in a container into which the condenser directs their flow.

Following the alkylation the products were distilled through a four foot fractionating column packed with stainless steel helices and the butyl phenols refractionated through a Concentric Tube Column with 75 theoretical plates. For the purpose intended in this study fractions were taken at temperatures corresponding to the boiling points of ortho secondary, ortho normal, para secondary, and para normal butyl phenols for comparison with each of these four pure isomers. In particular, attention was centered on whether this was a typical Friedel-Crafts reaction

which would result in the rearrangement of the n-butyl group to form a secondary butyl phenol. It is also possible that the normal butyl phenols might be formed. A typical example of the Friedel-Craft type of reaction is the reaction between benzene and n-propyl bromide using an aluminum chloride catalyst in which you get a rearrangement of the alkyl halide and form cumene (isopropyl benzene) in the reaction. According to Fieser (2) this is a result of the formation of a primary carbonium ion and rearrangement of the primary to the secondary carbonium ion.

In this light, attention was focused on the formation of the various isomers of butyl phenol shown below.



4

Past studies (3), (9) have been done on the reaction between methanol and phenol and it was found that mainly the ortho and para isomers with only a small percentage of meta are formed so that it is likely that this will also hold true in this case so that no particular attention is given to the possibility of meta substitution in the experimental work.

It should be pointed out that the actual mechanism in these cases is still somewhat in doubt but in the alkylation of phenol depending on the temperature, some alkyl phenyl ethers are obtained such as

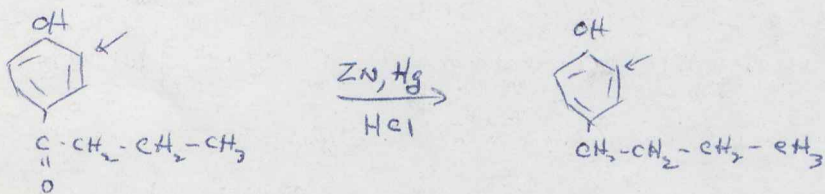
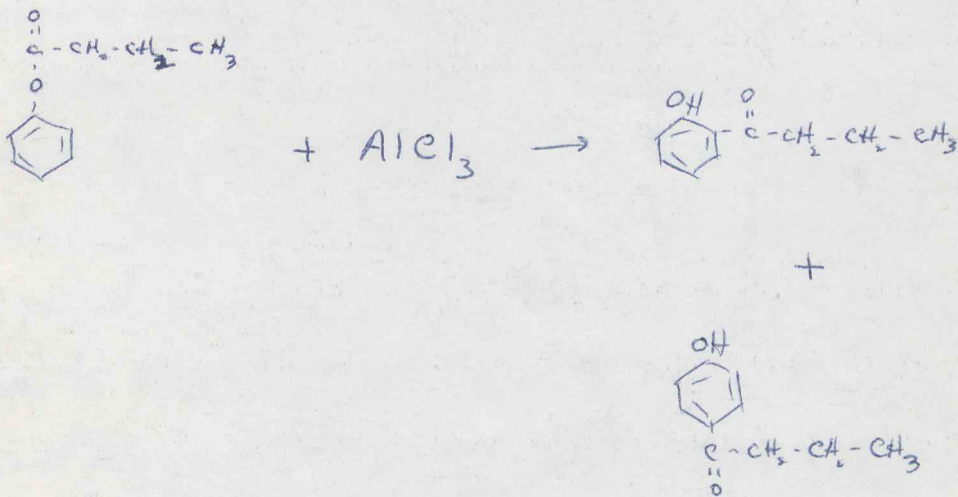
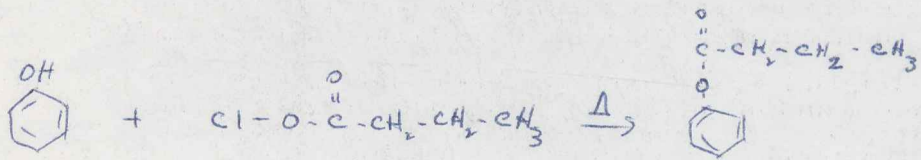


Less of this is obtained at high temperatures. However, since some ether is formed it has been suggested that it may be an intermediate and by some kind of rearrangement the butyl phenols may form from it.

The big problem of identification of the products stemmed from the fact that there is little or no data in the literature concerning derivatives of these compounds. Therefore, our best way of making a good comparison was

to prepare the normal isomers by another reaction and also to purify the secondary isomers which are available commercially.

For preparing the normal butyl phenols the following set of steps were carried out by Paskovich.



In the synthesis used phenol and butyryl chloride are reacted to form the phenyl butyrate ester which is rearranged to the ortho and para ketones. This mixture is in turn separated, purified and finally reduced to give ortho and para n-butyl phenols.

The first two steps are carried out in a 5 liter three neck flask fitted with thermometer, heavy duty stirrer, condenser and electric heating mantel. To the flask 188 grams of phenol (2 moles) are added and then melted by heating the flask to 50°C. The thermometer is replaced by a dropping funnel and 213 grams of butyryl chloride (2 moles) are added dropwise at such a rate as to complete the addition in an hour. The reaction is exothermic and no further heating is required. In this, as well as the next reaction, there is a large evolution of hydrogen chloride, hence the apparatus is placed in a hood. The mix is then further refluxed for one half an hour after addition of butyryl chloride by gentle heating.

After cooling 320 ccs. of carbon disulfide and 266 grams (2.2 moles) of aluminum chloride (anhydrous) are added in order, and the dropping funnel again replaced by a thermometer. The material is refluxed until hydrogen chloride evolution has ceased and at this point the carbon disulfide is distilled off. The flask contents are now heated to 150°C.

and stirred vigorously to prevent foaming. In this stage the aluminum chloride complex changes from a light orange to a dark cherry red and becomes extremely viscous. The reaction should be continued until either hydrogen chloride evolution ceases or the liquid becomes so viscous that it cannot be stirred.

The thermometer is again replaced by the dropping funnel and 500 ccs. of 50% hydrochloric acid is added cautiously after cooling the mix below 100°C . This reaction is highly exothermic. An additional 800 ccs. of water is added and the flask contents then refluxed until all resinous material has reacted to form a black oil. This oil is separated and fractionally distilled under 4 mm. pressure, the ortho boiling at $98-100^{\circ}\text{C}$. and the para at $168-172^{\circ}\text{C}$. The para butyryl phenol is a solid melting at about 92°C . and an adequately heated receiving system must be present on the column used.

The two isomers are purified by recrystallizing the para butyryl phenol from benzene (M.P. 92°C .) and by redistilling the ortho isomer. Due to the poor carbon-hydrogen analysis of Paskovich's samples the following Clemmenson reduction was repeated. The butyl phenols are reduced by a Clemmenson reduction similar to that described

in (6). The following quantities of material are used for about 45 grams of butyryl phenol. The use of a zinc amalgam is necessary and is prepared as follows. One hundred grams of mossy zinc are placed in a one liter round bottom flask. Five to ten grams of $HgCl_2$, 5 cc. of HCl and 125 cc. of H_2O are stirred for five minutes and the liquid is decanted away. The zinc is then covered with about 75 ml. of H_2O and 100 cc. of HCl . The butyryl phenol is added immediately and the mixture refluxed for 10 hours with the addition of 50 cc. of concentrated HCl every three hours. When reducing the ortho ketone 100 cc. of acetic acid was added just before the phenol as suggested in (10). After the reaction is complete about 120 cc. of toluene is added and the phenol which goes into the toluene layer is separated. The toluene layer is washed a few times with water and filtered. The next step is to distill off most of the toluene and then finally fractionally distill to get the pure ortho or para normal butyl phenol.

By a careful distillation the secondary isomers which as mentioned, are available commercially, were purified and the following results were obtained on duplicate carbon-hydrogen analysis. (14)

			Average	
	Carbon	Hydrogen	Carbon	Hydrogen
OSBP	80.12	9.38	80.02	9.29
	79.94	9.20		
ONBP	79.93	9.51	79.91	9.51
	79.88	9.52		
PSBP	79.60	9.54	79.96	9.49
	79.91	9.44		
PNBP	79.65	9.37	79.82	9.29
	79.98	9.21		

Actual Values: Carbon: 79.96%
Hydrogen: 9.39%

In our analysis, one possible derivative, the p-nitro phenyl urethane, was found which gave reproducible results but it wasn't felt that we would get a clear enough indication of the quantity of various isomers in each fraction by this method.

The boiling points of the four isomers are given below:

OS butyl phenol	227-228°
ON " "	234-237°
PS " "	240°
PN " "	247-248°

It is easily seen from this table that the boiling points of the four isomers assuming they are all present differ by not more than ten degrees so that some degree of impurity of one fraction in another is unavoidable. In addition, the column used had apparently reached its

capacity when the temperature got to around 240°C. so that it was rather difficult to get a very clear separation of the last two isomers.

The eight samples were now put in solution with chloroform at a concentration of 20% by volume. These eight include the four pure isomers and the four fractions from the alkylation which correspond to the boiling points of the pure isomers. The curves were run in the region from two to fifteen microns. In drawing conclusions we have concentrated mainly on the region from about 8 or 9 microns to 15 microns since in this region are the absorptions due to molecular rotation of the molecules. On the whole we found three wavelengths from which we have made some conclusions and speculations. It must be kept in mind that each of these fractions may well contain a little of each isomer but if a certain isomer does result from the alkylation it would undoubtedly be the major component of the corresponding fraction.

The first point considered was at a wavelength of 12.18 microns. Pure OSBP shows a very clear peak and an absorption of about 80%. On the fraction curves this peak appears as a very clear shoulder from an absorption which occurred at about 12.00 microns on F-1 and F-2. The notations

refer to fractions number 1 and 2 which correspond in turn to the two lowest boiling isomers of butyl phenol. On F-3 and F-4 no such peak or shoulder occurs. This is perfectly consistent with the presence of OSBP since it is the first fraction which boils over in the fractionation and would therefore be the first isomer to disappear entirely as the infrared indicates.

Our best point for analysis comes at a wavelength of 10.05 microns. At this point the following data was obtained.

	%absorption	base line absorbance	
		5% solution	20% solution
OS	35	.005	.097
ON	-	-	-
PS	35	.029	.095
PN	-	-	-

	base line absorbance	% secondary isomer (calc)
F-1	.067	76%
F-2	.072	83%
F-3	.088	93%
F-4	.084	88%

The percentages for the fractions are obtained by plotting the base-line absorbance of the pure isomers in 5% and 20% solutions and then finding the absorbance which the 20% fraction solutions gave and calling 20% solution strength equal to 100% pure isomer.

The results given for F-2 and F-4 were gotten by using pure OS and PS respectively as the standards.

The values obtained tend to indicate that fraction 3 was purer than fraction 1 due to the fact that only two isomers are left at the point when F-3 is collected in the distillation.

The last point is at 14.50 microns. In this case the pure PSBP gives a sharp peak at 14.50 microns with about 50% absorption. The only other isomer which shows any absorption in this region is the ONBP which absorbs a little above and below this point. The curves for the fractions all give a wide band in the region from about 14.25 to 14.45 microns with the band expanded somewhat through the 14.50 wavelength as shown in spectrums 1-4. Therefore, no clear quantitative determination of the percentage of the PSBP isomer can be made. However, there is a definite indication that para secondary is a product of the alkylation. Careful examination of the F-2 and F-3 curves finds the appearance of a shoulder from the absorption in the region above. This shoulder is quite small for F-2 but on F-3 which corresponds to PSBP it is more pronounced. It could also be speculated that some meta isomer may also be present since the region of the infrared from about 14.20 to 14.40 is very characteristic of meta substituted compounds. The meta isomers do also boil in this same region from about 225-250 so that they would be collected

along with the four being tested if they were present. The possibility of meta orientation could come from the reaction since it is known that no groups are perfect ortho-para orienting groups but that some meta substitution will always occur.

Another piece of evidence which indicates the secondary isomer is the major product is the distillation curve obtained from the fractional distillation of the alkylation products. The curve is reproduced on page 21. From the curve it is easily seen that definite plateaus appear at the boiling point corresponding to the para secondary isomer and in the region where the ortho secondary isomer boils.

The conclusions arrived at from the research are that the primary products of the alkylation are the secondary butyl phenols. In addition there is substantial proof of the presence of both the ortho and para isomers. There must, however, be some of the normal isomer present since the percentage of secondary isomers differs considerable from 100%.

In addition the possibility of meta substitution is pointed out.

Finally, a rough determination of the relative amounts of ortho and para isomers was made by taking 237.5 as the break point between ortho and para isomers. Doing this the distillation curve indicates that the ortho and para isomers were obtained in about equal amounts.

A final comment should also be made about a result which is seen in the chart on the following page. It is evident that the percentage yield of the butyl phenols is extremely low. This is attributed to the fact that the catalyst may have lost its effectiveness since it was only changed once during the 22 hour reaction run.

Alkylation Data:

Run Number PB-21

Time: 22 hours

Temperature: 349°C.

Contact Time: about 1 second

Catalyst: Type: $AlPO_4-Al_2O_3$

Number: P-43

Feed Rate: 77.8 cc./hr.

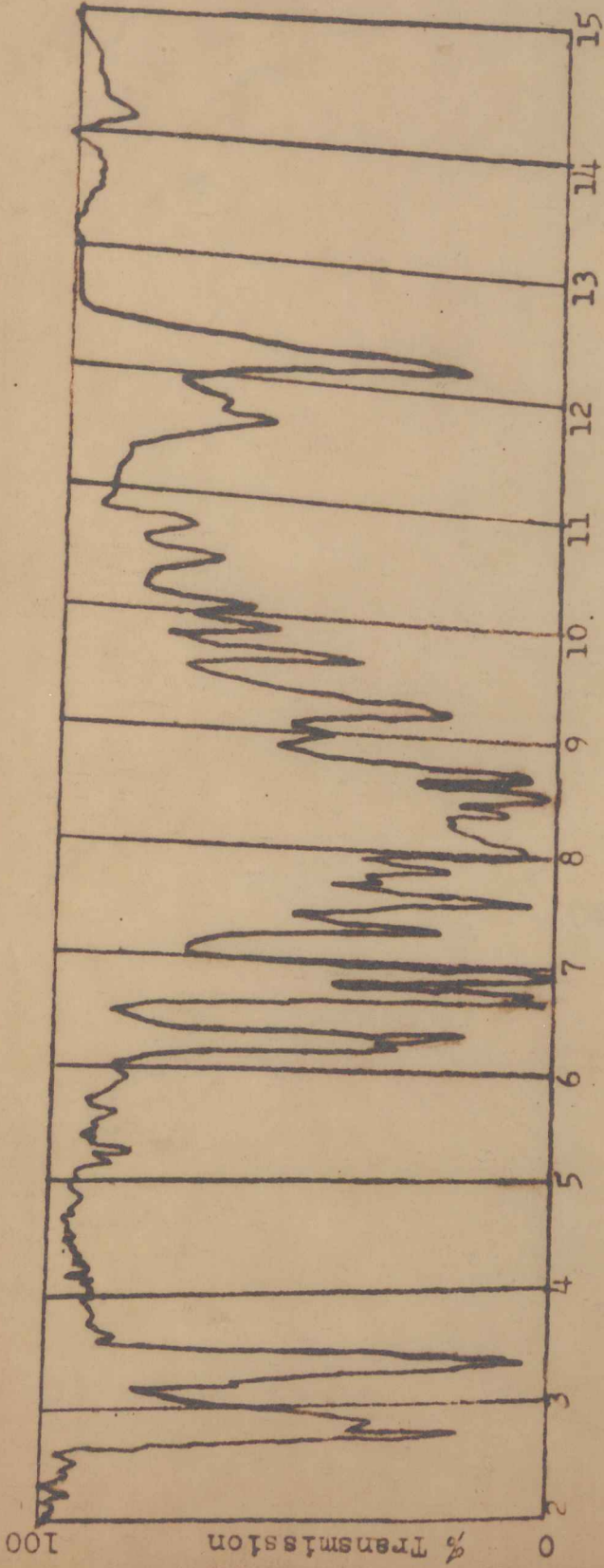
Products:

phenolic ethers: 64 wt. %

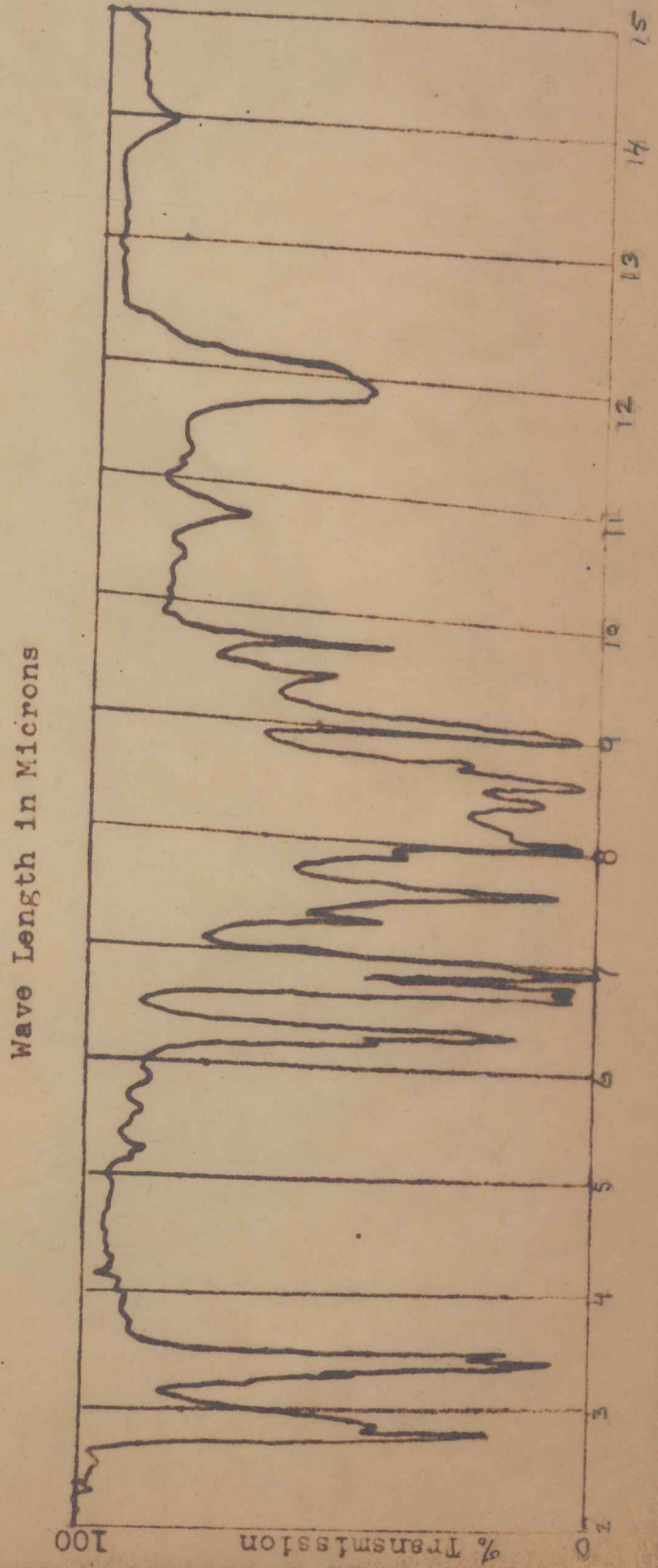
recovered phenol: 4.6 wt. %

butyl phenols: 3.1 wt. %
(assumed)

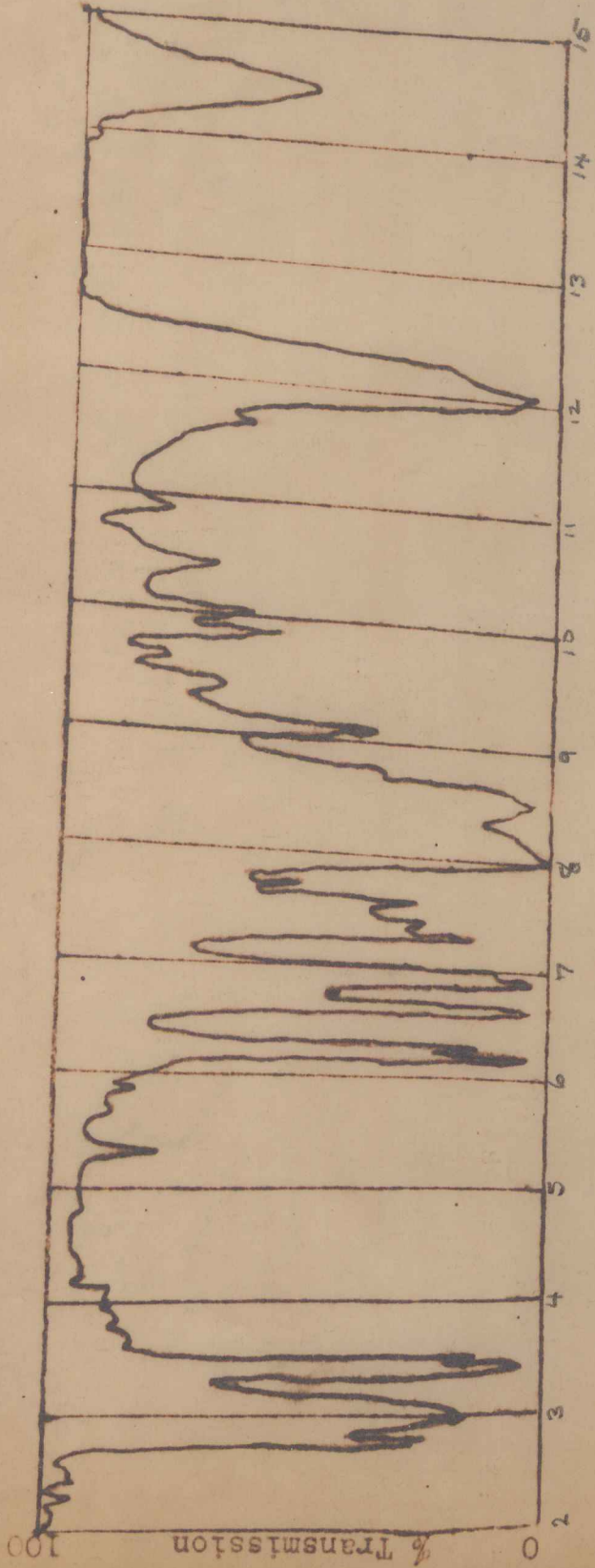
Spectrum #1
Pure OSRP
20% in CHCl₃
NaCl cells
Origin: Dow
Chemical Co.



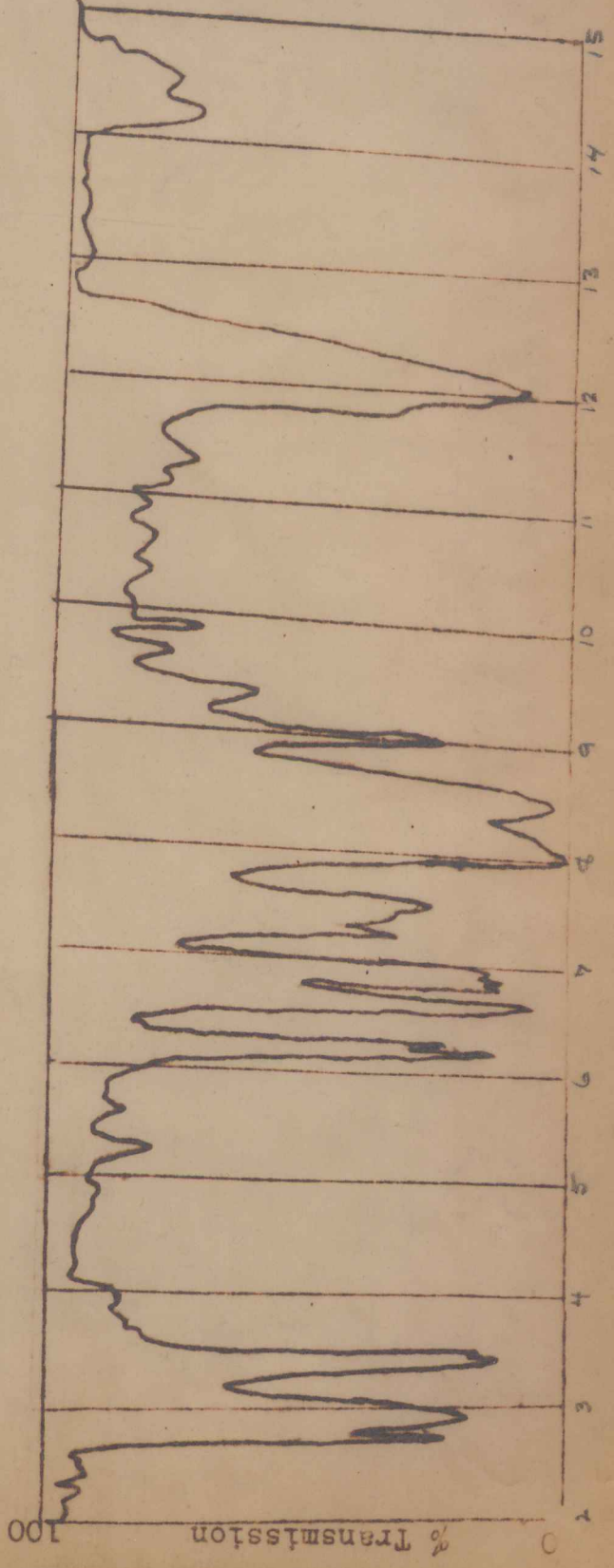
Spectrum #2
Pure ONBP
20% in CHCl₃
NaCl cells
Origin: Research
Prep.



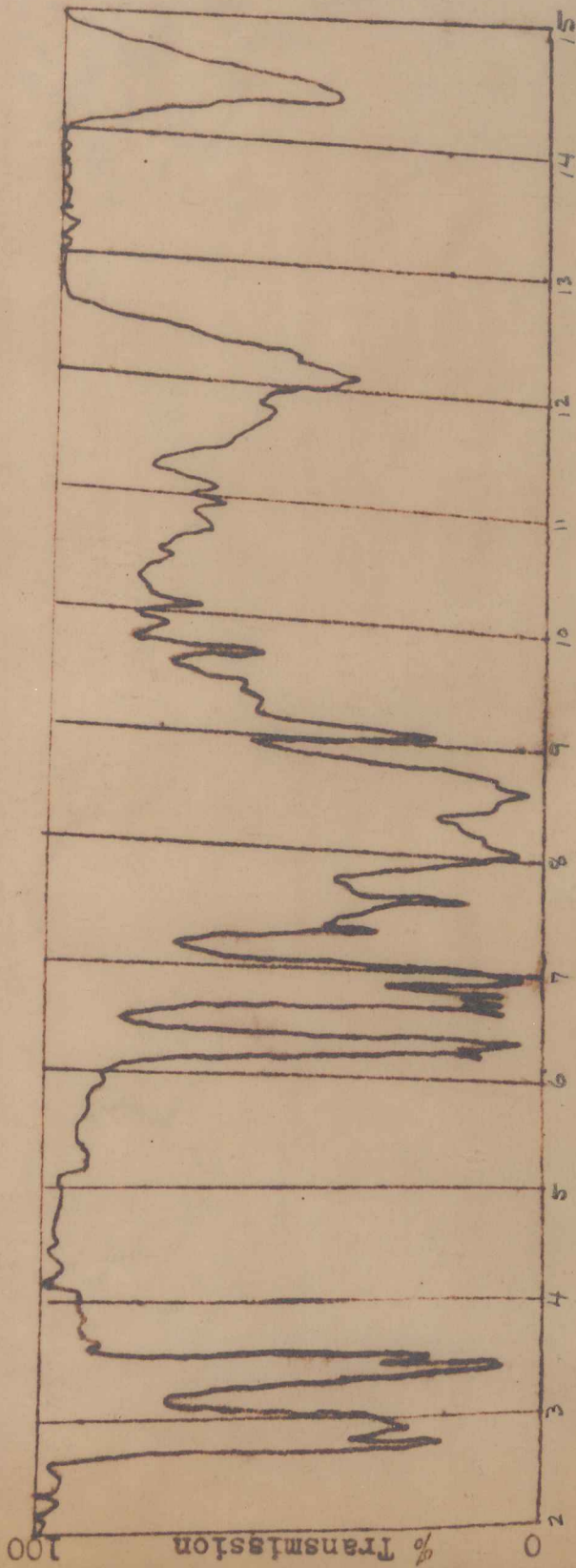
Spectrum #3
Pure PSRP
20% in CHCl₃
NaCl cells
Origin: Dow
Chemical Co.



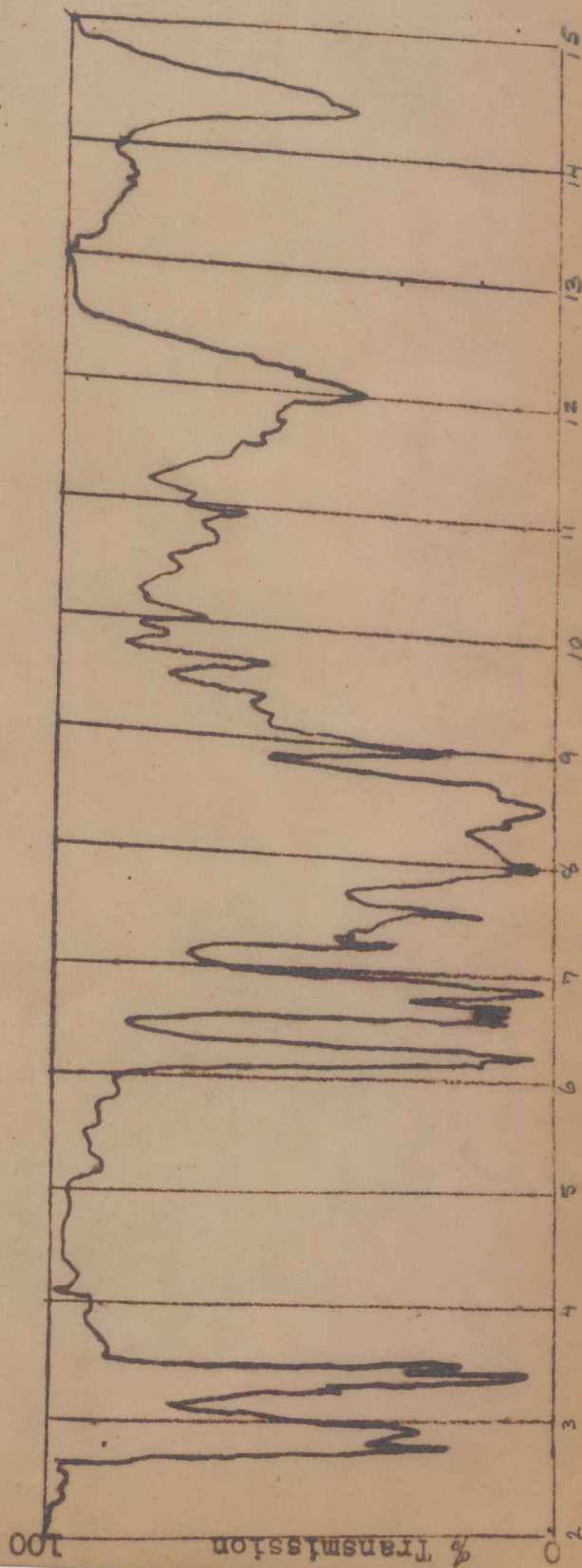
Spectrum #4
Pure PNBPF
20% in CHCl₃
NaCl cells
Origin: Research
Prep.



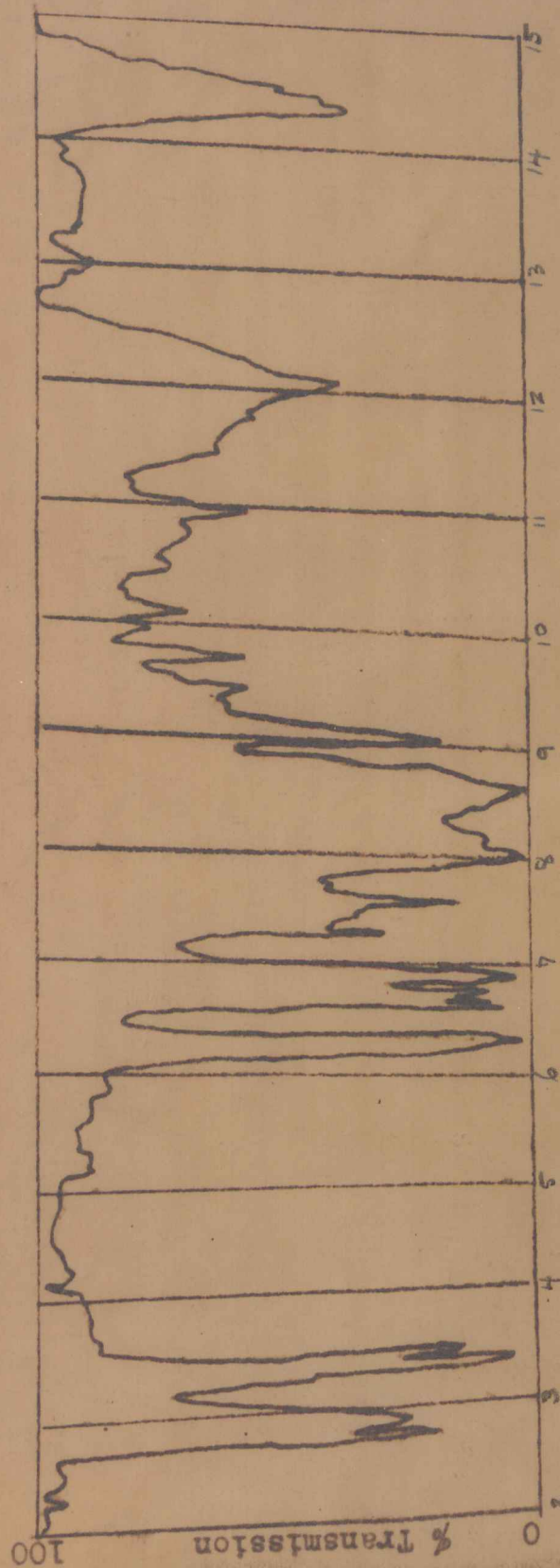
Spectrum #5
Fraction #1
20% in CHCl₃
NaCl cells
Boiling Point:
231°C.
Origin: Alkylation



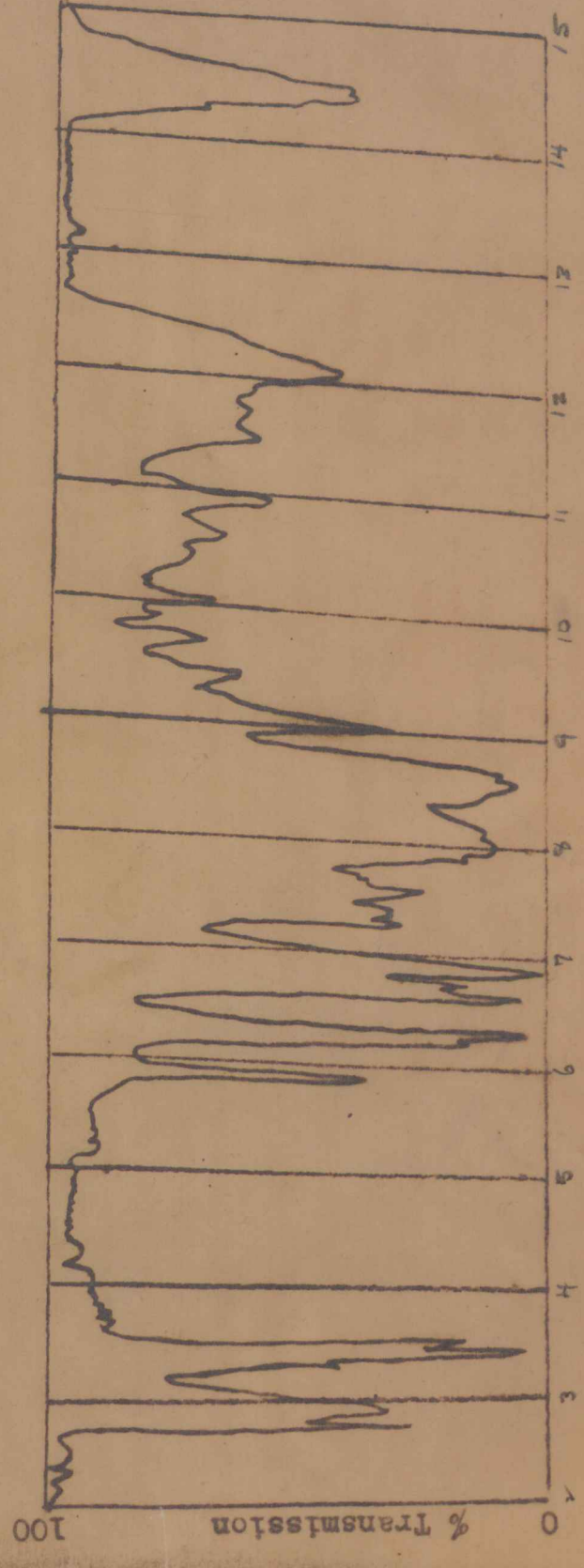
Spectrum #6
Fraction #2
20% in CHCl₃
NaCl cells
Boiling Point:
236°C.
Origin: Alkylation



Spectrum #7
 Fraction #3
 20% in CHCl₃
 NaCl cells
 Boiling Point:
 240°C.
 Origin: Alkylation



Spectrum #8
 Fraction #4
 20% in CHCl₃
 NaCl cells
 Boiling Range:
 249-255°C.
 Origin: Alkylation

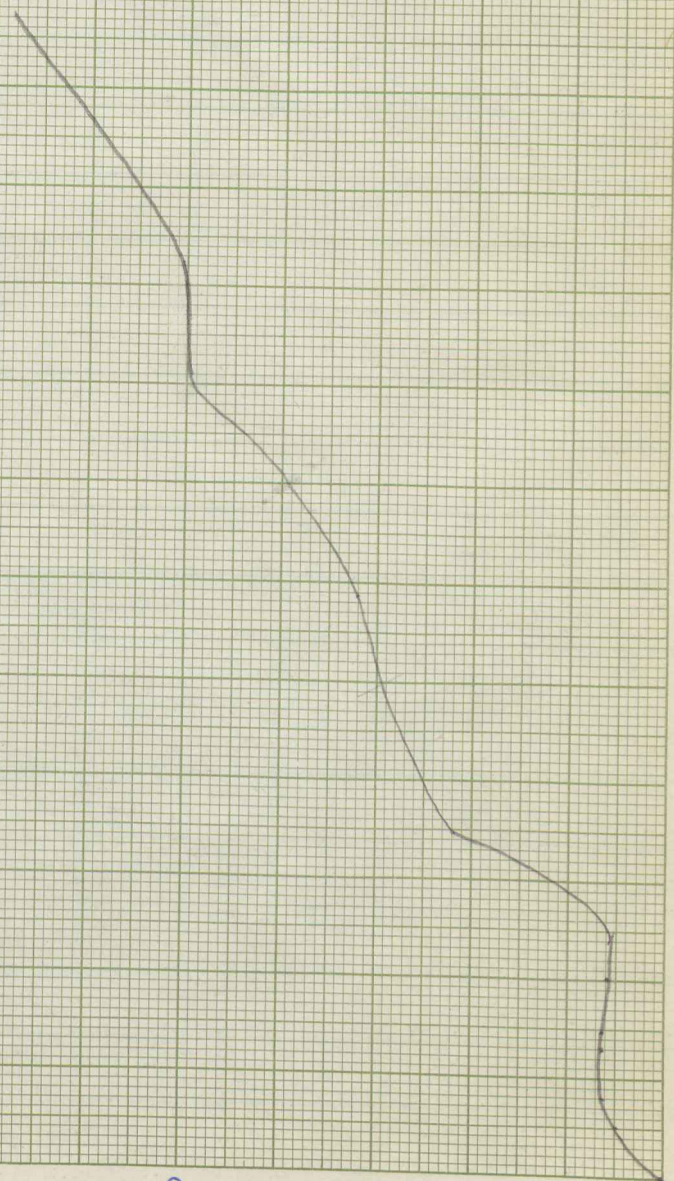


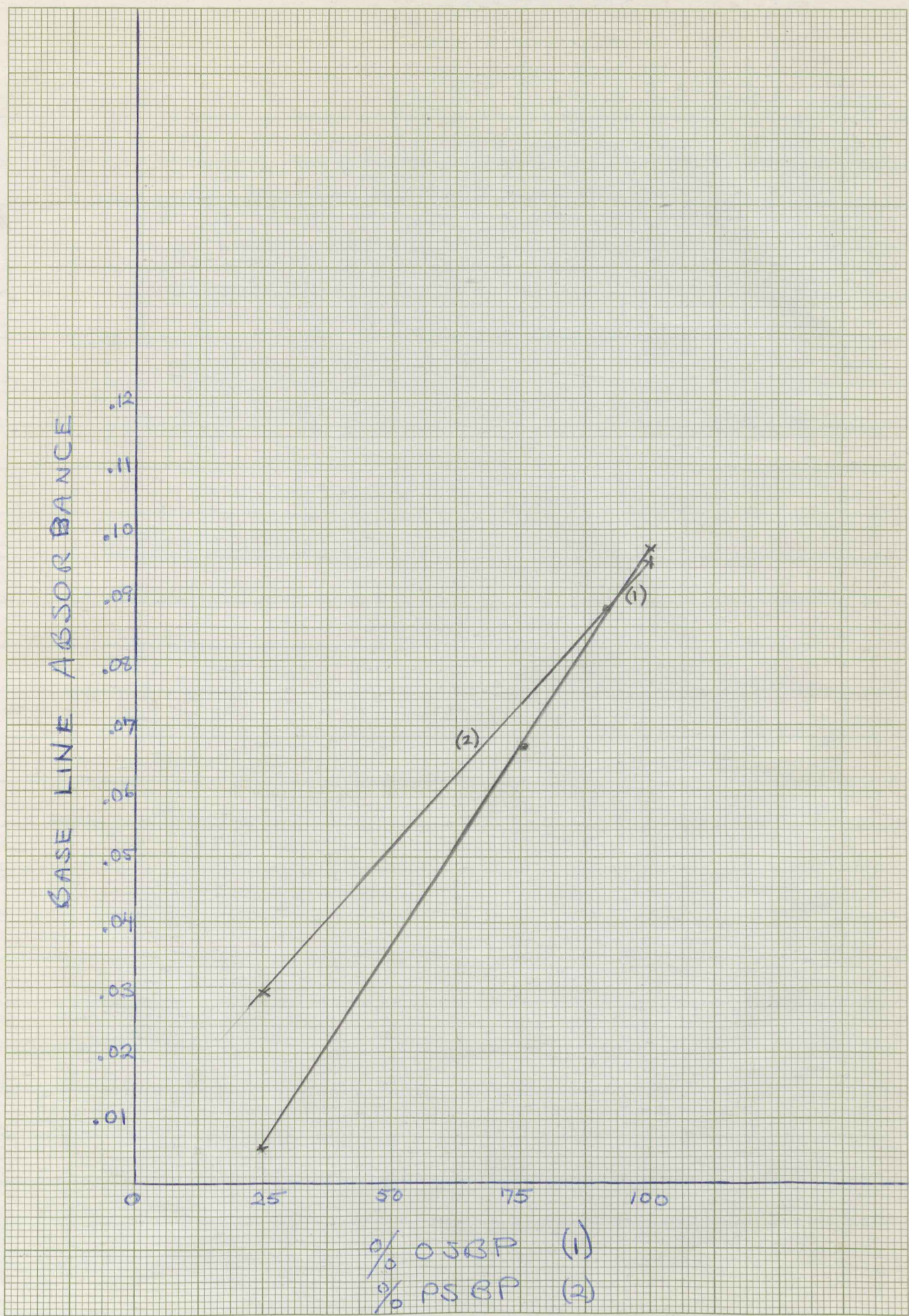
Distillation of Alkylation
Products in the Range
230-250°C.

5780-20
20 SQUARES TO THE INCH

250 Boiling Point (°C.) 240 230 0

30
20
10
0
Volume Collected (cc.)





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