

THE DEHYDRATION OF ALCOHOLS IN THE PRESENCE OF  
CHLOROFORM AND ALKALI

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Master of Science in Chemistry

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THE DEHYDRATION OF ALCOHOLS IN THE PRESENCE OF  
CHLOROFORM AND ALKALI

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## INTRODUCTION

It has been reported by previous workers that in the reaction between ethyl alcohol, chloroform and potassium hydroxide in the presence of various amounts of water, not only ethyl orthoformate and potassium formate are formed, but also ethylene, carbon monoxide and diethyl ether.

It was thought that this procedure might possibly lead to a new method for the dehydration of alcohols, especially useful in cases where other methods cause rearrangements.

An attempt was made to obtain the optimum conditions for the formation of ethylene from ethyl alcohol and also investigate the behavior of other alcohols under these conditions.

## SUMMARY

The formation of olefin and carbon monoxide from alcohol and chloroform by the action of alkali has been studied.

Runs with ethyl alcohol have been conducted in which the amounts of the reagents used and the composition of the solvent were varied.

When dropping an 11% potassium hydroxide solution into an excess of chloroform, using ethyl alcohol of various strength as solvent, a maximum yield of ethylene was obtained when 78% ethyl alcohol was used. The amount of carbon monoxide formed rose as the solution became more aqueous. Lower rates of addition of the alkali caused a decrease of the yield of ethylene. It was found that the reaction proceeds very slowly at low pH ranges.

When pyridine, methyl alcohol or diethyl ether were used instead of water as solvents lower yields of ethylene were obtained.

Neither ultraviolet light nor pressure showed any large influence on the reaction.

Using 74%, 57% and 40% aqueous potassium hydroxide solution in excess, and constant amounts of alkali, alcohol and chloroform, the yield with 57% potassium hydroxide solution was found to be the highest. The use of higher amounts of alcohol caused a decrease in the percent yield of the olefin. Under optimum conditions 7% of the ethyl alcohol was converted into olefin.

These conditions were then applied to the propanols, butanols, cyclohexanol and isoborneol.



In general it was found that primary alcohols give yields of olefins of the same order as ethyl alcohol. Secondary and tertiary alcohols give yields of the order of 30%. Cyclohexene is formed from cyclohexanol in a yield of 14%. In case of the isoborneol infrared measurements indicated that camphene rather than bornylene is formed.

A possible mechanism for this reaction has been discussed.

THE DEHYDRATION OF ALCOHOLS IN THE PRESENCE OF  
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## HISTORICAL

In 1855 Hermann<sup>1</sup> investigated a reaction between bromoform and an alcoholic solution of potassium hydroxide. Unfortunately, this reference is not available, but some of the results may be deduced from quotations in later reports by other workers.

He found that during this reaction gas is given off, which he identified as a mixture of carbon monoxide and ethylene. A quantitative determination showed that there was a constant ratio of 3 : 1 between the carbon monoxide and ethylene, independent of the concentration of the potassium hydroxide. In one case, however, using very concentrated potassium hydroxide he found a ratio of 5 : 2 . This ratio 5 : 2 is quoted by Long<sup>2</sup> , however, no details about the concentrations used are available.

In 1862, Geuther<sup>3</sup> decomposed chloroform by alcoholic potassium hydroxide. He reported an evolution of gas during the reaction. Studies showed that if the solution was more aqueous or contained less potassium hydroxide more gas was given off. He identified the gas as carbon monoxide by its typical flame. From the description of his procedure it might be judged that he overlooked the ethylene. The gas he obtained burned with a green flame - probably due to chloroform vapors. After bubbling through water the gas burned with a bright flame. When the gas was shaken

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<sup>1</sup>Hermann, Liebigs Annalen der Chemie, 95, 211 (1855).

<sup>2</sup>Long, H., Annalen der Chemie und Pharmacie, 194, 23 (1878).

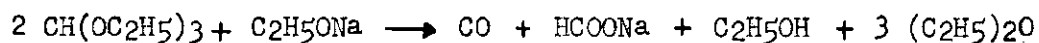
<sup>3</sup>Geuther, A., Liebigs Annalen der Chemie, 123, 121 (1862).

with water for a while or stored over water for a long time, the typical carbon monoxide flame was observed. It might be assumed that the ethylene was dissolved in the water. Geuther assumed that formic acid was formed from carbon monoxide and potassium hydroxide. He used this as an explanation for the fact that in more dilute solutions more carbon monoxide was given off.

In 1864, Bassett<sup>4</sup> prepared triethyl orthoformate by variations of the method given by Williamson and Kay<sup>5</sup>. The latter workers reported the formation of orthoformate and "vinous ether" from sodium ethylate and chloroform with and without alcohol as solvent. They also used potassium hydroxide instead of sodium ethylate as reactant. They do not mention the evolution of any gas.

Bassett, however, observed that a rather great amount of gas was given off when an alcoholic solution of sodium ethylate was added to chloroform. The gas evolution was not noticed when sodium was added to a mixture of chloroform and alcohol.

Bassett explains the formation of carbon monoxide and ether by the action of the ethylate ion on the orthoformate, according to the following equation:



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<sup>4</sup>Bassett, H., Liebigs Annalen der Chemie, 132, 54 (1864)

<sup>5</sup>Williamson, A. W., and Kay, Proceedings of the Royal Society of London, Vol. VII, 135 (1856).

It might be mentioned here that Hulleman<sup>6</sup> found that the ether formed in the reaction of sodium ethoxide and chloroform does not come from a reaction between sodium ethoxide and ethyl orthoformate, since these two compounds do not react under the conditions used.

Bassett also reports a small residue of gas after the absorption of carbon monoxide by cuprous chloride solution. This gas residue burns, and he assumed it to be ethylene, since Hermann<sup>7</sup> found ethylene in the similar reaction between bromoform and alcoholic potassium hydroxide. Bassett, however, did not report any ratio between carbon monoxide and ethylene.

In 1878 Long<sup>8</sup> checked Hermann's work. He mixed bromoform (no amount given) with alcoholic potassium hydroxide solution (30, 20 and 10 g. potassium hydroxide respectively in 200 ml. solution). The amount of ethylene and carbon monoxide in the mixture was determined by combustion. The ratio found was in all cases 3 : 1 (he actually found a little more carbon monoxide than the ratio would give. 3.16 : 1 is the highest value obtained).

Long assumed that two of the reactants form an intermediate which is decomposed by the third reactant.

In a publication in 1897, Nef<sup>9</sup> discusses the reaction as part of a long article on methylene compounds. According to him, haloforms may

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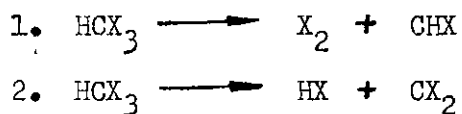
<sup>6</sup>Hulleman, M. T., Recueil des Travaux Chimiques des Pays-Bas, 8, 386 (1889).

<sup>7</sup>Hermann, Loc. cit.

<sup>8</sup>Long, Loc. cit.

<sup>9</sup>Nef, J. U., Liebigs Annalen der Chemie, 298, 367 (1897).

dissociate in two ways:



The difference between chloroform and the other haloforms is explained by the assumption that chloroform dissociates mainly by the second way. It is for this reason that it forms salts of formic acid and orthoesters. But it also decomposes to carbon monoxide in more dilute alkali.

It appears that the only experimental work upon which Nef's discussion is based is that of Geuthner.

He does not take into account the "small gas residue" - presumably ethylene - reported by Bassett<sup>10</sup>.

Nef explains the formation of ethylene from bromoform as reported by Hermann<sup>11</sup> and Long<sup>12</sup> by the dimerization of the "CHX" which is formed from bromoform by the reaction 1 above, the acetylene dibromide being finally reduced. It is apparently for this reason that the 3 : 1 ratio of carbon monoxide to ethylene is found in all cases. His reasoning is not entirely clear. His assumption that the olefin is formed by the dimerization of fragments of the bromoform molecule is proved wrong by

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<sup>10</sup>Bassett, Loc. cit.

<sup>11</sup>Hermann, Loc. cit.

<sup>12</sup>Long, Loc. cit.

the formation of propylene when isopropyl alcohol is used instead of ethyl alcohol. This was shown by an unpublished investigation of J. Hine.

Thiele and Dent<sup>13</sup> investigated the formation of carbon monoxide from chloroform and aqueous potassium hydroxide. They found that higher temperatures and higher concentrations of alkali supported the formation of formic acid. They assumed that the formic acid is formed by a secondary reaction from carbon monoxide and potassium hydroxide.

The most intensive work on this reaction, however, has been done by Mossler<sup>14</sup>. He analyzed for ethylene using bromine water and for carbon monoxide using a solution of cuprous chloride in ammonia. The formic acid was determined with mercuric chloride.

He made runs mixing chloroform in excess with 20, 5 and 1% solutions of potassium hydroxide in absolute and 50% ethyl alcohol. In all six runs he reported a 3 : 1 ratio between carbon monoxide and ethylene. In the runs with 50% alcohol the reaction mixture was heterogenous. The yield of formic acid, in the runs with absolute alcohol, rose from 20% to 38% as the potassium hydroxide solution became more dilute. In the runs with 50% alcohol the yield of formic acid decreased from 42% to 37% as the strength of the potassium hydroxide solution decreased from 20 to 1%. It can be seen that under the more aqueous conditions more formic acid was formed. Mossler then made runs with the same potassium hydroxide solutions

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<sup>13</sup>Thiele, J. and F. Dent, Liebigs Annalen der Chemie, 302, 273 (1898).

<sup>14</sup>Mossler, G., Monatshefte fuer Chemie, 29, 573 (1908).

but with the alkali in excess. Here also the 3 : 1 ratio was obtained in every run. In the runs with absolute alcohol the yield of formic acid dropped from 52% to 34% as the potassium hydroxide solution became more dilute. In the runs with 50% alcohol the yields ranged between 54 and 47%, the yield of the run with 5% potassium hydroxide being the highest.

Another series of runs was made by dropping a mixture of chloroform and ethyl alcohol on powdered dry potassium hydroxide. The ratio between chloroform and alcohol was varied. This series showed that the ratio of 3 : 1 was obtained only as long as there were five moles of alcohol to one mol of chloroform in the reaction mixture. If less alcohol was present more carbon monoxide was formed than would be expected from the 3 : 1 ratio. But in none of the runs reported by Mossler was more ethylene formed, i.e. no ratio lower than 3 : 1 was ever obtained.

Another run was made using potassium hydroxide in lumps and 1% alcohol in chloroform, in order to obtain knowledge about the rate of the reaction. It was found that as the alcohol was used up by the reaction the rate of the gas evolution became smaller and the ratio between carbon monoxide and ethylene became greater.

Mossler also treated chloroform with dry potassium hydroxide. The reaction proceeded slowly at room temperature, but better at elevated temperatures. The amount of formic acid formed was relatively small. At room temperature 14%, and when heated only about 5% of the chloroform was converted to formic acid.

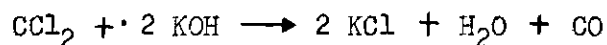
Mossler's proposed mechanism involves the intermediate formation of  $\text{CCl}_2$ . This compound is not stable, but reacts as an acid chloride.



Carbon monoxide is considered to be the anhydride of this acid. This acid chloride reacts only with the alcohol, forming two series of esters:  $\text{Cl-C-OC}_2\text{H}_5$  and  $\text{C}(\text{OC}_2\text{H}_5)_2$ . The latter ester is saponified to alcohol and carbon monoxide. The other ester decomposes to carbon monoxide and ethyl chloride. By the action of potassium hydroxide on the ethyl chloride, ethylene is formed. It might be mentioned here that under similar conditions ethyl chloride gives only about 1% elimination reaction, most of the ethyl chloride being converted into ethyl alcohol by a substitution reaction.

To explain the constant ratio of 3 : 1 Mossler assumes that there is an equilibrium between both esters in which two  $\text{C}(\text{OC}_2\text{H}_5)_2$  molecules are present for each  $\text{Cl-C-OC}_2\text{H}_5$  molecule. It must be assumed that the  $\text{CCl}_2$  reacts only with the alcohol even in the presence of water.

When chloroform reacts with dry potassium hydroxide, or as in the runs of Thiele and Dent<sup>15</sup> with an aqueous solution of potassium hydroxide, the reaction proceeds according to the following equation:



The same reaction will take place in the presence of alcohol if there are less than five mols of alcohol for each mol of chloroform.

The formation of the formic acid is a separate reaction - a saponification of the chloroform. This seems indicated, since under conditions which favor a saponification reaction - more aqueous solutions, lower concentrations of alkali and slower reaction - more formic acid is

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<sup>15</sup>Thiele and Dent, Loc. cit.

formed. Under conditions which favor the dissociation of the chloroform into  $\text{CCl}_2$  and hydrochloric acid more carbon monoxide is formed.

Reviewing the results reported here it is to be seen that they are not always in agreement with each other: Geuthner<sup>16</sup> overlooked the ethylene, which certainly would not have happened if, while shaking the gas sample with water, one quarter of it dissolved. It might be expected that he would have reported such an observation. Bassett<sup>17</sup> speaks of a "small gas residue", while Hermann<sup>18</sup> reports a 5 : 2 ratio. All these reports indicate that also ratios other than 3 : 1 have been found. On the other hand we find little agreement about the conditions which favor the formation of formic acid. The results of Geuthner and those of Thiele and Dent<sup>19</sup> do not agree with the results of Mossler<sup>20</sup>.

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<sup>16</sup>Geuthner, Loc. cit.

<sup>17</sup>Bassett, Loc. cit.

<sup>18</sup>Hermann, Loc. cit.

<sup>19</sup>Thiele and Dent, Loc. cit.

<sup>20</sup>Mossler, Loc. cit.

## EXPERIMENTAL WORK

## I

## APPARATUS

A three-necked flask heated by a heating mantle was equipped with a glass sealed stirrer, dropping funnel, inlet for nitrogen and reflux condenser. Ground joints were used for all connections. The vapor space above the liquid in the dropping funnel was connected to the vapor space in the three-necked flask to maintain equal pressure in both and to obtain constant dropping rates. On top of the reflux condenser a cold finger was attached. After passing through the reflux condenser and around the cold finger, the gases were passed through a trap and a bubble counter and were finally collected.

In the runs with ethyl alcohol, the reflux condenser was cooled by ice water circulated by means of a pump. The cold finger and trap were filled, however, with a dry ice-acetone mixture. In the other runs the cooling agents used are listed under the details for the individual runs.

In runs in which chloroform was placed in the three-necked flask and alcoholic potassium hydroxide solution was dropped into the boiling chloroform, it was necessary to prevent the chloroform from condensing at the outlet of the dropping funnel since the sodium chloride formed would stop the dropping. A cooling tube (10 cm. by 2 cm.) was placed between the three-necked flask and the dropping funnel. The vertical tube was wide enough to allow the potassium

hydroxide solution to drop without touching the walls.

Between the reflux condenser and the cold finger, a short adapter of straight glass tubing was introduced. It was filled with glass pieces and served to collect vapors which formed in the reflux condenser and were driven by the gas stream past the cold finger if the gas evolution was vigorous. The size of this adapter was, however, only one centimeter in order to keep the holdup of condensed liquid small.

The gas was collected in two outlet bottles, whose volume (bottle I 4492 ml., bottle II 4425 ml.) was determined by their weight with and without water. The bottles were held with their necks down by stainless steel wire (to prevent corrosion) and a counter weight was attached to allow them to be raised and lowered into ceramic containers which were filled with saturated sodium chloride solution as confining liquid. The outlet openings of the bottles were equipped with stopcocks. The stopcocks were at the highest point of the bottles so that it was possible to fill the bottles completely with confining liquid by means of a suction pump. The special features of this setup are that a drawback of liquid into the system during the run is prevented and that it is possible to maintain a slightly diminished pressure in the system.

The collecting bottles were connected to the bubble counter by a three-way stopcock so that it was possible to connect either bottle to the system.

## II

## GENERAL PROCEDURE

The following procedure is used unless it is stated otherwise for the individual run: The starting materials, according to the details given for each run, were placed in the dropping funnel and the three-necked flask. Cooling agents were applied and both collecting bottles were filled with confining liquid. Then a slow stream (approximately two bubbles per second) of dry nitrogen was passed through the system in order to sweep out all oxygen. It was sufficient to fill about one-half of a collecting bottle. Then the nitrogen was shut off and the other completely filled collecting bottle was connected to the system. When the bottle was completely filled with confining liquid and settled at the bottom of the container, the level of the confining liquid in the bottle was about ten centimeters above the level of the liquid in the container, thus a slightly diminished pressure was obtained in the system. Any leak was detected by bubbles in the bubble counter after the pressure equilibrium was reached.

If raised temperatures were to be used, the three-necked flask was heated and when no more expansion of the gas was seen, the liquid of the dropping funnel was dropped into the three-necked flask. Approximate dropping rates are given under the details for each run. In some cases, both bottles were filled before the gas analysis of the first bottle was completed. In such a case, the dropping was shut off for a while but heating and stirring was continued.

During the entire run, the level of the confining liquid in the bottle was kept a few centimeters higher than the level in the container, thus maintaining a slightly diminished pressure in order to prevent any loss of gas by leaking.

After all of the liquid was dropped in, heating and stirring was continued for an additional two hours. No more gas was given off after this time. Then the system was again swept with nitrogen. At least one more bottle was filled with nitrogen. The stream velocity of the nitrogen was about two bubbles per second in order to maintain equilibrium of vapor pressures in the trap. Heating and stirring was continued while sweeping to prevent dissolving of the olefin and carbon monoxide in the reaction mixture.

### III

#### ANALYSIS OF GASES

After each bottle was filled, the room temperature and barometric pressure were noted. Each bottle was allowed to sit for a short time before a sample was taken in order to insure a uniform mixture of the gas.

The gas analysis was carried out by means of an Orsat apparatus with a 100 ml. burette and mercury as confining liquid. For general instructions about the gas analysis Altieri's book<sup>21</sup> was used as a reference.

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<sup>21</sup>Altieri, V. J., Gas Analysis - Testing of Gaseous Materials (New York: American Gas Association, Inc., First Edition, 1945).

The ethylene was absorbed first in a solution of mercuric sulfate in diluted sulfuric acid as recommended by Francis and Lukasiewicz<sup>22</sup> (56.4 g. mercuric sulfate dissolved in 200 g. of 22 % sulfuric acid). The solution was filtered before use. Residues in the pipettes after absorption of ethylene were easily removed by use of mixtures of hydrochloric and nitric acids.

The results were found to be in general reproducible within 0.2 ml. The absorption was relatively fast.

The carbon monoxide was next absorbed in acidic cuprous chloride solution<sup>23</sup> (75 g. cuprous chloride and 600 ml. of concentrated hydrochloric acid diluted with water to 1000 ml.). Hydrochloric acid vapors given off by this solution were found to be negligible. When a gas sample which has been passed through the cuprous chloride solution was bubbled through potassium hydroxide solution the contraction that occurred was within the experimental error of 0.2 ml. Thus, there was no necessity to use potassium hydroxide solution during the runs.

Two pipettes were filled with cuprous chloride solution, the first one to absorb the main part of the carbon monoxide and the second to remove the last traces.

To avoid any mistake due to oxygen which was left in the system, or which may have entered the system by a leak or as an impurity

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<sup>22</sup>Francis, A. W., and S. J. Lukasiewicz, Industrial and Engineering Chemistry, Analytical Edition, 17, 703 (1948).

<sup>23</sup>Altieri, V. J., Loc. cit., p. 104.

of the nitrogen used, a determination of oxygen was made before carbon monoxide was absorbed, since oxygen would also be absorbed by cuprous chloride solution.

Since Altieri<sup>24</sup> states that alkaline solutions of pyrogallol would give off small amounts of carbon monoxide under certain conditions, an alkaline solution of sodium hyposulfite was used, as recommended by Franzen<sup>25</sup>. Reproducibility of the results was not too good.

Starting with Run XVI, Fieser's solution<sup>26</sup> was used as absorption liquid for oxygen. This consisted of 32 g. sodium hydrosulfite, 13 g. sodium hydroxide, and 4 g. sodium anthraquinone beta sulfonate dissolved in 200 ml. of water. The color changes from red to brown when the solution is exhausted. Propylene and n-butylene were absorbed in 87% sulfuric acid<sup>27</sup>. Isobutylene was absorbed in 64% sulfuric acid<sup>27</sup>. To re-establish the original water vapor pressure, the gas sample was passed through saturated salt solution after passing through the sulfuric acid.

In run XXVI with n-propyl alcohol where this is not done, a correction factor was introduced instead.

Starting with Run XXVIII the olefin was also determined by using bromine water in order to check the results. 13 ml. of bromine were dissolved in 985 ml. of water containing 50 g. of potassium bromide and

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<sup>24</sup>Altieri, V. J., Loc. cit., p. 183.

<sup>25</sup>Franzen, H., Berichte der Deutschen Chemischen Gesellschaft, 39, 2069 (1906).

<sup>26</sup>Fieser, L. F., Journal of the American Chemical Society, 46, 2639 (1924).

<sup>27</sup>Altieri, V. J., Loc. cit., p. 184.



the solution used as absorber<sup>27</sup>.

The bromine vapors were removed by a solution of 97 g. sodium hydroxide and 90 g. sodium bisulfite in 980 ml. of water<sup>27</sup>.

The absorption of the olefins by sulfuric acid is very slow, so that some errors may be introduced due to change of room temperature during the determination, since the Orsat was not equipped with a pressure compensator. The reproducibility of results with sulfuric acid and their agreement with results obtained with bromine water can best be judged from the data presented later.

For the calculations of the results of the gas analysis the barometric pressure was first corrected for the partial water vapor pressure over saturated sodium chloride solution. Values of this vapor pressure were taken from the Handbook of Chemistry and Physics.

The volumes were then corrected to 760 mm. Hg and 0° C.

The following terms are used as table headings in the data presented below:

"Burette reading" refers to the actual reading of the burette after passing through the corresponding absorption liquid until no further contraction of the gas volume is observed.

Under "mol", given figures are calculated on the basis of the average of all readings.

"Av. dev." gives the average deviation of the readings from the calculated average expressed in per cent of the average.

"Ratio" refers to the ratio of carbon monoxide to olefin. The average values are used for this calculation.

"Yield" refers to the alcohol which is transformed into olefin.

## IV

## DETAILS OF RUNS

## Run I

Starting Materials:	Room temperature 23° C
32 g. (1.39 mols) Sodium	Barometric pressure 747 mm Hg.
41.5 g. (0.348 mol) Chloroform	
600 ml. absolute ethyl alcohol	
No water	

The alcohol was placed in the three-necked flask and the sodium was dissolved in the alcohol. The solution of sodium ethoxide was almost clear, only slightly yellow. The chloroform was added at the rate of about one drop per second. The temperature of the three-necked flask was maintained at 20° C by means of a water bath. The solution was stirred for an additional three hours at this temperature and finally boiled for one and one-half hours. One-half of the reaction liquid was distilled off and the distillate was cooled with dry ice. After fractionation, 1.2 g. of a liquid, B. P. 32-40° C - presumably ether were obtained. The rest of the reaction liquid was filtered to remove the sodium chloride. Then most of the alcohol was distilled off and the residue was treated with water to remove the sodium formate. The triethyl orthoformate was extracted with ether and after drying with anhydrous sodium sulfate, the ether was distilled off. Yield of ester after distillation - 15 g. B. P. 144-147° C .

The odor of ether was also noticed in the gases given off after these had been passed through a dry ice trap.

Gas analysis:

Bottle II	Burette Readings				Mols	Av. dev.	Ratio
ethylene	11.8	11.6	11.7	11.7	0.0205	1%	1.67 : 1
CO	30.0	31.2	31.1	31.1	0.0336	0.5%	

## Run II

Starting Materials: Room temperature 25° C  
 36 g. (1.56 mols) sodium Barometric pressure 740 mm Hg.  
 46 g. (0.385 mol) chloroform  
 600 ml. ethyl alcohol 99.35%  
 0.78 mols water (0.65% contained in the alcohol and 10.9 g. added)

The sodium was dissolved in the water-alcohol mixture. The temperature of the three-necked flask was maintained at 20° C. The chloroform was dropped in at the rate of one drop per second. After the addition was complete, the mixture was stirred for three hours and finally boiled for an hour and a half. Determinations of ether and orthoester were tried, but no reasonable results were obtained due to the very small yields.

## Gas analysis:

Bottle II	Burette Readings				Mols	Av. dev.	Ratio
ethylene	15.0	16.0	15.0	15.2	0.026	2%	133 : 1
CO	36.0	36.0	35.2	35.6	0.0347	1.5%	

## Run III

Starting Materials: Barometric pressure 740 mm Hg.  
 39 g. (1.7 mols) sodium Room temperature 25° C  
 51 g. (0.427 mol) chloroform  
 600 ml. ethyl alcohol 92.7%  
 1.97 mols water (7.3% contained in the alcohol)

The sodium was dissolved in the alcohol-water mixture. The temperature of the three-necked flask was maintained at 20° C. The chloroform was dropped in at the rate of one drop per second. After three hours of additional stirring at 20° C the solution was boiled for one and one-half hours. Determinations of ether and orthoester gave no reasonable results.

## Gas analysis:

Bottle I	Burette Readings		Mols	Av. dev.	Ratio
ethylene	16.0	15.8	0.0278	0.6%	1.37 : 1
oxygen	19.3	19.2			
CO	41.2	41.3	0.0384	0.5%	

## Run IV

Starting Materials:	Barometric pressure 737 mm Hg.
30 g. (0.45 mol) KOH	Room temperature 26° C
42.5 g. (0.354 mol) chloroform	
300 ml. ethyl alcohol (absolute)	

The KOH was dissolved in the alcohol contained in the three-necked flask. The resulting solution was pale yellow. It was heated to the boiling point and the chloroform was added within 3 minutes. The reaction was very vigorous. Boiling was continued for 3 more hours but only small amounts of gas were given off. The color of the solution did not change very much. After the reaction, the liquid was "acid" to phenolphthalein as indicator.

## Gas Analysis:

Bottle I	Burette Readings		Mols	Av. dev.	Ratio
ethylene	7.7	7.9	0.0133	1.4%	3.1 : 1
oxygen	9.0	8.5			
CO	32.6	32.8	0.0409	1.5%	

## Run V

## Starting Materials:

50 g. (0.419 mol) chloroform

0.5505 mol KOH

Enough absolute ethyl alcohol to make 300 ml. solution with the above amount of KOH.

Barometric pressure 741 mm Hg.

Room temperature 25° C

Potassium hydroxide was dissolved in absolute ethyl alcohol. 10 ml. of this solution used 17.20 and 17.21 ml. of 1.0667 n. HCl. This solution was dropped within three quarters of an hour into the boiling chloroform. Added phenolphthalein showed that the reaction liquid was alkaline during the reaction. The reaction mixture was boiled until the color of the indicator changed.

## Gas Analysis:

Bottle I	Burette readings	Mol	Av. dev.	Ratio
ethylene	6.8 6.8	0.0119	0.5%	3.84 : 1
oxygen	7.8 7.8			
CO	35.0 35.0	0.0457		

## Run VI

Starting Materials: Barometric pressure 743 mm Hg.  
 41.2 g. (0.337 mol) chloroform Room temperature 26° C  
 250 ml. alcoholic KOH solution made up of  
 91.2% ethyl alcohol containing  
 0.453 mol KOH

KOH was dissolved in the alcohol and the strength of the solution was determined by titration with HCL using phenolphthalein as indicator. 10 ml. of the KOH solution used 18.09 and 18.11 ml. of 1.0667 n. HCl . The KOH solution was dropped into the boiling chloroform at the rate of one drop per second.

## Gas analysis:

Bottle I	Burette readings					Mol	Av. dev.	Ratio
ethylene	8.0	8.1	7.9	7.8	7.6	0.0137	2.2%	3.8 : 1
oxygen	9.2	11.5	9.2	8.8	9.0			
CO	39.2	39.2	38.6	38.9	38.8	0.0519	2.5%	



## Run VII

Starting Materials: Barometric pressure 742 mm Hg.  
 43.7 g. (0.366 mol) chloroform Room temperature 24° C  
 250 ml. KOH solution made up of  
 78.4% ethyl alcohol containing  
 0.477 mol KOH

The KOH was dissolved in the alcohol and the strength of the solution was determined by titration with HCl using phenolphthalein as indicator. 10 ml. of the KOH solution used 17.87 and 17.83 ml. of 1.0667 n. HCl. The KOH solution was dropped into the boiling chloroform at a rate of one drop per second.

## Gas Analysis:

Bottle I	Burette Readings				Mol	Av. dev.	Ratio
ethylene	9.0	9.0	9.0	9.2	0.0158	0.6%	3.9 : 1
oxygen	10.2	12.2	11.0	11.0			
CO	46.6	46.6	46.8	46.4	0.0624	3%	

## Run VIII

Starting Materials: Barometric pressure 734 mm Hg.  
 43.8 g. (0.367 mol) chloroform Room temperature 25° C  
 250 ml. KOH solution made up of  
 49.3% ethyl alcohol and containing  
 0.477 mol KOH

The KOH was dissolved in the alcohol and the strength of the solution was determined by titration with HCl using phenolphthalein as indicator. 10 ml. of the KOH solution used 17.92 and 17.85 ml. of 1.0667 n. HCl. The KOH solution was dropped into the boiling chloroform at the rate of one drop per second.

## Gas Analysis:

Bottle I	Burette Readings				Mol	Av. dev.	Ratio
ethylene	8.6	8.4	8.4	8.4	0.0145	0.6%	4.5 : 1
oxygen	10.5	11.4	9.2	9.2			
CO	47.8	47.8	47.0	47.4	0.0652	1.5%	

## Run IX

Starting Materials: Barometric pressure 740 mm Hg.  
 40.4 g. (0.338 mol) chloroform Room temperature 25° C  
 250 ml. KOH solution made up of  
 33.1% ethyl alcohol and containing  
 0.440 mol KOH

The KOH was dissolved in the alcohol and the strength of the solution was determined by titration with HCl using phenolphthalein as indicator. 10 ml. of the solution used 16.55 and 16.45 ml. of 1.0667 n. HCl. The KOH solution was dropped into the boiling chloroform at the rate of one drop per second. The mixture of chloroform and KOH solution was heterogenous.

## Gas Analysis:

Bottle I	Burette Readings			Mol	Av. dev.	Ratio
ethylene	6.8	6.8	6.8	0.0119		6.9 : 1
oxygen	9.0	8.0	8.0			
CO	55.2	55.8	55.2	0.0821	1.2%	

## Run X

Starting Materials: Barometric pressure 741 mm Hg.  
 40.5 g. (0.339 mol) chloroform Room temperature 25° C  
 250 ml. KOH solution made up of  
 8.1% ethyl alcohol and containing  
 0.441 mol of KOH

The KOH was dissolved in the alcohol and the strength of the solution was determined by titration with HCl using phenolphthalein as indicator. 10 ml. of the solution used 16.51 and 16.58 ml. of 1.0667 n. HCl. The KOH solution was dropped into the boiling chloroform at the rate of one drop per second. The mixture of chloroform and KOH solution was heterogenous.

## Gas Analysis:

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
ethylene	2.6	2.8	2.8	0.00468	2.5%	25 : 1
oxygen	4.4	4.0	4.2			
CO	72.0	72.2	72.0	0.1177	0.3%	

## Run XI

## Starting Materials:

42.6 g. (0.357 mol) chloroform  
 250 ml. KOH solution made up of  
 38% ethyl alcohol and containing  
 0.464 mol KOH

Barometric pressure 741

Room temperature 26° C

The KOH was dissolved in the alcohol and the strength of the solution was determined by titrating with HCl using phenolphthalein as indicator. 10 ml. samples of the solution required 17.43, 17.39 and 17.37 ml. of 1.0667 n. HCl. The KOH solution was added to the boiling and vigorously stirred chloroform within 6 minutes. Finally the solution was boiled for an additional 4 hours. The solution was heterogenous.

## Gas Analysis:

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
ethylene	7.8	7.1	7.2	0.0127	3.6%	6.5 : 1
oxygen	16.4	14.4	15.0			
CO	62.8	62.0	62.5	0.0320	1.2%	

## Run XII

Starting Materials: Barometric pressure 743 mm Hg.  
 42.6 g. (0.351 mol) chloroform Room temperature 28° C  
 250 ml. KOH solution made up of  
 38% ethyl alcohol and containing  
 0.464 mol KOH

The KOH was dissolved in the alcohol and the strength of the solution was determined by titrating with HCl using phenolphthalein as indicator. 10 ml. samples of the solution required 17.43, 17.49 and 17.37 ml. of 1.0667 n. HCl. (Same solution as in Run XI)

The KOH solution was added at a rate of about one drop per ten seconds. 23 hours were used to complete the addition.

## Gas Analysis:

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
ethylene	6.0	6.0	6.0	0.0102	1.6%	8.0 : 1
oxygen	12.4	13.8	10.6			
CO	61.0	60.2	60.8	0.0823	2.7%	

Run XIII Not made

No superstition - but it was Friday too . . . . .

## Run XIV

Starting Materials:	Barometric pressure 743 mm Hg.
45 g. (0.67 mol) KOH	Room temperature 25° C
15 ml. (0.188 mol) chloroform	
15 ml. (0.25 mol) ethyl alcohol	

This run was carried out under pressure. The KOH solution was placed in a 175 ml. bomb. The chloroform was placed in a test tube which was floated on the KOH solution. After the bomb was closed, the liquids were mixed by shaking the bomb. The bomb was heated by means of a steam jacket to 100° C for a period of 48 hours. During this time the bomb was shaken several times. The obtained pressure was 150 lb. per square inch (10.2 atm.). At room temperature this corresponded to 100 lb. per square inch (6.8 atm.). The bomb was opened and the gases were released into the setup which was used for the previous runs. To expel the gas from the bomb, the bomb was heated until the solution in the bomb was boiling. The apparatus was then swept out with nitrogen as described previously. The residue in the bomb had a very dark brown color.

## Gas Analysis:

Bottle I	Burette readings		Mols	Av. dev.	Ratio
ethylene	6.0	6.0	0.0105		5.7 : 1
oxygen	8.6	8.6			
CO	34.4	33.8	0.0598	0.9%	
Yield ethylene:	4.2%				



## Run XV

Starting Materials: Barometric pressure 744 mm Hg.  
 100 g. (1.5 mols) KOH Room temperature 28° C  
 50 ml. (0.63 mol) chloroform  
 20 ml. (0.34 mol) ethyl alcohol

The dry KOH was placed in the three-necked flask and the mixture of chloroform and alcohol was dropped in at the rate of one drop per second. The reaction was carried out at elevated temperatures - about 110 - 120° C. Shortly after the first few drops of chloroform-alcohol mixture were added, the KOH turned brownish-black. The KOH forms a very viscous liquid. The gas evolution starts very vigorously and slows down somewhat while the second part of the chloroform-alcohol mixture is added.

## Gas Analysis:

Bottle II	Burette Readings		Mol	Av. Dev.	Ratio
ethylene	7.4	7.6	0.0128	1.3%	10.1 : 1
oxygen	10.2	10.3			
CO	86.8	86.6	0.129	0.3%	

## Bottle I

ethylene	2.2	2.2	0.0038		26 : 1
oxygen	2.7	2.9			
CO	60.0	60.0	0.0989		

## Sum of Bottles I and II

ethylene			0.0166		16.6 : 1
CO			0.229		

Yield olefin: 4.1%

## Run XVI

Starting Materials: Barometric pressure 737 mm Hg.  
 42.6 g. (0.351 mol) chloroform Room temperature 26° C.  
 250 ml. KOH solution made up of  
 38% ethyl alcohol and containing  
 0.464 mol of KOH

The KOH was dissolved in the alcohol and the strength of the solution was determined by titrating with HCl, using phenolphthalein as indicator. 10 ml. samples of the solution used 17.43, 17.49, and 17.37 ml. of 1.0667 n HCl (same solution as in runs XI and XII). The KOH solution was added to the chloroform at the rate of one drop per second. During the run the three-necked flask was exposed to ultraviolet light. The light source was a General Electric AH 4 bulb, 100 watts. The three-necked flask was pyrex glass, so that the light above the following frequencies was transmitted to the given extent:

$\lambda$	% transmitted
3400	80
3170	50
3090	25
3000	10

## Gas Analysis:

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
ethylene	6.6	6.6	6.6	0.0112	1.5%	7.8 : 1
oxygen	9.2	8.4	8.4			
CO	59.8	60.0	60.1	0.0874	0.9%	

## Run XVII

## Starting Materials:

200 g. (3.0 mols) KOH

50 ml. (0.63 mol) chloroform

20 ml. (0.34 mol) ethyl alcohol

Barometric pressure 744 mm Hg.

## Room temperatures:

Bottle IIa 26° C

Bottle I 31

Bottle IIb 29

The KOH was placed in the three-necked flask and the alcohol was added. The alcohol was insufficient to dissolve the KOH entirely. The chloroform was added to the heated solution at the rate of one drop per second. The reaction was very vigorous. The solution solidifies somewhat during the first part of the reaction, finally it becomes more liquid again.

## Gas Analysis:

Bottle IIa	Burette Readings			Mol	Av. Dev.	Ratio
ethylene	5.4	5.0	5.4	0.00906	3.4%	7.7 : 1
oxygen	9.0	10.0	9.2			
CO	50.6	50.2	49.6	0.0700	1.4%	
Bottle I						
ethylene	3.0	2.8	3.0	0.00494	5.6%	30 : 1
oxygen	5.8	5.8	6.6			
CO	94.2	94.0	94.5	0.1502		
Bottle IIb						
ethylene	1.4	1.4		0.00237		2.9 : 1
oxygen	2.8	2.8				
CO	6.8	6.8		0.0678	1.4%	
Sum of Bottles IIa, I, IIb						
ethylene				0.01637		17.6 : 1
CO				0.288		

Yield olefin: 4.8%

## Run XVIII

Starting Materials:	Barometric pressure 745 mm Hg.
200 g. (3.0 mols) KOH	Temperature 26° C
50 ml. (0.63 mol) chloroform	
20 ml. (0.34 mol) ethyl alcohol	
75 ml. pyridine	

The KOH, pyridine and alcohol were placed in the three-necked flask. The chloroform was added at a rate of about one drop per second. At room temperature only very little gas is involved. When heated after a few ml. of chloroform had been added, the reaction suddenly becomes very vigorous and the mixture is colored deep brown. Despite this fact, the gas evolution is very small.

## Gas Analysis:

Bottle II	Burette Readings			Mol	Ave. Dev.	Ratio
ethylene	2.6	2.2	2.4	0.0042		4.2 : 1
oxygen	6.8	6.4	6.6			
CO	16.8	16.6	16.7	0.0176	0.6%	

Yield Olefin: 1.2%

## Run XIX

Starting Materials: Barometric pressure 742 mm Hg.  
 100 g. (1.5 mols) KOH Room temperature 26° C  
 25 ml. (0.313 mol) chloroform  
 10 ml. (0.170 mol) ethyl alcohol  
 75 ml. methyl alcohol

KOH, methyl alcohol and ethyl alcohol were placed in the three-necked flask and the chloroform was dropped in at the rate of one drop per second. The flask was heated during the reaction. The amount of alcohol was sufficient to dissolve the KOH entirely.

## Gas Analysis:

Bottle II	Burette Readings			Mol	Ave. dev.	Ratio
ethylene	1.2	1.2	1.2	0.00206		19.9 : 1
oxygen	2.6	2.8	2.7			
CO	26.6	26.8	26.4	0.0410	0.8%	

Yield Olefin: 1.2%

## Run XX

Starting Materials: Barometric pressure 742 mm Hg.  
 100 g. (1.5 mols) KOH Room temperature 23° C  
 25 ml. (0.313 mol) chloroform  
 10 ml. (0.170 mol) ethyl alcohol  
 75 ml. water

KOH, water and alcohol were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second.

## Gas Analysis:

Bottle I	Burette Readings			Mol	Av. dev.	Ratio
ethylene	4.8	4.8	4.8	0.0083		8.9 : 1
oxygen	6.8	7.0	7.1			
CO	50.0	49.2	49.8	0.0738	0.6%	
Bottle II						
ethylene	0.4	0.4	0.4	0.0007		
oxygen	1.8	1.8	1.6			
CO	24.0	23.6	23.3	0.0384	1%	
Sum of Bottles I and II						
ethylene				0.0090		
CO				0.112		12 : 1

Yield Olefin: 5.3%

## Run XXI

Starting Materials: Barometric pressure 739 mm Hg.  
 100 g. (1.5 mols) KOH Room temperature 27° C  
 25 ml. (0.313 mol) chloroform  
 10 ml. (0.170 mol) ethyl alcohol  
 100 ml. diethyl ether

KOH, diethyl ether and alcohol were placed in the three-necked flask and the flask was heated. The chloroform was dropped in at the rate of one drop per second. After all the chloroform had been added, the mixture was boiled for 11 additional hours. The ether layer was separated and boiled for a short time with an excess of alcoholic KOH. The resulting solution showed no significant reaction for chloride ions.

## Gas Analysis:

Bottle I	Burette readings			Mol	Ave. dev.	Ratio
ethylene	1.0	1.2	1.1	0.0019	9.1%	29.9 : 1
oxygen	3.0	2.8	3.0			
CO	36.0	35.8	36.0	0.0569	0.6%	

Yield olefin: 1.1%

## Run XXII

Starting materials: Barometric pressure 740 mm Hg.  
 100 g. (1.5 mols) KOH Room temperature 27°  
 25 ml. (0.313 mol) chloroform  
 10 ml. (0.170 mol) ethyl alcohol  
 150 ml. water

KOH, alcohol and water were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second.

## Gas analysis:

Bottle I	Burette readings			Mol	Ave. dev.	Ratio
ethylene	1.4	1.4	1.4	0.00245		11 : 1
oxygen	2.4	2.8	2.6			
CO	18.0	18.2	18.0	0.0272	0.3%	

Yield of olefin: 1.4%



## Run XXIII

Starting Materials: Barometric pressure 742 mm Hg.  
 100 g. (1.5 mols) KOH Room temperature 28° C  
 25 ml. (0.313 mol) chloroform  
 10 ml. (0.17 mol) ethyl alcohol  
 35 ml. water

KOH, water and alcohol were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second. The KOH was not completely dissolved.

## Gas analysis:

Bottle I	Burette readings			Mol	Ave. dev.	Ratio
ethylene	3.2	3.2	3.2	0.0055		7.4 : 1
oxygen	4.6	4.6	4.8			
CO	28.4	28.2	28.8	0.0411	0.9%	

Yield olefin: 3.1%

## Run XXIV

Starting materials: Barometric pressure 738 mm Hg.  
 200 g. (3.0 mols) KOH Room temperature 29° C  
 50 ml. (0.63 mol) chloroform  
 10 ml. (0.17 mol) ethyl alcohol  
 150 ml. water

KOH, water and alcohol were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second.

## Gas analysis:

Bottle I	Burette readings			Mol	Ave. dev.	Ratio
ethylene	7.0	6.6	7.0	0.0117	2.4%	9.2 : 1
oxygen	9.2	10.1	8.4			
CO	72.9	73.2	72.8	0.108	0.4%	
Bottle II						
ethylene	0.6	0.6	0.6	0.0010		108 : 1
oxygen	2.0	2.0	2.0			
CO	66.4	66.5	66.3	0.108	0.1%	
Sum of Bottles I and II						
ethylene				0.0127		1 : 17
CO				0.216		

Yield olefin: 7.5%

## Run XXV

Starting Materials: Barometric pressure 738 mm Hg.  
 400 g. (6.0 mols) KOH Room temperature 29° C  
 25 ml. (0.31 mol) chloroform  
 5 ml. (0.085 mol) ethyl alcohol  
 300 ml. water

KOH, alcohol and water were placed in the three-necked flask which was heated during the reaction. The chloroform was added at a rate of one drop per second.

## Gas analysis:

Bottle I	Burette readings			Mol	Av. dev.	Ratio
ethylene	1.0	1.4	1.0	0.0019	15%	57 : 1
oxygen	3.0	3.4	3.0			
CO	70.8	80.1	70.8	0.109	0.2%	
Bottle II						
ethylene	0	0	0			
oxygen	1.0	1.0	1.0			
CO	7.5	7.4	7.5	0.010	0.9%	
Sum of Bottles I and II						
ethylene				0.0019		64 : 1
CO				0.119		

Yield olefin: 2.2%

## Run XXVI

## n - Propyl alcohol

Starting Materials:	Barometric pressure 743 mm Hg.
200 g. (3.0 mols) KOH	Room temperature 25° C.
10.2 g. (0.17 mol) n-propyl alcohol	
50 ml. (0.63 mol) chloroform	
150 ml. water	

The KOH, alcohol, and water were placed in the three-necked flask, which was heated during the reaction. The chloroform was added at the rate of one drop per second. During the reaction and while sweeping the apparatus with nitrogen the cold finger and the trap were filled with dry ice-acetone mixture. In the gas analysis the gases were not bubbled through saturated salt solution after they had been bubbled through sulfuric acid. It was learned in later runs where this had been done, that the expansion of the gas due to the reestablished original water vapor pressure would be about 1.5 ml. ( $\pm 0.5$  ml.). A corresponding correction has been made in the results obtained in this run.

## Gas Analysis:

Bottle I	Burette Readings			Mol	Av. dev.	Ratio
olefin (H <sub>2</sub> SO <sub>4</sub> )	8.4	8.6	8.4			
corrected	6.9	7.1	6.9	0.0122	8%	9.3 : 1
oxygen	9.5	9.7	9.4			
CO	75.4	75.0	75.4	0.114	0.5%	

## Run XXVI (Continued)

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
olefin (H <sub>2</sub> SO <sub>4</sub> )	2.5	2.6	2.6			
corrected	1.0	1.1	1.1	0.00189	45%	
oxygen	2.9	2.8	3.0			
CO	55.4	55.9	55.7	0.0910	0.8%	48 : 1
<u>Total gas</u>						
olefin (H <sub>2</sub> SO <sub>4</sub> )				0.0141		15 : 1
CO				0.205		
<u>Yield olefin:</u>	8.3%					

## Run XXVII

## Isopropyl alcohol

Starting Materials:	Barometric pressure 737 mm Hg.
200 g. (3.0 mols) KOH	Room temperature 31° C.
50 mL. (0.63 mol) chloroform	
10.2 g. (0.17 mol) isopropyl alcohol	
150 mL. water	

The KOH, water, and alcohol were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second. During the reaction the cool finger and the trap were filled with dry ice-acetone mixture. While sweeping the apparatus, the cool finger and trap were filled with ice-salt mixture.

## Gas Analysis:

Bottle Ia	Burette Readings			Mols	Av. dev.	Ratio
Olefin (H <sub>2</sub> SO <sub>4</sub> )	17.8	17.6	17.7	0.030	0.4%	3.5 : 1
oxygen	19.0	19.0	19.1			
CO	81.4	81.4	81.4	0.105	0.1%	
Bottle IIa						
Olefin (H <sub>2</sub> SO <sub>4</sub> )	8.4	8.6	8.5	0.0141	0.7%	9.8 : 1
oxygen	9.0	8.8	8.9			
CO	93.0	93.0	92.9	0.139		

## Run XXVII (Continued)

Bottle Ib	Burette Readings			Mol	Av. dev.	Ratio
Olefin (H <sub>2</sub> SO <sub>4</sub> )	7.2	6.8	7.0	0.0116	2%	3.5 : 1
oxygen	7.8	7.7	7.7			
CO	32.1	32.0	32.0	0.0410		
Bottle IIb						
Olefin (H <sub>2</sub> SO <sub>4</sub> )	3.2	3.2		0.0053		0.9 : 1
oxygen	3.6	3.6				
CO	3.9	3.9		0.0005		
Total gas						
Olefin				0.0610		4.5 : 1
CO				0.276		
Yield olefin:	34.9%					

## Run XXVIII

## Isopropyl alcohol

Starting Materials:	Barometric pressure 740 mm Hg.
200 g. (3.0 mols) KOH	Room temperature:
50 ml. (0.63 mol) chloroform	Bottle Ia 24° C.
10.2 g. (0.17 mol) isopropyl alcohol	Bottle II 23° C.
150 ml. water	Bottle Ib 23° C.

The KOH, alcohol, and water were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second. During the reaction and while sweeping the apparatus, the cool finger and trap were filled with dry ice-acetone mixture. The reaction mixture was dark brown after a short time, and later very viscuous. The gas evolution was slow at the beginning of the reaction.

## Gas Analysis:

Bottle Ia	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	14.1	14.0	14.1	0.0247	0.7%	4.6 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	14.4	14.4	14.4	0.0252		4.6 : 1
oxygen	15.3	15.4	15.3			
CO	80.6	80.7	80.6	0.115	0.1%	
Bottle II						
Olefin (Br <sub>2</sub> )	12.9	12.8	13.0	0.0223	0.5%	5.7 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	12.9	12.9	12.9	0.0223		5.7 : 1
oxygen	13.4	13.4	13.5			
CO	87.0	87.0	87.0	0.128		



## Run XXVIII (Continued)

Bottle Ib	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	0.5	0.5	0.5	0.0009		2.3 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	0.5	0.5	0.5	0.0009		2.3 : 1
oxygen	2.0	2.0	2.1			
CO	3.2	3.2	3.3	0.0021		
Total gas						
Olefin (Br <sub>2</sub> )				0.0479		5.1 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )				0.0484		5.1 : 1
CO				0.245		
Yield olefin:	(Br <sub>2</sub> )	28.2%				
	(H <sub>2</sub> SO <sub>4</sub> )	28.4%				

## Run XXIX

## Isopropyl alcohol

Starting Materials:	Barometric pressure 736 mm Hg.
200 g. (3.0 mols) KOH	Room temperature:
50 ml. (0.63 mol) chloroform	Bottle Ia 30° C.
10.2 g. (0.17 mol) isopropyl alcohol	Bottle II 31° C.
20 ml. water	Bottle Ib 28° C.

The KOH, alcohol, and water were placed in the three-necked flask which was heated during the reaction. The solvents were insufficient to dissolve the KOH entirely. During the reaction and while sweeping the apparatus, the cool finger and trap were filled with dry ice-acetone mixture.

## Gas Analysis:

Bottle Ia	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	11.2	11.2	11.2	0.0190		5.1 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	11.4	11.4	11.4	0.0193		5.1 : 1
oxygen	14.4	14.4	14.5			
CO	72.0	72.0	72.0	0.0975		
Bottle II						
Olefin (Br <sub>2</sub> )	11.1	11.1	11.1	0.0184		7.7 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	11.1	11.1	11.1	0.0184		7.7 : 1
oxygen	11.1	11.2	11.1			
CO	97.0	97.2	97.0	0.143		

## Run XXIX (Continued)

Bottle Ib	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	4.0	4.0	4.1	0.0068	0.8%	17 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	4.0	4.5	4.0	0.0071	5%	16 : 1
oxygen	4.6	5.0	4.4			
CO	70.0	71.0	72.0	0.114	1.8%	
Total gas						
Olefin (Br <sub>2</sub> )				0.0439		8.1 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )				0.0448		7.9 : 1
CO				0.354		
Yield olefin:	(Br <sub>2</sub> )	25.8%				
	(H <sub>2</sub> SO <sub>4</sub> )	26.3%				

## Run XXX

## n-Butyl alcohol

Starting Materials: Barometric pressure 734 mm Hg.  
 200 g. (3.0 mols) KOH Room temperature:  
 50 ml. (0.63 mol) chloroform Bottle I 28° C.  
 12.6 g. (0.17 mol) n-butyl alcohol Bottle II 25° C.  
 150 ml. water

The KOH, alcohol, and water were placed in the three-necked flask which was heated during the reaction. The chloroform was added at the rate of one drop per second. During the run and while sweeping the apparatus with nitrogen the reflux condenser was cooled by ice water. The cold finger and the trap were filled with ice-salt mixture.

## Gas Analysis:

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	6.4	7.2	6.8	0.0114	3.4%	9.6 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	8.0	8.0	8.0	0.0134		8.2 : 1
oxygen	8.0	8.2	8.1			
CO	76.0	71.0	73.5	0.110	2.5%	
Bottle I						
Olefin (Br <sub>2</sub> )	1.0	1.0	1.0	0.00174		43 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	1.0	1.0	1.0	0.00174		43 : 1
oxygen	4.8	4.8	4.6			
CO	48.0	48.8	48.2	0.0754	0.7%	

## Run XXX (Continued)

Total gas	Burette Readings	Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )		0.0131		14 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )		0.0151		12 : 1
CO		0.1854		

Yield olefin: (Br<sub>2</sub>) 7.7%  
(H<sub>2</sub>SO<sub>4</sub>) 8.8%

## Run XXXI

## Isobutyl alcohol

Starting Materials:	Barometric pressure 748 mm Hg.
200 g. (3.0 mols) KOH	Room temperature:
12.6 g. (0.17 mol) isobutyl alcohol	Bottle I 28° C.
50 mL. (0.63 mol) chloroform	Bottle II 27° C.
150 mL. water	

For procedure see Run XXX.

## Gas Analysis:

Bottle I	Burette Readings			Mols	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	9.4	9.0	9.2	0.0160	1.4%	7.6 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	7.0	6.8	7.0	0.0121	1.3%	10 : 1
oxygen	8.0	8.0	8.1			
CO	78.4	78.5	78.4	0.122	0.1%	

## Bottle II

Olefin (Br <sub>2</sub> )	1.5	1.4		0.0026	2%	17 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	1.2	1.3	1.3	0.00217	3.5%	20 : 1
oxygen	2.0	2.8	2.6			
CO	28.0	28.2	28.3	0.0441	0.8%	

## Total gas

Olefin (Br <sub>2</sub> )	0.0186	8.9 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	0.0142	11.7 : 1
CO	0.166	

## Run XXXI (Continued)

Yield olefin: (Br<sub>2</sub>) 10.9%  
(H<sub>2</sub>SO<sub>4</sub>) 8.4%

## Run XXXII

sec. Butyl alcohol

Starting Materials: Barometric pressure 738 mm Hg.  
 200 g. (3.0 mols) KOH Room temperature 30° C.  
 50 ml. (0.63 mol) chloroform  
 12.6 g. (0.17 mol) sec. butyl alcohol  
 150 ml. water

For procedure see Run XXX.

## Gas Analysis:

Bottle Ia	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	24.6	24.4	24.5	0.0426	0.3%	2.0 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	24.4	24.4	24.4	0.0424		2.0 : 1
oxygen	25.0	25.1	25.0			
CO	75.0	75.1	75.2	0.0869	0.1%	

## Bottle II

Olefin (Br <sub>2</sub> )	8.8	8.6	8.7	0.0149	0.7%	8.0 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	8.6	8.6	8.8	0.0147	0.7%	8.0 : 1
oxygen	9.6	10.0	9.5			
CO	79.8	80.4	79.7	0.120	0.1%	

## Total gas

Olefin (Br <sub>2</sub> )	0.0580	3.6 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	0.0572	3.6 : 1
CO	0.209	



## Run XXXIII (Continued)

Yield olefin: (Br<sub>2</sub>) 34.1%  
(H<sub>2</sub>SO<sub>4</sub>) 33.6%

## Run XXXIII

tert. Butyl alcohol

Starting Materials:	Barometric pressure 742 mm Hg.
200 g. (3.0 mols) KOH	Room temperature:
50 ml. (0.63 mol) chloroform	Bottle II 31° C.
12.6 g. (0.17 mol) tert. butyl alcohol	Bottle I 28° C.
150 ml. water	

For procedure see Run XXX.

## Gas Analysis

Bottle II	Burette Readings			Mol	Av. dev.	Ratio
Olefin (H <sub>2</sub> SO <sub>4</sub> )	24.8	24.8	25.0	0.0415	0.3%	2.4 : 1
oxygen	26.2	25.4	25.7			
CO	84.0	84.0	84.0	0.0977	0.7%	

## Bottle I

Olefin (H <sub>2</sub> SO <sub>4</sub> )	7.2	7.4	7.0	0.0124	1.8%	6.3 : 1
oxygen	8.6	8.2	8.2			
CO	54.2	54.0	53.8	0.1%		

## Total gas

Olefin (H <sub>2</sub> SO <sub>4</sub> )	0.0539	3.3 : 1
CO	0.176	

Yield olefin: 31.7%

## Run XXXIV

tert. Butyl alcohol

Starting Materials:	Barometric pressure 734 mm Hg.
200 g. (3.0 mols) KOH	Room temperature:
50 ml. (0.63 mol) chloroform	Bottle I 31° C.
12.6 g. (0.17 mol) tert. butyl alcohol	Bottle II 27° C.
150 ml. water	

For procedure see Run XXX.

## Gas Analysis

Bottle I	Burette Readings			Mol	Av. dev.	Ratio
Olefin (Br <sub>2</sub> )	24.8	24.8	24.8	0.0417		1.8 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	27.6	27.2	26.2	0.0454	1.9%	1.7 : 1
oxygen	31.6	32.0	32.2			
CO	78.0	76.6	77.4	0.0760	2.0%	

## Bottle II

Olefin (Br <sub>2</sub> )	8.3	8.2	8.0	0.0138	1.2%	7.8 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	10.0	9.2	9.8	0.0162	2%	6.6 : 1
oxygen	10.4	9.8	10.5			
CO	72.6	75.0	74.2	0.1073	1.5%	

## Total gas

Olefin (Br <sub>2</sub> )	0.0555	3.3 : 1
Olefin (H <sub>2</sub> SO <sub>4</sub> )	0.0616	3.0 : 1
CO	0.183	

## Run XXXIV (Continued)

Yield olefin: (Br<sub>2</sub>) 32.6%  
(H<sub>2</sub>SO<sub>4</sub>) 36.3%

Run XXXV

## Cyclohexanol

## Starting Materials:

400 g. KOH (6.0 mols)  
100 ml. (1.26 mols) chloroform  
34.5 g. (0.34 mol) cyclohexanol  
300 ml. water

The alcohol, KOH and water were placed in the three-necked flask and the chloroform was dropped in at the rate of one drop per second. Dry ice - acetone mixture was used as drying agent in the cold finger and the trap. The solution was finally boiled for six additional hours and then 250 ml. of purified isooctane were added. See below for details about the purification of isooctane. From the reaction mixture about 150 ml. liquid were distilled. Stirring was continued during this time to prevent bumping of the liquid. The distillate was cooled by dry ice because of the relatively high volatility of the cyclohexene. Analogous precautions were also taken during the other manipulations in this run. The distillate was dried with anhydrous sodium sulfate. After filtration the sodium sulfate was washed with isooctane and the washings were added to the main part.

From this sample about 75 ml. were distilled off in a fractionating column and the distillate was filled up with more isooctane to 100 ml. in a volumetric flask. The cyclohexene contained in this solution was determined by titration with bromine. By investigation employing

quantitative infrared spectroscopic methods it was detected that the amount of benzene in this solution was less than 0.005%.

#### Analysis of cyclohexene:

Stanerson<sup>28</sup> has described a method for the determination of olefins but he does not especially recommend this method for the determination of cyclohexene. Therefore, first a check was made with a sample of cyclohexene in isooctane with known strength. 12 ml. of the cyclohexene solution were added to 25 ml. chloroform in an iodometric flask. Then the standardized bromine solution was dropped in from a burette until a slight excess had been added. This excess was determined iodometrically by adding 2 g. potassium iodide, 1 g. sodium carbonate (to expel the oxygen) and 10 ml. HCl ( 1 : 1 ). After standing five minutes, the sample was diluted with water and the liberated iodine was titrated with standardized sodium thiosulfate solution, using starch solution as indicator.

The bromine solution employed was a 1% solution of bromine in glacial acetic acid. It was standardized with sodium thiosulfate solution after diluting a sample 1 : 10 with glacial acetic acid. The same procedure was used as described above for the determination of the cyclohexene. The strength of the bromine solution, however, has to be determined a short time before use, since the solution is not stable.

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<sup>28</sup>Stanerson, B. R., and H. Levin, Industrial and Engineering Chemistry, Analytical Edition, 14, 782 (1942).

Check of the method used:

Concentration bromine solution 0.3717 n.

Concentration sodium thiosulfate solution 0.01560 n.

Sample of 100 ml. containing 2.7610 g. (0.02975 mol) of cyclohexene. (Isooctane was used as solvent)

12 ml. used	I	II	III
Br <sub>2</sub> - solution	19.90 ml.	19.90 ml.	20.00 ml.
sodium thiosulfate	4.28 ml.	8.05 ml.	13.75 ml.
calculated mol			
cyclohexene in 100 ml.	0.03054	0.03029	0.03053
average			0.03030 mol.
av. dev.			0.3%
deviation from the theoretical value			0.00055 mol.
expressed in per cent of the theoretical value			1.8%

The results are slightly too high.

Analysis of the product:

Concentration bromine solution 0.3710 n.

Concentration sodium thiosulfate solution 0.01560 n.

10 ml. used	I	II	III
Br <sub>2</sub> - solution	25.46 ml.	25.53 ml.	26.15 ml.
sodium thiosulfate	4.80 ml.	10.90 ml.	18.38 ml.
calculated mol			
cyclohexene in 100 ml.	0.04651	0.04651	0.04711
average	0.04682 mol.		
av. dev.	0.45%		
% yield olefin	13.8%		

### Purification of the Isooctane

For this run isooctane had to be used which would not decolorize bromine solution, that is, which should be free of unsaturated compounds. Treatment with alkaline solution of potassium permanganate failed to give satisfactory results. It was, however, possible to purify the isooctane by means of acid potassium permanganate solution.

The crude isooctane was shaken for three hours with a solution of potassium permanganate in 10% sulfuric acid. After separation, the isooctane layer was washed several times with water, dried and fractionated. The isooctane thus purified did not decolorize bromine solution within 5 minutes.



## Run XXXV

## Isoborneol

## Starting Materials:

400 g. (6.0 mols) KOH  
100 ml. (1.26 mols) chloroform  
52.5 g. (0.34 mol) isoborneol  
300 ml. water  
25 ml. benzene

The KOH, alcohol, water and benzene were placed in the three-necked flask. The alcohol did not dissolve in the KOH solution. Therefore, benzene was added in order to dissolve the isoborneol which would be deposited in the condenser if such precautions were not taken.

The chloroform was added at the rate of one drop per second while the three-necked flask was heated. After all chloroform had been added, the solution was boiled for an additional six hours. Then the reaction mixture was steam-distilled.

In the distillate the organic material was collected with benzene and part of the benzene was distilled after previous drying with anhydrous sodium sulfate. It was not possible to determine the olefin formed in this solution by bromine since the isoborneol itself was not stable against bromine.

An attempt was made to determine what olefin is formed - camphene, bornylene or tricyclene - by means of infrared investigation. No reliable

results were obtained. There is some indication that camphene might be formed. It must be considered, however, that there might be a loss of bornylene while distilling the benzene due to the extremely high volatility of this compound.

## V

## INFRARED MEASUREMENTS

For this work Beckmann infrared spectrophotometer (model IR2) was used with a wave length range 2 to 15 microns. The samples were placed in sodium chloride cells of 0.2 mm. thickness. The absorption was recorded automatically on a Brown, high speed, strip chart recorder.

Determination of benzene in Run XXXV. (cyclohexanol)

First the absorption spectrum of benzene, cyclohexene and isooctane were determined to get information about their characteristic absorption peaks. Benzene showed a strong, broad adsorption between 14.5 and 15 microns in which area none of the other compounds absorbed significantly.

A 4% solution of purified cyclohexene in purified isooctane was made up - this corresponded to the solution of cyclohexene in isooctane obtained by Run XXXV - and the spectrum of this sample was determined. On the same chart absorption curves were recorded of samples of the same concentration of cyclohexene but containing also 0.4, 0.9 and 1.5% benzene, respectively.

The build-up of the absorption peak of benzene in the area of 14.5 to 15 microns was evident to be seen as the amount of benzene in the solution was increased.

This area was then more carefully investigated to get correct information about the height of the peak and its dependence on the amount of the benzene contained in the solution.

A slower chart velocity and a greater damping period was used to obtain smoother curves.

#### Investigation of the Products Obtained in Run XXXVI

The infrared absorption spectrum of benzene and isoborneol was determined. Unfortunately, none of the products which were to be expected, camphene, bornylene and tricyclene, was available so that it was not possible to record their spectrum also. But some previous work with these compounds was done by Swann and Cripwell<sup>29</sup>. These workers investigated the spectra of camphene, tricyclene and bornylene and report the following absorption peaks of camphene and tricyclene.

Approximate wave length in microns	% Absorption
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#### Absorption peaks of tricyclene

11.0	25
11.6 - 11.8	50
12.3	66

#### Absorption peaks in camphene

11.5 - 11.4	100
12.3	27
13.16	45
13.33	30
13.4	42

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<sup>29</sup>Swann, G. and Cripwell, F. J., The Industrial Chemist and Chemical Manufacturer, 24, 576 (1948).

Their attempts to record the spectrum of bornylene were not successful because of difficulty of obtaining this compound in a pure state. They, however, report a peak probably at 14.2 microns.

We examined the spectrum of the following samples in order to get information as to which of the three possible compounds might possibly be formed:

1. 3% solution of isoborneol in benzene
2. Saturated solution of isoborneol in benzene
3. Products of Run XXXVI in benzene as described in the details of this run.

All three spectra were recorded on the same chart. The curve 3 lies in general between the curves 1 and 2 due to the concentration of isoborneol in this sample. But there are, however, two areas in which sample 3 shows slightly higher absorption than the saturated solution of isoborneol. The results are reproducible, as shown by repetition of these measurements. The wave lengths of these areas are:

1. 13.1 - 13.2 microns
2. 11.2 - 11.4 microns

The fact that these two areas correspond to peaks of the spectrum of camphene as reported by Swann and Cripwell<sup>30</sup> might be taken as an indication that this compound is present among the products of this run.

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<sup>30</sup>Swann, G. and Cripwell, F. J., Loc. cit.

## DISCUSSION OF RESULTS

Some of the results of this work appear to differ from those reported by Mossler. But we have to consider that in general the runs were made under conditions differing from those used by the latter worker. Mossler added all his reactants at the beginning of the reaction while here one reactant was generally added to the other at a definite rate.

However, two runs were made using conditions approaching those of Mossler.

In Run IV the chloroform was added within three minutes to a 10% solution of potassium hydroxide in absolute alcohol. Here the ratio of 3 : 1 between ethylene and carbon monoxide is actually obtained.

If calculated by the following formula:

$$\text{mols formate} = \frac{\text{mols KOH} - 3 \times \text{mols CO}}{4}$$

the percent yield of formate based on the chloroform used up is about 68%.

According to Mossler the yield of formic acid is about 20% and 28% in runs with 20% and 5% potassium hydroxide respectively and with chloroform in excess. This would correspond to conditions at the end of our run when all the chloroform had been added. Considering the beginning of the reaction where the potassium hydroxide was actually in excess the percent of formic acid formed should lie

between 51% and 43%, i.e., between Mossler values for 20% and 5% potassium hydroxide solutions with the base present in excess.

The comparison shows that the percent formic acid formed in Run V is at least 20% higher than would be expected from Mossler's work.

The other run which might be compared is Run XI. Here a 10% solution of potassium hydroxide in 38% ethyl alcohol was dropped within 6 minutes into an excess of chloroform. The carbon monoxide-ethylene ratio obtained here was 6.5 : 1. The amount of formic acid formed calculated by the above procedure is about 43%. This agrees with the results of Mossler. He reports a yield of 42% and 38% using 20% and 5% potassium hydroxide solutions respectively in 50% alcohol. The chloroform was present in excess. This corresponds to conditions in Run XI since here the potassium hydroxide solution was dropped into the chloroform. The difference in the carbon monoxide-ethylene ratio might be explained by the fact that in the first part of the reaction the ratio between chloroform and ethyl alcohol was lower than Mossler's limiting value of 1 : 5. For such cases Mossler himself reports ratios differing from the usual 1 : 3 ratio.

However, the results of a few runs show a carbon monoxide-ethylene ratio lower than 1 : 3 (Runs I, II, and III), although the conditions there do not differ appreciably from those used by Mossler.

Several facts may be seen from the results obtained in this work. Results of Runs V through X are shown in Table I and Graphs

I, II, and III. These runs have been made dropping potassium hydroxide solution (11% potassium hydroxide on the average) into an excess of chloroform.

In Run V where absolute alcohol was used the ratio of chloroform to alcohol was above 1 : 5 until about 100 ml. of the 250 ml. total potassium hydroxide solution have been added. In Runs VI and VII even more solution had to be added before this ratio 1 : 5 was reached. In Run VIII through X the 1 : 5 ratio between chloroform and alcohol was never reached.

These considerations might explain the fact that the ratio of carbon monoxide to olefin is about 3.8 : 1 in Runs V through VII and falls gradually from Run VIII through Run X.

The ratio mols olefin to mols potassium hydroxide has been used for the comparison of the amount of olefin formed in the different runs, since the amount of potassium hydroxide in the starting material varies slightly. The corresponding ratio is used to compare the yields of carbon monoxide.

It is evident that there is a dependence of the yield of ethylene upon the percentage of the alcohol, since the amount rises first, reaches a maximum in Run VII (78% alcohol) and then decreases. The amount of carbon monoxide on the other hand rises as the solution becomes more aqueous.

A similar dependence of the yields of olefin formed was also found in the series of Runs XVII, XX, XXII, and XXIII (Table II). Here the chloroform was dropped into an excess of potassium hydroxide



contained in a few ml. of alcohol and varying amounts of water. The maximum yield of ethylene was found in Run XX and the yields in Runs XXII and XXIII using more or less water were found to be smaller. In Run XVII where no water was added to the starting materials the yield of ethylene is higher than in Run XXIII but smaller than in Run XX.

However, we must consider the fact that the conditions - especially the temperature - differ in the various runs. Also in Runs XVII and XXIII the potassium hydroxide was not completely dissolved in the starting materials, so that a comparison of the runs in detail does not seem justified.

It was thought that the products might possibly depend on the pH value (or the alkoxide ion concentration) of the reaction mixture. It was attempted to use an indicator in order to maintain a constant concentration of hydroxyl and alkoxide ions during the reaction. Several indicators were tested, but all of them were either chemically unstable under the reaction conditions used or their pH range was such that the potassium hydroxide had to be dropped in at an excessively slow rate in order to keep within that range.

However, the tests did show that there has to be a relatively high concentration of hydroxide and alkoxide ions before the reaction proceeds at a reasonable rate.

Despite the fact that it was not possible to maintain controlled concentrations of hydroxide and alkoxide ions, runs were made in which the potassium hydroxide solution was added at different rates.

These are listed in Table III. In both cases the same amount of carbon monoxide is formed. The amount of olefin formed is different. The yield of olefin is smaller in the run with the slower dropping rate. The yield in the run with the higher dropping rate was 24% higher. This difference cannot be accounted for by experimental errors alone.

The ratio of carbon monoxide to olefin is 6.5 : 1 in the fast run and 8 : 1 in the slow run. It must be considered that the chloroform to alcohol ratio is consistently higher in the fast run.

A comparison of the fast run and the series of runs V through X with dropping rates of one drop per second (and different alcohol concentrations) shows that the yield of olefin in the fast run is of the same order - even somewhat smaller - compared with these runs. This seems to be some indication that above a certain pH value the course of the reaction no longer depends on the concentration of the hydroxide and alkoxide ions.

Runs XVIII, XX, and XXI were made using the same amount of potassium hydroxide, chloroform, and alcohol. In each run a different solvent was added. Run XVIII was made with pyridine, which should be more basic than water. In Run XX water was added, and in Run XIX methyl alcohol was added (methyl alcohol is more acid than water). Previous work showed that methyl alcohol reacts with chloroform only at an extremely slow rate. In Run XXI diethyl ether was added to the reaction mixture. Another run which might be considered

for this comparison is Run XVII where no solvent was used.

The results of these runs are shown in Table IV. Yields of about the same order of magnitude are obtained with methanol, ether, and pyridine. This yield is about 23% of the yield obtained in the run with water as solvent. This might suggest that hydroxide or alkoxide ions will enter in the reaction to a much greater extent than the water molecule. If the water would enter the reaction as an acid or a base, then methanol being more acid or pyridine being more basic should be more effective if they take the place of the water in the reaction.

In the case of ether we also have to consider the lower temperature of the reaction mixture, when comparing this run with Run XVII where no water was present in the starting material. Another fact which is important is that the alcohol is diluted by the solvent. This might explain the difference in the yields in Runs XVII and XVIII where the potassium hydroxide in both cases was present as a solid phase and the temperatures were of the same order of magnitude.

The yield of carbon monoxide is especially low in the run with pyridine. Here only 29% of the chloroform occurs as carbon monoxide.

There are photochemical reactions of chloroform reported. Therefore Run XVI was made to learn whether exposing the reaction mixture to ultraviolet light would have any influence on the yield. Unfortunately no quartz flask was available so a pyrex flask had to be used instead. This of course will absorb light with a wave length below  $3000 \text{ \AA}$ . A comparison of the results of this run with closely

related runs shows that the yield of carbon monoxide is higher. The yield of olefin on the other hand is smaller. It might be that the higher yield of carbon monoxide is due to a photochemical decomposition of the chloroform. The yield of the ethylene indicates that the formation of the olefin does not include any free radical mechanism.

Run XIV was carried out under pressure, to test whether pressure would have any influence on the formation of the olefin. No unusual results were obtained. The yield of olefin (4.3%) is of about the same order of magnitude as in similar runs without pressure. The yield of carbon monoxide is considerably lower, i.e., more formate is formed. It must be considered that the carbon monoxide might react with the base under the influence of applied pressure.

Some runs were made varying the amounts of potassium hydroxide and chloroform used. The use of alcohol as a solvent was avoided since this would result in a very small percentage yield of olefin.

All of the following runs were made by adding the chloroform to the other reactants at the rate of one drop per second.

In Run XX and Run XXV the amount of chloroform and alcohol used was held constant and in Run XXV a larger volume of aqueous potassium hydroxide solution of the same strength was used as a starting material. The yield of olefin was smaller in this run than in Run XX (Table V). The amount of carbon monoxide formed was about 6% higher. That means that in a more diluted solution of alcohol in aqueous potassium hydroxide less olefin is produced by the same amount

of chloroform.

In Run XXIV and Run XX the amount of all other reactants was the same but the amount of alcohol used was varied. In Run XXIV, where less alcohol was present in the starting materials a greater percentage of it was changed to olefin, the amount of carbon monoxide formed being about 3% smaller.

It might of course be possible by using still less alcohol to obtain even higher percentage yields of olefin. But if we consider the mols olefin formed per mole chloroform or potassium hydroxide used we see that less olefin per mole of these starting materials is formed, i.e., despite the fact that the percentage yield of olefin based on alcohol is improved, the method becomes less economical with respect to the other starting materials used. It is for this reason that the conditions of Run XXIV were used for the higher alcohols - they gave the highest yield in the case of ethyl alcohol without being too wasteful of the other starting materials. The results using higher alcohols are compiled in Table VI.

As the table shows, the yield of olefin depends mainly on whether the alcohol is primary or secondary and tertiary. There is no dependence on the kind of olefin, which is presumably formed as to be seen by Table VII.

The difference within the groups might be neglected to some extent due to the experimental error in the determination.

The determination of the olefin has been carried out for most of the alcohols using sulfuric acid and bromine water both. The

relationship between these determinations is not entirely clear. In general the results obtained by both methods are close together, the values obtained with sulfuric acid being somewhat higher, but in some runs a considerable difference was found. The reason why the bromine water values were chosen for the comparison was based on the following test: Nitrogen saturated at room temperature with chloroform vapors was bubbled through the sulfuric acid which was used for the absorption of the olefin. A contraction of a few milliliters was observed in several gas samples. It is not entirely clear what reaction causes this contraction.

It is possible that the conditions used are not the optimum for the different alcohols. Not all of these alcohols form a homogeneous solution with the aqueous potassium hydroxide. The reaction with the chloroform might take place in both layers, but it might of course be assumed that the greater part of the chloroform will enter the alcoholic layer.

Tests showed that tertiary butyl alcohol does not form two layers under the conditions of the reaction. It is also not separated from the aqueous solution by the decreasing alkalinity during the reaction or the circumstance that the solution becomes saturated with potassium chloride. That means that in the run with tertiary butyl alcohol we do not have a layer which contains the alcohol in a more concentrated form. Another consideration in connection with the fact that the tertiary butyl alcohol does not give higher yields than the secondary alcohols might be that the reaction of the dehydration

might proceed by an E2 mechanism in the case of primary and secondary alcohols and will shift partially to an E1 mechanism in case of the tertiary alcohol, a fact which would be in agreement with the behavior of substances with primary, secondary or tertiary functional groups in other elimination reactions.

Considering the fact that the reaction mixture forms two layers of unknown composition, it is not possible to predict what influence any change of the concentrations of the potassium hydroxide, water, etc., will have on the composition of the different layers and to what extent the reaction will take place in each of them. We have to keep these considerations in mind when we compare the Runs XXVIII and XXIX - runs with isopropyl alcohol using different amounts of water in the starting material. A similar effect was expected as in the case of ethyl alcohol with the same change of the conditions (Runs XX and XXIII) where smaller amount of water caused a drop of the yield of about 40%, while in the run with isopropyl alcohol the drop in the yield was only about 8%.

Although this work was not designed to obtain information about the mechanism of the reaction some possibilities for such a mechanism may be pointed out.

Run XVI, where the reaction mixture was exposed to ultraviolet light, did not show any increase in the yield of the olefin, but a slight decrease. This might be taken as an indication that the reaction which leads to the formation of the olefin does not proceed by a free radical mechanism, since in such a case a positive effect of the ultra-

violet light might be expected.

As to the basic hydrolysis in aqueous solution, J. Hine<sup>32</sup> cited evidence that the first step is the formation of a  $\text{CCl}_3^-$  ion, the next step being the  $\text{S}_{\text{N}}1$  removal of a chloride ion leading to the formation of the  $\text{CCl}_2$  intermediate. This compound is stabilized by resonance. The nucleophilic attack of hydroxide ions on the  $\text{CCl}_2$  intermediate will lead to the formation of carbon monoxide and formate ions as final products.

In the case of aqueous alcoholic solutions there are also alkoxide ions present in the solution, which act as nucleophilic reagents and will compete with the hydroxide ions.

An attack of the alkoxide ion could lead to the formation of  $\text{RO-C-Cl}$ , the same intermediate which Mossler<sup>33</sup> postulated. This intermediate might then undergo  $\text{E1}$  or  $\text{E2}$  elimination reactions resulting in the formation of the olefin, but also  $\text{S}_{\text{N}}2$  (or  $\text{S}_{\text{N}}1$ ) substitution reactions.

The data obtained by this work do not enable a decision to be made as to whether the formation of the olefin proceeds via a carbonium ion ( $\text{E1}$ ) or consists of the removal of a proton by a base and the simultaneous loss of the functional group ( $\text{E2}$ ).

The facts that the yield does not depend on the olefin which is presumable formed and that no benzene has been found among the

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<sup>32</sup>Hine, J., Journal of the American Chemical Society, 72, 2438 (1950).

<sup>33</sup>Mossler, Loc. cit.



products of the run with cyclohexanol does not decide this question without additional assumptions. The same is true of the fact that the yield of the olefin depends on the range of the reaction mixture, since the pH value has influence on various competing reactions of unknown rate constants.

Other workers<sup>34</sup>, however, have pointed out that alkaline solutions favor E2 reactions relative to E1. They also showed that secondary compounds undergo E2 eliminations easier than primary compounds. This suggests that - at least in the case of primary and secondary alcohols - the reaction proceeds by an E2 mechanism. We must however, keep in mind that there is some possibility for tertiary compounds to react via carbonium ions.

The indication that camphene is formed from isoborneol would suggest an E1 mechanism in this special case, since this reaction involves a molecular rearrangement and these most commonly proceed via carbonium ions.

The E2 elimination reaction would consist of a nucleophilic attack of hydroxide or alkoxide ions on the beta hydrogen and the simultaneous removal of the  $\text{COCl}^-$  - the latter ion breaking up into chloride ion and carbon monoxide. In summary this E2 reaction would yield ethylene and carbon monoxide in the ratio 1 : 1.

On the other hand we have also to consider possible  $\text{S}_{\text{N}}2$  replace-

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<sup>34</sup>Dhar, M.L., E. J. Hughes, C. K. Ingold, A. M. M. Mandour, G. A. Maw, and L. I. Woolf, Journal of the Chemical Society, London, 1948, 2093.

ment reactions, which this RO-C-Cl intermediate might undergo. We might first consider the replacement of the COCl<sup>-</sup> by hydroxide or ethoxide ions. The latter ion would cause the formation of ether, while an attack of the hydroxide ions would reproduce the alcohol. The COCl<sup>-</sup> would break up into carbon monoxide and chlorine ions.

The other way of a S<sub>N</sub>2 reaction would be the replacement of the chlorine of the intermediate Cl-C-OR. The action of hydroxide ions could cause - via an intermediate enolform - the formation of ethyl formate, which of course would be saponified under the conditions of the reaction, regenerating the alcohol.

If the chlorine ion is replaced by an alkoxide ion the compound RO-C-OR would be obtained.

Action of alcohol - or alkoxide ions - could cause the formation of triethyl formate, action of water - or hydroxide ions - could cause the formation of ethyl formate, which would be saponified to ethyl alcohol and formic acid.

If we consider the steps which lead to the different products, we see that there are various possibilities for the formation of carbon monoxide aside from the formation of carbon monoxide in direct connection with the formation of the olefin. Any deviations from the ratio 1 : 1 between carbon monoxide and olefin are due to the formation of carbon monoxide in other steps of the reaction. We do not see so far any reason for a constant ratio between carbon monoxide and ethylene other than 1 : 1, if not by coincidence, i.e., that the change of concentrations, etc., causes the same effect on the forma-

tion of the olefin as on the formation of the carbon monoxide.

As to the formation of the ether and the orthoformate these mechanisms would suggest that the yield of these compounds will be low as soon as hydroxide ions are present in the reaction mixture, i.e., as soon as water is among the starting materials.

The yield of olefin on the other hand should depend on the amount of alcohol or alkoxide ions which become attached to the intermediate, and on the relative ease of the  $S_N2$  and E2 reactions described.

The amount of alcohol attached to the intermediate would depend on the amount of alcohol present in the starting material, the acidity of the alcohol, and the nucleophilicity of the alkoxide ions.

On the other hand, as has already been mentioned, it is reported that secondary compounds undergo E2 elimination reactions easier than primary compounds.

Since this effect and the probable greater nucleophilicity of secondary alkoxide ions affect the yield of olefin in the same direction, it is so far not possible to decide whether the higher yield of olefin obtained is due to the higher amount of the RO-C-Cl intermediate or due to the fact that the elimination reaction is favored relative to the replacement reaction, although the amount of the intermediate RO-C-Cl did not increase.

Except in runs where little or no water is present in the starting materials, this mechanism demands that every replacement reaction leads to the regeneration of the alcohol. This consideration might explain the fact that by using more chloroform and alkali the percent

yield of olefin is increased, as it was to be seen by the comparison of Runs XX and XXIV.

The fact that the reaction proceeds slowly at low pH ranges will be explained by the low acidity of chloroform. Relatively high alkali concentrations are needed to form the  $\text{CCl}_3^-$  ion.

The fact that better yields of olefin are obtained, when limited amounts of water are present in the starting materials, is not so easily explained.

It is not very likely that the reason is that considerable amounts of alcohol are converted into orthoformate, since the best yield was obtained using 78% alcohol while the amount of orthoformate formed dropped very much when 98% alcohol was used instead of absolute alcohol. And in this series we even used alcohol as a solvent, but this of course is not true for the optimum run with 57% aqueous potassium hydroxide solution and only small amounts of alcohol.

Determinations of the rate constants of the different reactions might bring the explanation for this fact that in less alcoholic solutions more olefin is formed, since with ad hoc assumed rate constants for the different eliminations and substitution reactions it is possible to explain this increase of the yield of the olefin by the addition of water.

The final drop, of course, will be due to the fact that still less alkoxide ions are available to be attached to the  $\text{CCl}_2$  to form the  $\text{RO-C-Cl}$ , and still more of the chloroform will be hydrolyzed according to equations which apply for basic hydrolysis by aqueous alkali.

APPENDIX 1

TABLE 1

Effect of Solvent Composition on Formation of Carbon Monoxide and Ethylene in Aqueous Ethanol Solution.

Run Number	V	VI	VII	VIII	IX	X
Mol KOH	0.551	0.453	0.477	0.477	0.440	0.440
% of Alcohol in Solvent	abs.	91.2	78.4	49.3	33.4	8.1
Mol Olefin	0.0119	0.0137	0.0158	0.0145	0.0119	0.0047
Mol CO	0.0457	0.0519	0.0624	0.0652	0.0821	0.118
Ratio CO/olefin	3.84	3.8	3.82	4.5	6.9	25.2
Ratio CO/KOH	0.083	0.115	0.131	0.137	0.187	0.268
Ratio Olef./KOH	0.0216	0.0302	0.0331	0.0301	0.0268	0.0106

TABLE 2

Effect of Water Concentration on the Yield of Ethylene from a  
Given Amount of Ethanol.

Run Number	XVII	XX	XXII	XXIII
KOH g.	200	100	100	100
Chloroform ml.	50	25	25	25
Alcohol ml.	20	10	10	10
Water ml.	-	75	150	35
Mol CO	0.288	0.112	0.0272	0.0411
Mol Olefin	0.0164	0.0090	0.0025	0.0055
% Yield Olefin	4.8	5.3	1.4	3.1
Ratio CO to Olefin	17.6	12	11	7.4

TABLE 3

Results Obtained with Varying Rates of Addition of Alkali.

Run Number	XI	XII
Mol KOH	0.464	0.464
KOH Solution Added In	6 minutes	23 hours
% Alcohol	38	38
Ratio CO Olefin	6.5	8.0
Ratio CO KOH	0.177	0.177
Ratio Olefin KOH	0.0273	0.0220
Mol CO	0.0820	0.0823
Mol Olefin	0.0127	0.0102



TABLE 4

Effect of the Addition of Various Solvents on the Course of the Reaction.

Run Number	XVII	XVIII	XIX	XX	XXI
Solvent Used		pyridine	CH <sub>3</sub> OH	H <sub>2</sub> O	ether
KOH g.	200	200	100	100	100
Chloroform ml.	50	50	25	25	25
Alcohol ml.	20	20	10	10	10
Solvent ml.	-	75	75	75	100
Mol CO	0.288	0.0176	0.041	0.112	0.0569
Mol Olefin	0.0164	0.0042	0.0026	0.0090	0.0019
% Yield Olefin	4.8	1.2	1.2	5.3	1.1
Mol CO Mol KOH	0.096	0.006	0.027	0.075	0.038
Ratio CO Olefin	17.6	4.2	19.9	12	29.9

TABLE 5

Economy of the Reaction in Dependence on the Amount of Alcohol

Run Number	XXV	XX	XXIV
KOH g.	400	100	200
Chloroform ml.	25	25	50
Alcohol ml.	5	10	10
Water ml.	300	75	150
Mol CO	0.119	0.112	0.216
Mol Olefin	0.0019	0.009	0.0127
% Yield Olefin	2.2	5.3	7.5
Ratio CO : Olefin	64	12	17
Ratio $\frac{\text{Mol Olefin}}{\text{Mol KOH}}$	-	0.006 : 1	0.0042 : 1

TABLE 6a

Yields of Olefin Obtained with Various Primary Alcohols.

Alcohols	Ethyl	n-Propyl	n-Butyl	iso-Butyl
Ratio CO Olef.	17	15	14	8.9
Bottle 1	9.2	9.3	9.6	7.6
Bottle 2	108	48	43	17
Bottle 3	-	-	-	-
Mol Olefin	0.0127	0.0141	0.0131	0.0186
Bottle 1	0.0117	0.0122	0.0114	0.0160
Bottle 2	0.0010	0.0019	0.0017	0.0026
Bottle 3	-	-	-	-
Mol CO	0.216	0.205	0.185	0.166
Bottle 1	0.108	0.114	0.110	0.122
Bottle 2	0.108	0.091	0.075	0.044
Bottle 3	-	-	-	-
% Yield	7.5	8.3	7.7	10.9

TABLE 6b

Yields of Olefin Obtained with Various Secondary and Tertiary Alcohols.

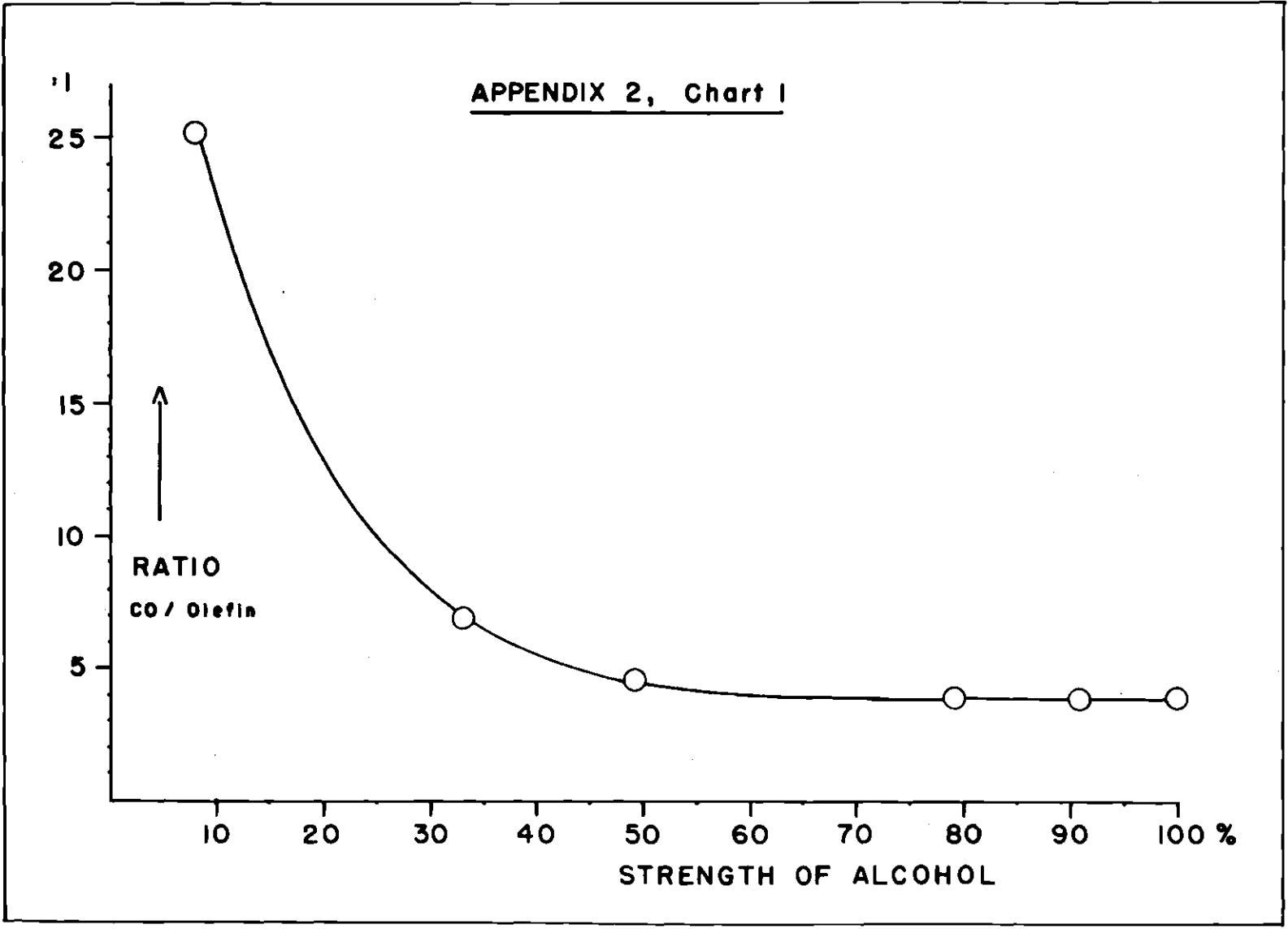
Alcohols		iso-Propyl	sec-Butyl	tert-Butyl	Cyclohexanol
Ratio CO	Olefin	5.1	3.6	3.3	
Bottle 1		4.6	2	1.8	
Bottle 2		5.7	8	7.8	
Bottle 3		2.3	-	-	
Mols Olefin		0.0479	0.0580	0.0555	
Bottle 1		0.0247	0.0426	0.0417	
Bottle 2		0.0223	0.0149	0.0138	
Bottle 3		0.0009	-	-	
Mols CO		0.245	0.209	0.183	
Bottle 1		0.115	0.0869	0.0760	
Bottle 2		0.128	0.120	0.1073	
Bottle 3		0.0021	-	-	
% Yield		28.2	34.1	32.6	13.8

TABLE 7

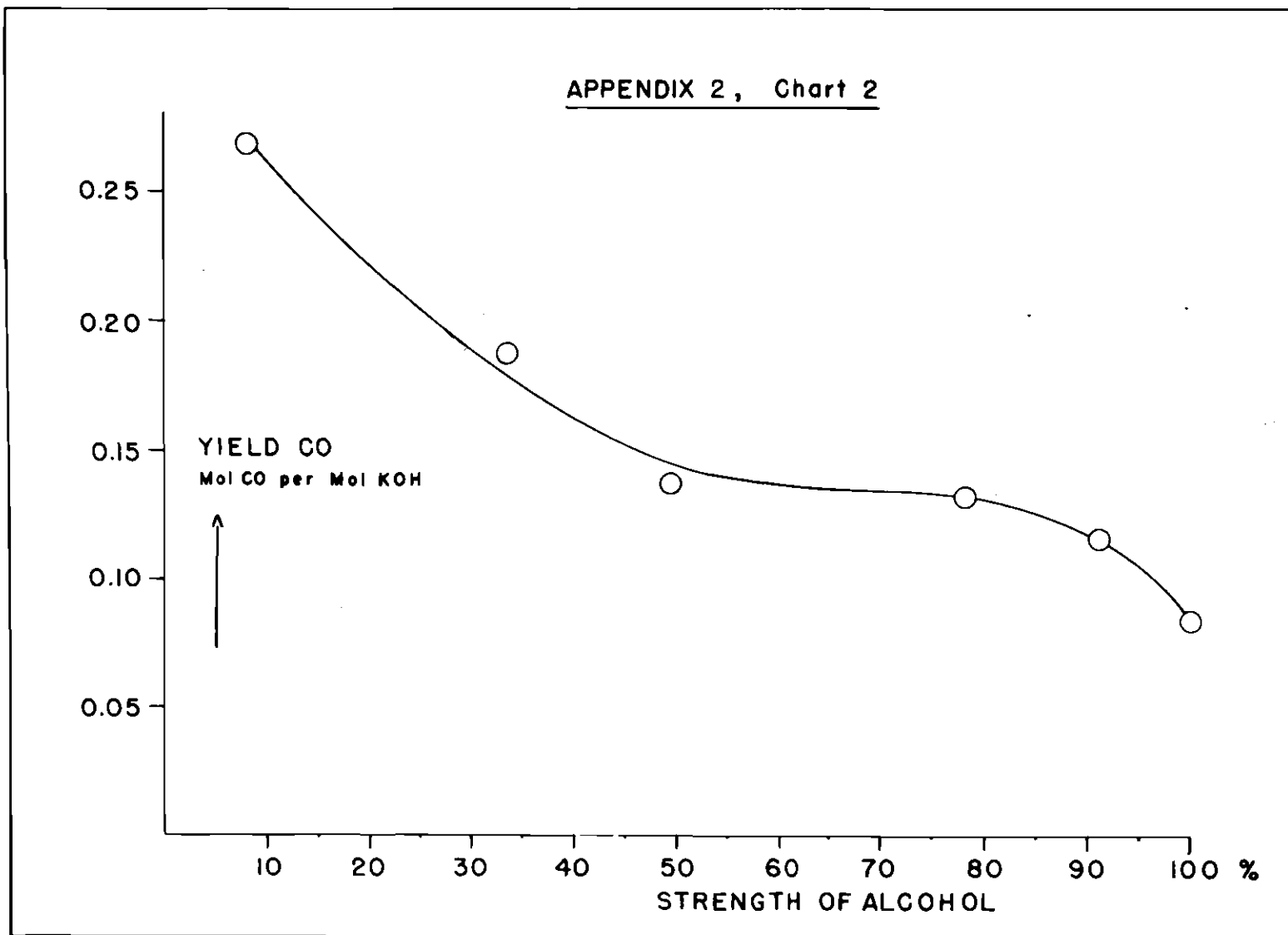
Yields of Olefin Which are Presumably Formed from Different Alcohols as Starting Materials.

Olefin	Alcohol	Yield
Ethylene	Ethyl Alcohol	7.5%
Propylene	n-Propyl Alcohol	8.3%
	iso-Propyl Alcohol	28.2%
n-Butylene	sec-Butyl Alcohol	34.1%
	n-Butyl Alcohol	7.7%
iso-Butylene	tert-Butyl Alcohol	32.6%
	iso-Butyl Alcohol	10.9%

APPENDIX 2

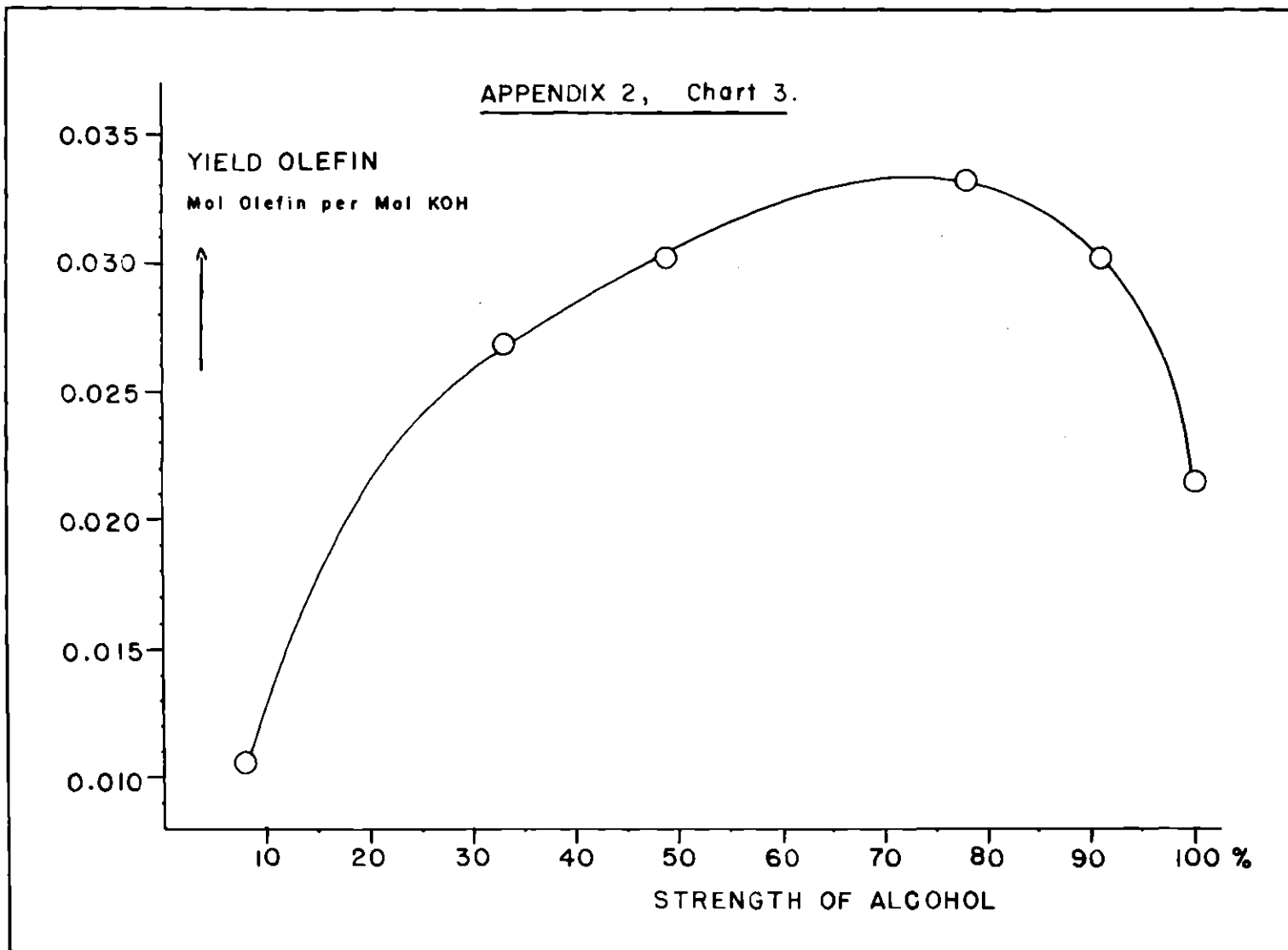


APPENDIX 2, Chart 2





APPENDIX 2, Chart 3.



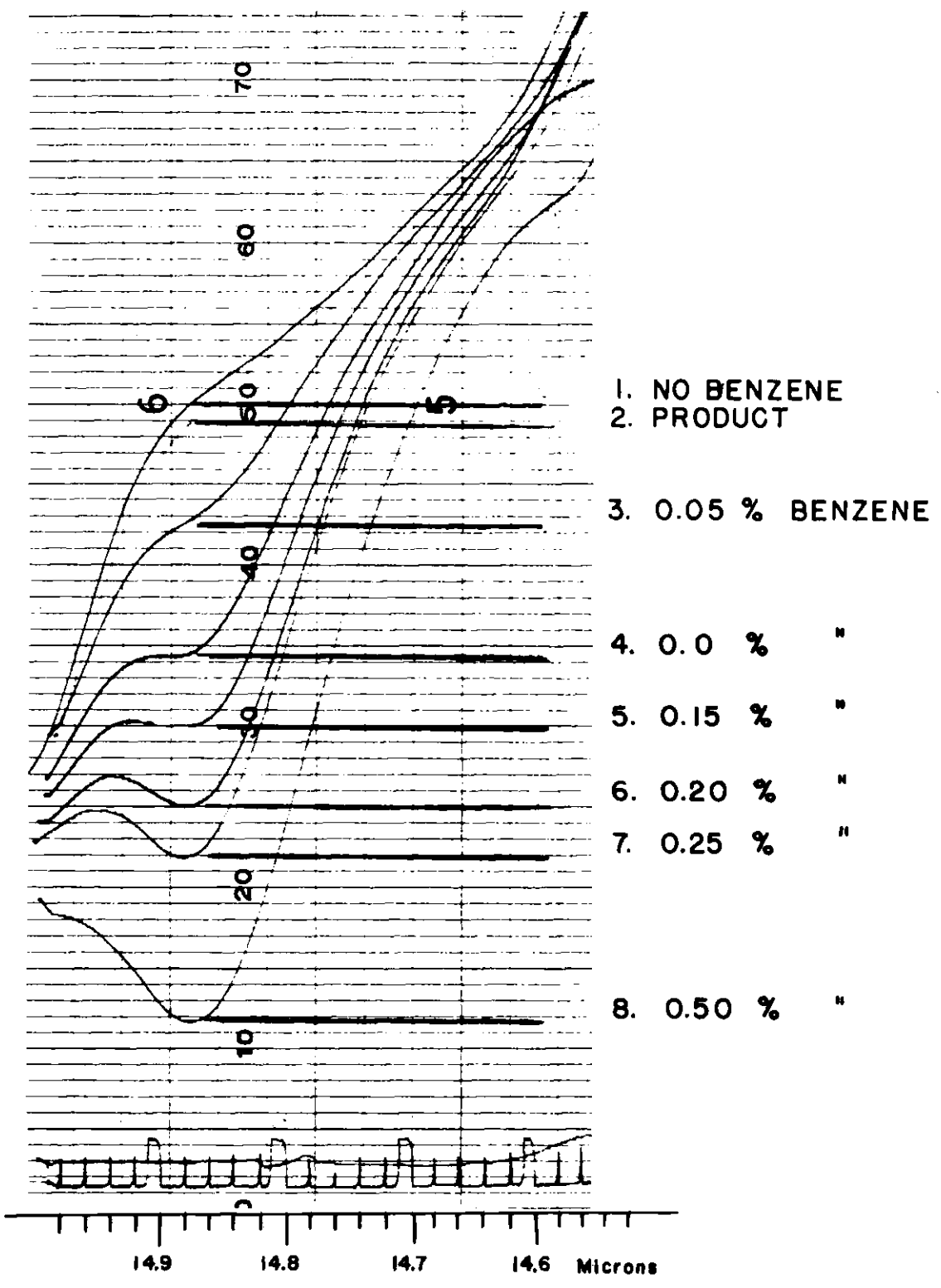
## NOTE TO CHART 4

The following samples were recorded on this chart:

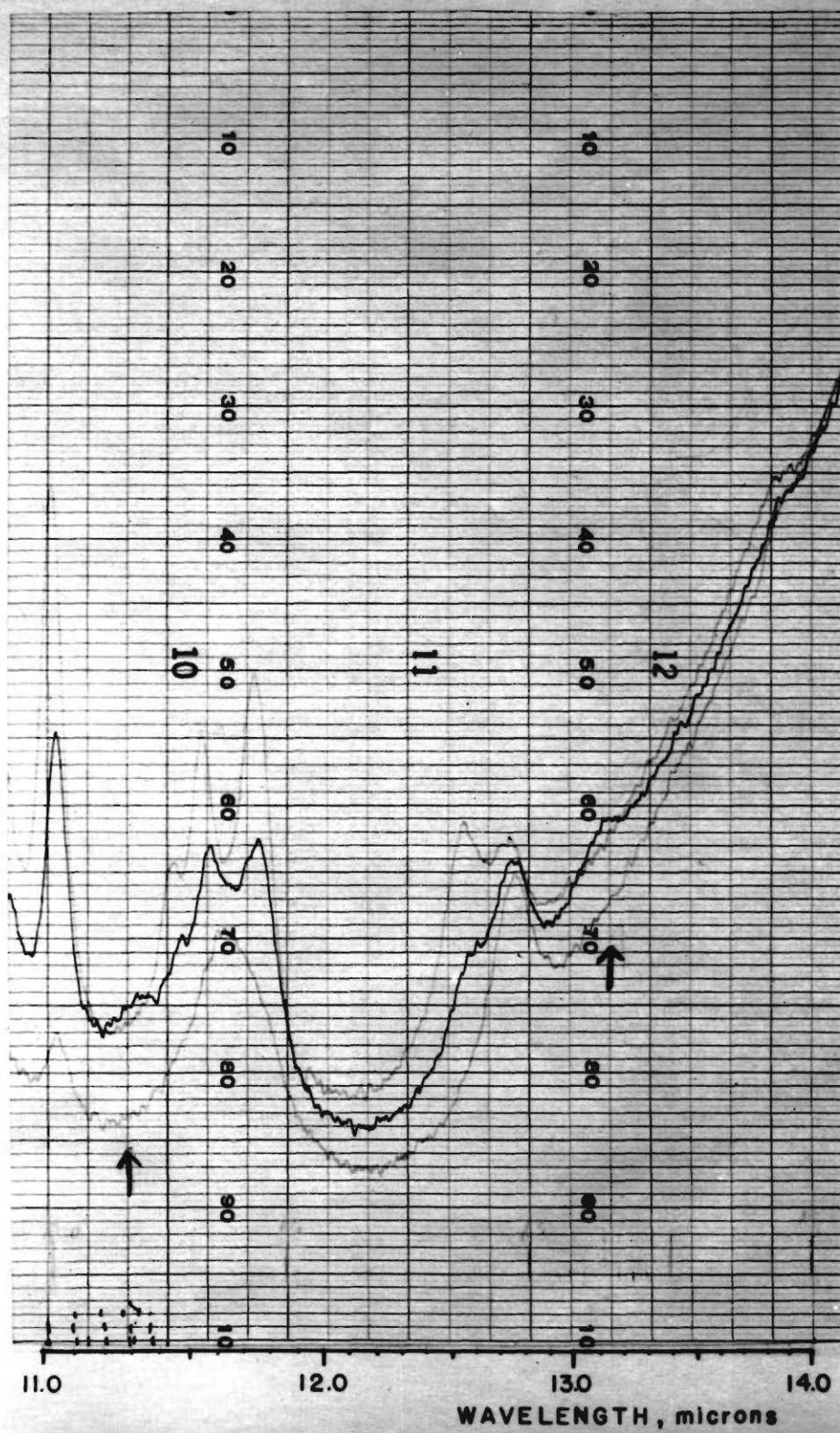
1. 3% solution of cyclohexene in iso-octane.
2. Solution of the product of Run XXXV as it was prepared for the titration of cyclohexene by bromine solution.
3. 3% solution of cyclohexene in iso-octane containing 0.05% benzene.
4. " " " " " " " 0.10% "
5. " " " " " " " 0.15% "
6. " " " " " " " 0.20% "
7. " " " " " " " 0.25% "
8. " " " " " " " 0.50% "

It is evident that there is less than 0.005% benzene in the solution of the products of Run XXXV. Compared with the yield of cyclohexene in these runs, this means that less than 0.2% of the elimination reaction has led to the formation of benzene.

APPENDIX 2, Chart 4 .



APPENDIX 2, Chart 5



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