# THE EFFECT OF MERCURY ON THE QUANTITATIVE BROMINATION OF UNSATURATED COMPOUNDS

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# INTRODUCTION

It has been shown that the simple bromide, bromate procedure for the determination of unsaturation is unsatisfactory for triple bonded compounds. Davis, Crandall and Hibee (1) have pointed out that in the case of acetylene, interference is due to the presence of oxygen. Quantitative bromination can be achieved by carrying out the reaction in an oxygen free system (evacuated). The authors also pointed out that the bromination of acetylene is catalysed by aluminum, nickel and mercury salts. Frieman, Kennedy and Lucas (2) have definitely shown that the use of a mercuric sulfate catalyst in the bromination of a sulfuric acid solution of acetylene yields theorectical results, each mole of acetylene adding two moles of bromine. Mulliken and Wakeman (3) attempted to determine liquid alkynes by bromination and obtained low results. The purpose of the work presented in this thesis is to find a general method for the quantitative bromination of unsaturated compounds by studying:

(a) The bromination of different triple bonded compounds.

(b) The effect of mercuric sulfate on these brominations.

(c) The effect of mercury upon the bromination of double bonded compounds, both those easily and those difficultly brominated in the absence of mercury.

(d) The effect of oxygen and peroxides on these systems.

## THE ANALYTICAL METHOD EVOLVED

The procedure finally evolved is based upon the method of analysis used by Frieman, Kennedy and Lucas (2). A calculated 10 - 15% excess of 0.1 N. potassium bromate-bromide (about 25 ml.) solution is run into a 300 ml. conical flask fitted with a ground glass stopper bearing a sealed-in stopcock. The flask is then evacuated by a water aspirator, 5 ml. of 6 N. sulfuric acid is added and the flask permitted to stand 2 - 3 minutes to permit the liberation of bromine. Next, there are added in order 10 - 20 ml. of .2 f$HgSO_4$ solution so that the ratio of the mercury concentration to the bromide concentration is more than 1, 5 ml. of the solution of the alkyne to be analysed in $CCl_4$ (the solution should contain about 2 milliequivalents of unsaturation), and 20 ml. of glacial acetic acid. The mixture is still under vacuum. The flask is wrapped in a black cloth and is shaken vigorously for about 7 minutes. Then 15 ml. 2 f.NaCl and 15 ml. of 20% KI solution are added and the shaking continued for ½ minute. The vacuum is broken and the titration made with .05 N. sodium thiosulfate solution to the starch end point. A blank is run at the same time to measure the bromination of acetic acid in the mercury medium. In the case that the substance to be brominated is water soluble, the unkown is added as an aqueous solution and the acetic acid is unnecessary.

## Discussion of Analytical Method

A large excess of bromine is avoided in order to reduce the possibility of substitution of either the hydrocarbon or the acetic acid. The first run on a sample will give an approximate value for the amount of bromine used, so that the next run may be made with only the slight excess required. The mercury concentration must be greater than that of the bromide, present as such, before efficient catalysis occurs. It has been found that acetic acid, even though it introduces a slight error, aids the bromination by increasing the distribution ratio of bromine and alkyne between the aqueous and the organic phases. This is helpful since the mercury catalyst appears to be active only in the aqueous phase. When acetic acid is not used, the results are not nearly as reproducible as when it is used and the increased time of bromination can introduce an appreciable substitution error. Sodium chloride has been found (2) to overcome the uncertainity of the starch-iodine endpoint in these solutions. It is impossible to use the carbon tetrachloride iodine endpoint since the acetic acid so enlarges the apparent distribution of iodine between the aqueous and the organic phases that the latter has only a faint pink while the former is a deep yellow. However, this effect makes for ease in the titration. The blank run with acetic acid must be made with discretion, since during the real run, the bromine concentration drops enormously in the first moments of the bromination and the substitution process is very dependent on the bromine concentration. The presence of peroxides in the hydrocarbon causes a shifting endpoint.

## Special Apparatus for Holding Hydrocarbon Solution

A means for working with dilute solution of hydrocarbons and for volumetric sampling was found in this device. The solution is made by breaking a sealed ampule, containing a weighed quantity of hydrocarbon, under carbon tetrachloride in a weighed glass stoppered bottle of 150 ml volume. After being filled with $CCl_4$ and after a thorough mixing of the contents, the bottle is again weighed. From the weights of the 2 liquids, their densities at the temperature of the mixture, and the assumption of perfect solution (additive volumes), it is possible to calculate a volume formality for the solution. Next the bottle is fitted with a two hole rubber stopper containing a separatory funnel and a glass tube through which the pipette can be introduced. The pipette used was similar to that described by Eberz and Lucas (4) and was lubricated with a water soluble stop cock grease (5) which would not be leached out by the $CCl_4$, introducing errors. The liquid was forced up into the pipette by mercury admitted through the separatory funnel. This procedure was adopted in order to avoid fractionating any volatile hydrocarbon from the solvent. Were air to be used to force the liquid up the pipette, this would happen, especially if the airspace above the liquid was appreciable, since then the air would be renewed at each sampling by the compression process. This error was observed in a mixture of pentene and carbon tetrachloride. Sucking up the solution would surely produce errors in the lighter hydrocarbon. Carbon tetrachloride was chosen for the solvent because of the great solvent power toward hydrocarbons, greater than acetic acid which would yield homogeneous systems, however.

# RESULTS OBTAINABLE

Mercury Present

| Substance | Acetic Acid | Time Min. | Average percent error |
|---|---|---|---|
| 1 Pentyne | 0 | 2 | + 2. |
| 1 Hexyne | 0 | 3 | + 1. |
| 1 Heptyne | 0 | 35 | + 1.5 |
| | 20 | 10 | - 1. |
| 2 Heptyne | 0 | 10 | - 4. |
| | 20 | 10 | - 2. |
| Phenyl Acetylene | 15 | 7 | - 2. |
| Propiolic Acid | 0 | 2 | +45. |
| Cyclohexene | 15 | 3 | + 0.5 |
| 1 Hexene | 15 | 3 | + 0.7 |
| 2,3 Dimethyl-butadiene | 15 | 5 | +20. |
| Dichloroethylene | 0 | 70 | - 1.0 |
| | Solution made with HOAc | 10 | - 1.5 |
| Mixture of phenyl acetylene and cyclohexene | | | |
| | 15 | 5 | - 1. |
| Maleic acid | 0 | 25 | 0. |
| Fumaric acid | 0 | 30 | 0. |
| Cinnamic acid | 0 | 5 | +67. |

## RESULTS OBTAINABLE

Mercury Absent

| Substance | Acetic Acid | Time Min. | Average Percent Error |
|---|---|---|---|
| 1 Hexyne | 0 | 30 | - 41. |
|  | 20. | 10 | - 44. |
| 1 Heptyne | 0 | 30 | - 39. |
|  | 15. | 5 | - 50. |
| 2 Heptyne | 0 | 10 | - 26. |
|  | 20. | 7 | - 23. |
| Phenyl Acetylene | 20. | 7 | - 11. |
| Propiolic Acid | 0 | 15 | - 78. |
| Cyclohexene | 0 | 3 | 0 |
| 1 Hexene | 0 | 5 | - 0.7 |
|  | 15. | 3 | - 0.3 |
| 2,3 Dimethyl-butadiene | 0 | 5 | - 29. |
|  | 15. | 5 | - 35. |
| Dichloroethylene | 0 | 100 | - 30. |
|  | Solution made with HOAc | 20 | - 98. |
| Maleic acid | 0 | 20 | - 98. |
| Fumaric acid | 0 | 10 | - 99. |
| Cinnamic acid | 0 | 3 | † 3.5 |

# CONCLUSIONS

I. Triple bonded hydrocarbons can be quantitatively brominated by the general procedure as has been shown in the case of 1 pentyne, 1 hexyne, 1 heptyne, 2 heptyne and phenyl acetylene.

II. The presence of mercury is necessary as has been shown by the fact that the compounds listed just above are only slightly effected by bromine in the absence of mercury.

III. Mercury does not effect the bromination of most double bonded hydrocarbons as has been shown in the bromination of cyclohexene and 1 hexene.

IV. Excessive substitution may be caused in certain compounds by the presence of mercury, as in the case with propiolic acid, cinnamic acid and 2,3 dimethyle butadiene.

V. Certain compounds which are substituted by the action of mercury may be quantitatively brominated in the absence of mercury which is the case of cinnamic acid.

VI. Certain double bonded compounds which are normally brominated with difficulty are quite readily brominated in the presence of mercury. Cases of the effect are dichloroethlyene, maleic acid and fumaric acid.

VII. A peculiar mercuric ion-bromide ion complex must be formed which contains equal moles of bromide and mercury, since the mercury is effective only if the mercury to bromide concentration is greater than unit. If the ratio is less than unity, the catalysis may be effected by the dissociation of this complex.

VIII. The bromination occurs in the aqueous phase, since it is only when an intimate contact of the two phases present occurs or acetic acid is present to increase the distribution ratio of the hydrocarbon between the aqueous and carbon tetrachloride phases that quantitative bromination occurs.

IX. It is possible that the formation of the stable emulsions of the carbon tetrachloride in the aqueous phase in the absence of acetic acid has something to do with the reactions taking place. Emulsions formed only with the 1 alkynes. The emulsions broke down after the bromination was over. Conditions that increased the rate of bromination such as excess mercury or bromine weakened the emulsion.

X. Perhaps a carboxyl group adjacent to an unsaturated linkage affects the ease of substitution farther along the molecule. This was the case with cinnamic and propiolic acids.

XI. Old acetylene compounds which have been exposed to air give variable results which are most likely due to the fact that slow oxidation has taken place to produce aldehydes. The peroxides formed must be of a very loose character since no peroxide test was obtained with the old hydrocarbons.

XII. The error due to substitution cannot be found by an extrapolation to zero time of the final rate of substitution which can be found by runs of various time lengths, since the bromine concentration varys appreciably during the initiation of the bromination.

## INDIVIDUAL ANALYSES

### 1 PENTYNE

The pentyne was made up as a carbon tetrachloride solution and the standard procedure was followed except that no acetic acid was added, since this technique had not been developed at that time. Several runs were made in order to improve my method of handling the hydrocarbons. When the carbon tetrachloride and the aqueous phases were shaken vigorously, a thick emulsion of great stability formed, which afforded a very large surface between the two phases. The pentyne brominated quantitatively in about 2 minutes. No runs were made without any mercury present. All of the errors were positive and indicated substitution. This must have been true since the enlengthened action of bromine upon the mixture increased the positive errors at rate of about ¼% per minute. The determination was quantitative under the conditions described and therefore should be quantitative under the conditions of the general procedure outlined above.

| # | Time Min. | Mercury to Bromide Ratio | excess $KBrO_3$ % | Percent error | |
|---|---|---|---|---|---|
| Solution #A | | | | | |
| 1 | 20 | 1.7 | 5 | +5.5 | |
| 2 | 20 | 1.7 | 12 | +7.5 | |
| 3 | 5 | 1.7 | | +5.0 | |
| Solution #B | | | | | |
| 1 | 2 | 1.3 | | +3.4 | |
| 2 | 2 | 1.3 | | +1.6 | |
| 3 | 4 | 1.3 | | +2.5 | |
| 4 | 1.5 | 1.3 | | +1.9 | |
| 5 | 2 | 1.3 | | +2.1 | |
| 6 | 2 | 1.3 | | +1.9 | |
| 7 | 20 | 1.0 | | +12. | 25% excess bromine was present. |

## 1 HEXYNE

The solutions used were made up in carbon tetrachloride according to the standard procedure. Solutions of the freshly prepared, old, refractionated old, and old refractionated materials were made up at different times. In all cases the two phases formed thick emulsions so it was deemed unnecessary to add any acetic acid except in the case of solution #E for reasons to be discussed under that heading. In solutions #A and #B we find that the bromination was quantitative within two or three minutes, and that only slight substitution occurred in a 20 minute bromination period. Without the aid of mercury, the bromination only proceeded 60% in a 30 minute period. This indicates that the general procedure should give quantitative results.

Solution #A

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 2 | 2.1 | + 1.0 |
| 2 | 3 | 1.1 | + 0.7 |
| 3 | 2 | 1.1 | + 1.65 |
| 4 | 3 | 1.1 | + 1.2 |
| 5 | 20 | 1.1 | + 3.2 |
| 6 | 30 | 0 | -41. |

Solution #B

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 2.5 | .9 | - 1.9 |
| 2 | 3. | .9 | - 3.3 |
| 3 | 3. | .9 | - 2.8 |

Solution #B (Cont'd)

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 4 | 3 | .9 | - 2.6 |
| 5 | 3 | .9 | - 1.4 |
| 6 | 3 | 1.0 | - 4.3 |
| 7 | 3 | 1.0 | 0.0 |

Solution #C was made from some of the Hexyne which had aged for 2½ months in a cork stoppered bottle. For some unexplainable reason the results were very errotic, being both positive and negative under what should be the same conditions.

Solution #C (2.5 mo. old)

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 5 | 1.0 | + 2.7 |
| 2 | 5 | 1.0 | -14. |
| 3 | 10 | 1.0 | - 5.3 |
| 4 | 10 | 1.0 | + 6.7 |
| 5 | 10 | 1.3 | - 5.8 |
| 6 | 30 | 1.0 | - 0.8 |
| 7 | 35 | 1.0 | + 3.5 |
| 8 | 30 | 1.0 | - 5.8 |

Solution #D was made up of a freshly refractionated portion of the hexyne used in #C, but the results were again errotic. Apparently the fractionation did not correct the cause of the errors. The only recognizable error is that of substitution in the longer time brominations.

Solution #D freshly distilled

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 5 | 1.1 | - 13. |
| 2 | 5 | 1.1 | - 1. |
| 3 | 5 | 1.1 | - 10. |
| 4 | 5 | 1.5 | - 12. |
| 5 | 30 | 1.1 | + 2.6 |
| 6 | 30 | 1.1 | + 4. |
| 7 | 40 | 1.2 | + 8. |

Solution #E was made up in carbon tetrachloride in order to test the use of acetic acid in ironing out the errors. The results obtained, omitting #2 indicate that the bromination is complete in about 4 minutes and that the substitution error is appreciable. Nevertheless this shows that the hexyne may be determined by the general procedure. No distillation was performed in an inert atmosphere which would have perhaps removed errors due to oxygen effects. See 1 Heptyne for discussion of Oxygen effects.

Solution #E (3 weeks old

| # | Time Min. | Mercury To Bromide Ratio | Acetic Acid | Percent error |
|---|---|---|---|---|
| 1 | 7 | 1.1 | 20. | + 6.6 |
| 2 | 6 | 1.1 | 20. | - 2.6 |
| 3 | 6 | 1.1 | 20. | + 2.6 |
| 4 | 5 | 1.1 | 20. | + 0.9 |
| 5 | 4 | 1.4 | 20. | + .9 |
| 6 | 1.5 | 1.1 | 20. | - 4.4 |
| 7 | 25 | 1.1 | 20. | + 7.1 |
| 8 | 10 | 0 | 20. | -44. |

1 HEPTYNE

The solutions analyzed were made up in carbon tetrachloride. Solutions A and B were made up with the freshly prepared heptyne and were run before the acetic acid technique was available. Solution #C was made of the hexyne when it was one month old, while #D was made the day after from a sample, which had been freshly distilled in an inert atmosphere. Solution #A shows that bromination is very slow in the absence of mercury and was fairly slow in the presence of mercury. The bromination was quantitative after about 10 minutes of bromine action. However, there must be an appreciable amount of substitution in that time. Solution #B was a check upon the time length chosen. A half hour gave quantitative results while the one run of an hour did not indicate excessive substitution.

Solution #C shows that the old solution which had been stored in a cork stoppered bottle did not brominate nearly as readily as the freshly prepared hydrocarbon. The bromination carried out at conditions similar to those of solution #B gave results which were 10% low while those conditions worked out in solution #D resulted 17% low.

Solution #D proves that distillation was able to remove any products which were interfering with the bromination. The bromination in that case, proceeded quite rapidly to completion within about ten minutes, and there was not much substitution there after. The lowness of the old heptyne must be due to peroxide formation with a subsequent slow decomposition to aldehydes or acids. However, the peroxide would have to be a loose one since the heptyne gave no peroxide test.

**Solution #A** recently syn. & dist.

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 2.5 | 1.2 | -20. |
| 2 | 5 | 1.2 | -13. |
| 3 | 5 | 1.2 | - 9. |
| 4 | 5 | 1.2 | -11. |
| 5 | 5 | 1.2 | - 7. |
| 6 | 5 | 1.2 | -13. |
| 7 | 15 | 1.2 | -10. |
| 8 | 15 | 2.0 | - 1.8 |
| 9 | 17 | 1.2 | + 1.3 |
| 10 | 35 | 1.2 | + 0.4 |
| 11 | 35 | 1.2 | + 1.4 |
| 12 | 40 | 1.2 | + 1.8 |
| 13 | 55 | 1.2 | - 3. |
| 14 | 75 | 1.2 | +11. |
| 15 | 30 | 0 | -39 |

**Solution #B**

| | | | |
|---|---|---|---|
| 1 | 35 | 1.2 | + 3.1 |
| 2 | 35 | 1.2 | 0.0 |
| 3 | 35 | 1.2 | + 2.3 |
| 4 | 65 | 1.2 | 0.0 |

**Solution #C** (old) 5 wks.

| # | Time Min. | Mercury To Bromide Ratio | Acetic acid ml | Percent error |
|---|---|---|---|---|
| 1 | 5 | 0 | 15. | -75. |
| 2 | 25 | 1.2 | 0 | -10. |
| 3 | 5 | 1.2 | 15. | - 6.7 |
| 4 | 5 | 1.2 | 15. | -10. |
| 5 | 5 | 1.2 | 15. | -12. |
| 6 | 15 | 1.2 | 15. | -17.5 |

**Solution #D** redistilled old sample

| | | | | |
|---|---|---|---|---|
| 1 | 5 | 0 | 15. | -50. |
| 2 | 5 | .9 | 0 | -29. |
| 3 | 5 | .9 | 15. | -11. |
| 4 | 7 | 1.5 | 15. | - 3.5 |
| 5 | 7 | 1.5 | 15. | - 1.2 |
| 6 | 8 | 1.5 | 15. | - 2.1 |
| 7 | 35 | 1.5 | 15. | + 2.7 |
| 8 | 60 | 1.5 | 15. | - 2.1 |
| 9 | 15 | 1.5 | 0 | -7. |
| 10 | 15 | 1.5 | 15. | +2.7 |

2 HEPTYNE

Three solutions were made up in carbon tetrachloride according to the standard procedure. The first was analyzed without any acetic acid present. In the second set of runs the procedures with and without acetic acid were compared. Since these solutions were consistently low in their analyses, the hydrocarbon was refractionated before the third solution was made up. Apparently the material had not been 100% heptyne, since the analysis after the distillation yielded a higher value for the analysis, but the reaction did not proceed with any more facility. No emulsions formed as in the case of certain other of the acetylenes, so the reaction was very dependent upon shaking in the case that no acetic acid was present, as can be shown from the case of solution #A. The absence of mercury results in a very slow bromination, only 75% being brominated in 10 minutes.

Solution #A

| # | Time Min. | Mercury To Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 5 | .95 | - 14. |
| 2 | 3 | 1.4 | - 3.8 |
| 3 | 6 | 1.4 | - 8.7 |
| 4 | 10 | 0 | - 26.6 |
| 5 | 12 | 1.4 | - 5.4 |
| 6 | 12 | 1.4 | - 6.5 |

Solution #B shows very clearly the effect of the vigor of shaking. The first four titrations show the variations occurring in runs under apparently similar conditions.

#4 was shaken by a machine for 35 minutes which was not as effective as 10 minutes shaking by hand. The addition of acetic acid very clearly smoothes out the bromination to a value, 4-5% low. Since these errors were consistent, it is quite probable that they were caused by an inert impurity.

Solution #B

| # | Time Min. | Mercury To Bromide Ratio | Acetic Acid | Percent error |
|---|---|---|---|---|
| 1 | 10 | 1.2 | 0 | - 5.8 |
| 2 | 10 | 1.2 | 0 | - 4.4 |
| 3 | 10 | 1.2 | 0 | - 8.3 |
| 4 | 35 | 1.2 | 0 | - 7.8 |
| 5 | 3 | 1.2 | 0 | -10.2 |
| 6 | 3 | 1.2 | 40. | - 6.8 |
| 7 | 10 | 1.2 | 20. | - 4.4 |
| 8 | 10 | 1.2 | 20. | - 3.9 |
| 9 | 10 | 1.2 | 20. | - 4.9 |

Solution #C checks the use of the acetic acid and mercury. This run proves that 2 heptyne can be determined by the general method evolved. After the first two runs were made the $CCl_4$ solution was exposed to the sunlight for 1 hour. This may be the reason why the first two determinations are theoretical while the others are low. A loose peroxide may be present that oxidizes some of the compound in the sunlight.

**Solution #C** Redistilled

| # | Time Min. | Mercury to Bromide Ratio | Acetic Acid | Percent error |
|---|---|---|---|---|
| 1 | 7 | 1.2 | 20. | - 0.2 |
| 2 | 7 | 1.2 | 20. | + 1. |
| 3 | 7 | 1.2 | 20. | -3.2 |
| 4 | 7 | 1.2 | 20. | -3.2 |
| ✓ 5 | 7 | 1.2 | 20. | -4.1 |
| ✓ 6 | 7 | 0 | 20. | -23. |
| ✓ 7 | 7 | 2.4 | 25. | - 3.2 |

## PHENYL ACETYLENE

The solution was made up in carbon tetrachloride. The action of mercury without the aid of acetic acid was not very appreciable even with long shaking since an emulsion with its tremendous surface did not form. With the aid of acetic acid mercury yielded quantitative results causing very little substitution, even over a period of ½ hour. Bromination with the aid of acetic acid, but without the mercury caused a negative error. Phenyl acetylene is quantitatively determined by the general procedure.

| # | Time Min. | Acetic Acid | Mercury to bromide conc. | Percent error |
|---|---|---|---|---|
| 1 | 5 | 0 | 1.5 | -13.7 |
| 2 | 7 | 0 | 1.1 | -22.6 |
| 3 | 25 | 0 | 1.2 | -20.3 |
| 4 | 7 | 25. | 1.1 | - 0.3 |
| 5 | 5 | 20. | 1.1 | 0.0 |
| 6 | 30 | 20. | 1.1 | + 3.7 |
| 7 | 7 | 20. | 0 | -11. |

## PROPIOLIC ACID

Since the propiolic acid used was a dilute aqueous solution of unknown strength, its concentration was determined by an acidimetric titration. The bromination without mercury was very slow proceeding only 20% in 15 minutes, whereas the bromination in the presence of mercury gave substitution which approached absorption of 50% excess bromine. This would correspond to the formation of pentabromopropionic acid.After a certain amount of mercury has been added, the solution suddenly faded. The end point seemed to shift quite rapidly,eqivalent to about three or four drops of thiosulfate per minute, an effect which might be due to any possible peroxides present, but the test solution gave no peroxide test with potassium iodide, sulfuric acid and starch. A quantitative test was made by permitting the brominated solution to stand with the added potassium iodide for 90 minutes and for 60 minutes before titration, the flask being evacuated. The results showed that the iodine thus liberated was not appreciable. There was no possibility for an impurity to be present in sufficient concentration to produce this error. It is impossible to quantitatively determine propiolic acid by bromination.

| # | Time Min. | Mercury to Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 2 | 1.3 | + 33. |
| 2 | 2 | 1.1 | + 42. |

| # | Time Min. | Mercury to Bromide Ratio | Percent error |
|---|---|---|---|
| 3 | 3 | 1.3 | + 47. |
| 4 | 15 | 0 | - 78. |
| 5 | 5 | 1.2 | + 47. |
| 6 | 7 | 1.3 | + 56. |
| 7 | 3 | 1.4 | + 41. * |
| 8 | 3 | 1.4 | + 36. ** |
| 9 | 3 | 1.4 | + 43. |
| 10 | 3 | 1.4 | + 51. |

*Permitted to stand 90 min. with KI before titration

** " " " 60 " " " " "

## CYCLOHEXENE

The cyclohexene was analyzed by the general method. Check runs were made without mercury or acetic acid, with mercury and without acetic acid, and with mercury and acetic acid. The different runs were found to check each other within the experimental error. Hence, it may be concluded that the general method of analysis as described may be used for cyclohexene.

| # | Time Min. | Acetic Acid | Mercury to Bromide Ratio | Percent Error |
|---|---|---|---|---|
| 1 | 3 | 0 | 1.2 | +0.2 |
| 2 | 3 | 0 | 1.2 | +0.2 |
| 3 | 3 | 0 | 0 | -0.2 |
| 4 | 3 | 15 | 1.2 | +0.6 |
| 5 | 3 | 15 | 1.2 | +0.2 |

## 1 HEXENE

The solution used was of an unknown concentration and was made up in carbon tetrachloride. Since bromination without mercury or acetic acid has been shown to be quantitative by Mr. S. Winstein, a comparison may be made with determinations in which mercury and acetic acid are factors. The experimental data shows that neither of these has any effect upon the bromination which is very rapid and proceeds in the carbon tetrachloride as well as in the water phase. Hence, the solution may be determined by the general procedure described.

| # | Time Min. | Mercury to Bromide Ratio | Acetic Acid | Percent Variation from mean |
|---|---|---|---|---|
| 1 | 6 | 0 | 0 | -0.7 |
| 2 | 5 | 0 | 0 | +0.7 |
| 3 | 3 | 0 | 15. | -0.7 |
| 4 | 3 | 0 | 15. | 0.0 |
| 5 | 3 | 1.3 | 15. | +1.0 |
| 6 | 3 | 1.3 | 15. | +0.7 |

## 2,3 DIMETHYLEBUTADIENE

The sample of dimethylbutadiene used was sealed in an ampule immediately after it was distilled and the solution was made up in carbon tetrachloride. The bromination in the absence of mercury was very slow even in the presence of acetic acid. Mr. Winstein has found that acetic acid is effective in the bromination of more concentrated solutions of the dimethylbutadiene in carbon tetrachloride. However, a rough calculation of the concentrations of the unsaturated compound in the carbon tetrachloride at the end of a five minute bromination for a dilute and a concentrated initial solution, yields approximately the same value, indicating that the error is due to slow reaction at low concentrations. The bromination without mercury according to the following data indicates that the bromination was 70% complete in five minutes and 90% complete in 30 minutes. The presence of mercury caused a very rapid bromination. Without the aid of acetic acid, the bromination proceeded readily to a positive error, the magnitude of which may be due to the fact that a 30% excess of bromine was present. With the aid of acetic acid, the mercury caused substitution to proceed so rapidly that a positive error of 8% occured in a bromination period of less than 1 minute, and an error of 35% in 15 minutes. In the brominations involving mercury, a 60% excess of bromine was present, since it was found that a 20% excess was completely used up within 5 minutes. These runs merely show the magnitude of the error introduced by mercury.

Hence, it may be concluded that dimethylbutadiene cannot be determined by the general method since excessive substitution occurs.

| # | Time Min. | Mercury to Bromide Ratio | Acetic acid | Percent Error |
|---|---|---|---|---|
| 1 | 5 | 0 | 0 | -29. |
| 2 | 5 | 0 | 15. | -36. |
| 3 | 5 | 0 | 15. | -35. |
| 4 | 5 | 0 | 15. | -13. |
| 5 | 7 | 1.1 | 0 | + 8. |
| 6 | 5 | 1.1 | 15. | +27. |
| 7 | 5 | 1.1 | 15. | +21. |
| 8 | 15 | 1.1 | 15. | +35. |
| 9 | .75 | 1.2 | 15. | + 8. |

TRANS-DICHLOROETHYLENE

Two different solutions of dichloroethylene were analyzed, one in carbon tetrachloride and the other in glacial acetic acid. This was done before the general procedure, in which acetic acid is added to the brominating flask, was developed. The bromination in carbon tetrachlorid was very slow in the presence of mercury, 90% bromination taking place in a quarter of an hour and 100% in an hour. There was little or no substitution as is shown by the bromination over a period of an hour and a half. Bromination without mercury proceeded very much slower since the bromination only went 70% in 1½ hours.

| # | Time Min. | Ratio of Mercury to Bromide | Percent error |
|---|---|---|---|
| 1 | 12 | 1.5 | - 12 |
| 2 | 70 | 1.4 | - 0.5 |
| 3 | 90 | 1.4 | - 1.2 |
| 4 | 100 | 0 | - 30. |

The bromination of the acetic acid solution proceeds quite rapidly in the presence of mercury, there action being complete in 5-10 minutes. Peculiarly, no bromination appeared to have taken place in the absence of mercury, while appreciable bromination had taken place with the carbon tetrachloride solution. Since mercury and acetic acid have such a pronounced effect upon the bromination of dichloroethylene, I think that I can say that the general procedure evolved would give quantitative results.

| # | Time Min. | Mercury to Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 2 | .8 | - 8.6 |
| 2 | 3 | .8 | - 6.6 |
| 3 | 2 | 1.6 | - 3.4 |
| 4 | 5 | 1.2 | 0.0 |
| 5 | 8 | 1.6 | - 1.0 |
| 6 | 10 | .8 | - 3.0 |
| 7 | 20 | 0 | -98. |

## MIXTURE OF PHENYL ACETYLENE AND CYCLOHEXENE

A solution of .42 g. of phenyl acetylene and 1.3 g. of cyclohexene in 140 ml of carbon tetrachloride was used to demonstrate the fact that the general procedure of analysis for unsaturation is applicable to mixtures. Run #4 shows that mercury is effective in the bromination of triplebonded compounds. The error may seem small but it must be remembered that a large portion of the unsaturation is contributed by the cyclohexene which is not dependant on bromination in the aqueous phase in the presence of mercury. The 4% apparent error is really a 12% error in the acetylene determination.

| # | Time Min. | Mercury to Bromide Ratio | Acetic acid | Percent error |
|---|---|---|---|---|
| 1 | 4 | 1.3 | 15. | -1.0 |
| 2 | 5 | 1.3 | 15. | +1.1 |
| 3 | 5 | 1.3 | 15. | +1.6 |
| 4 | 5 | 0 | 15. | -4.1 |

## MALEIC ACID

The unsaturated compound was made up as an aqueous solution. The bromination is greatly effected by the presence of mercury, since then it brominates quantitatively while negligible bromination takes place without mercury.

The bromination in the presence of mercury is somewhat slow, nevertheless. It is 95% brominated in 10 minutes and 100% brominated in 30 minutes. Hence, maleic acid may be determined by the general procedure with a slight modification to allow for the longer time necessary for complete bromination.

| # | Time Min. | Mercury to Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 20 | 0 | - 98. |
| 2 | 10 | 1.3 | - 4.5 |
| 3 | 25 | 1.3 | - 1.1 |
| 4 | 30 | 1.3 | + 1.1 |

FUMARIC ACID

The solution to be analyzed was made up with water. This substance analyzes very like its isomer, maleic acid. The bromination in the absence of mercury is nil while the bromination in the presence of mercury is 90% complete in ten minutes and is quantitative in one-half hour. Hardly any substitution takes place in sixteen hours. Hence, fumaric acid may be determined by the general method if time is allowed for complete bromination.

| # | Time Min. | Mercury to Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 10 | 2.4 | -9.3 |
| 2 | 10 | 0 | -99. |
| 3 | 35 | 2.4 | 0 |
| 4 | 960 | 1.7 | +2.8 |
| 5 | 30 | 1.7 | +0.4 |

## CINNAMIC ACID

An aqueous solution of the sodium salt of the acid was prepared by dissolving a weighed amount of cinnamic acid in a few ml. of dilute sodium hydroxide solution and making the resulting solution up to a definite volume. When this solution was acidified, the cinnamic acid formed immediately. Apparently this freshly precipitated acid was very readily brominated, because it was found by a slightly modified procedure that the bromine was used up as fast as it was formed from an acidified bromide-bromate mixture. This modification, which was used in the runs #1, 2, 8, consisted of the addition of the unsaturated compound to the bromide bromate solution before evacuation and subsequent acidification. In none of these runs was mercury present initially. When the acidification took place, the cinnamic acid precipitated, but no bromine color appeared. The acid then slowly redissolved and was completely in solution at the end of 2 minutes. At the end of an additional minute the bromine color began to appear. The bromination was complete at this point as can be shown by the fact that #2 was titrated immediately after the bromine color appeared and gave quantitative results. When the sodium cinnamate was added to an already acidified bromine solution, no cinnamic acid precipitated. The slightly high results without mercury were due to either the presence of an impurity in the sample or substitution of an intermediate product in the bromination, since run #7 shows that the substitution does not increase radically with the time, thus indicating that the final product is stable.

On the other hand, the presence of mercury caused erratic results by introducing very great substitution errors of the magnitude of at least 150%. The bromination was very rapid since a 16% error occurred within 1 minute. In all of the runs with mercury almost all of the excess bromine was used up. Run #9 proves that the substitution can very readily take place on the cinnamic acid dibromide, since in that run the cinnamic acid was first converted to the dibromide by bromination without mercury. Then the mercury was added and the excess bromine titrated, showing that a 31% substitution error had been introduced. The benzene ring was not responsible for the substitution, since it had been shown that phenyl acetylene can be quantitatively determined in the presence of mercury. A proof of the fact that a definite ration of mercury to bromide must be exceeded was shown by the fact that after a certain amount of mercury had been added, a sudden fading of the bromine color occurred.

| # | Time Min. | Mercury to Bromide Ratio | Percent error |
|---|---|---|---|
| 1 | 6 | 0 | +3.3 |
| 2 | 4 | 0 | +4.0 |
| 3 | 3 | 0 | +3.3 |
| 4 | 1 | 1.3 | + 16. |
| 5 | 5 | 1.2 | + 67. |
| 6 | 35 | 1.5 | +157. |
| 7 | 35 | 0 | +4.0 |
| 8 | 4<br>1 | 0<br>1.4 | + 31.* |

*Direct bromination,first,followed by the addition of mercury.

# MATERIALS

## Carbon Tetrachloride

The carbon tetrachloride used was the technical product which had been specially purified by treatment with chlorine for a three day period in the light, in order to remove materials which might react with bromine. The chlorine was thoroughly removed by shaking with sodium hydroxide solution. The organic liquid was dried and fractionated. The product boiled at $75.6^{\circ}$ uncor. without any range.

## 1 Pentyne

The preparation was made by the method of Bourguel (a). A suspension of excess sodamide in xylene was refluxed with 2,3 dibromopentane to yield the sodium salt of 1 pentyne according to the reaction,

$$3\ NaNH_2 + C_2H_5CHBrCHBrCH_3 \rightarrow 2\ NaBr + 3\ NH_3 + NaC{\equiv}CC_3H_7$$

The sodium salt can then be hydrolysed to yield the hydrocarbon. The sodamide was prepared by the method of Vaughn, Vogt, and Nieuwland (b) in which liquid ammonia is reacted with sodium in the presence of ferric nitrate and sodium oxide. About 300 ml. of liquid ammonia were collected. To this was added 0.4 g. powdered ferric nitrate and 1 g.

of sodium. Dry air was passed through to form the sodium oxide catalyst. Then the remainder of the 2 moles of sodium was added slowly, producing a copper colored solution. By the end of two hours, the color had changed from copper to blue, and back to copper, the color due to the iron. The mixture was then poured into 300 ml. of xylene and the ammonia was permitted to evaporate, leaving a finely divided suspension of sodamide. Then .58 moles of 2,3 dibromopentane were added to the xylene and the mixture refluxed for three hours. Care was taken not to loose much of the very volatile ethyl methyl acetylene which is first formed and which must be kept in the flask so that it may rearrange to the 1 pentyne.

The reaction mixture was subjected to a fractionation to remove any volatile products which might contaminate the pentyne. The mixture was reacted with water to decompose the excess sodamide, provision being made to absorb the evolved ammonia in water so that all evaporated hydrocarbons carried by the ammonia would condense. The oil mixture was dried with potassium carbonate and fractionated through a 3 foot Claison neck column filled with beads and equipped with a reflux condenser. The fraction, 38° - 40° uncor., was collected, weighing 3.4g., consisting of a 17% yield. The low yield may be partially due to the fact that the preparation was made over a period of two months, and the escape of ethyl methyl acetylene. The pentyne was no further purified, since the fractionation from the high boiling xylene was considered complete.

### 1 Hexyne

The method of Lebeau and Picon (c) was followed in which sodium acetylide and an alkyl halide are reacted to form the substituted acetylene.

$$HC \equiv CH \xrightarrow{Na} HC \equiv CNa \xrightarrow{BuBr} HC \equiv CBu$$

1.75 moles of sodium were dissolved in 300 ml. of liquid ammonia, and acetylene was rapidly passed in until the ammonia solution became white, due to suspended sodium acetylide. The acetylene was obtained from a Prestolyte cylinder and washed in four spiral wash bottles, two of which contained saturated sodium bisulfite solution to remove acetone, while the second two were filled with 30% sodium hydroxide solution to remove any sulfur dioxide evolved from the bisulfite solution. The gas was dried by passage through a calcium chloride tower and a tower of sodium hydroxide flakes. No attempt was made to remove phosphine since it would be a weaker acid than ammonia, and hence a weaker acid than acetylene and would not interfere.in the formation of sodium acetylide. The 1.7 moles of butyl bromide were slowly run in and the mixture was refluxed for two hours. The ammonia was allowed to evaporate over night, provision being made for its absorbtion in water in order to trap any evolved vapors. The reaction product still contained some sodium acetylide which was decomposed by hydrolysis. Enough water was added to dissolve the sodium bromide and the two phases were separated. The organic phase was washed with water and dilute sulfuric acid, and dried with potassium carbonate. The material was fractionated through an eighteen inch column of glass spiral~~e~~s, making a 46% yield of hexyne. Upon refractionation, 42.5 g. of hexyne (.51 moles) boiling in the range of $69.7^\circ$ - $70.1^\circ$ uncor. was recovered. A later redistillation for the preparation of solution #3 took place through a 12 inch Vigreaux column and boiled $69.9^\circ$ - $70.1^\circ$.

## 1 Heptyne

The procedure for the preparation of Hexyne was followed, substituting amyl bromide for butyl bromide. The product was fractionated twice, yielding 24 g. boiling in the range of $98^\circ$ - $100^\circ$ uncor. The yield was 37%. A later fractionation through a Vigreaux column in an atmosphere of nitrogen was carried out to remove peroxides, (see analytical data), yielding 4 cc. of liquid boiling between $97.5^\circ$ - $97.9^\circ$, uncor.

## Phenyl Acetylene

The hydrocarbon was prepared from beta bromostyrene according to the procedure described in Organic Synthesis (d). The product was fractionated through a Vigreaux column, the portion boiling between $139.8^\circ$ - $140.6^\circ$ uncor. considered as being pure. The fractionation was carried out in an atmosphere of nitrogen.

An attempt to prepare the phenyl acetylene from iodobenzene and sodium acetylide in liquid ammonia was a failure, but most of the reagent was recovered. Another attempt at this preparation consisted of refluxing sodium acetylide and iodobenzene on an oil bath. Apparently this yielded phenyl acetylene, which polymerized because a rubbery mass was obtained. (It may be well to mention here that the iodination of benzene with nitric acid and iodine (e) proceeds quite smoothly to a 82% yield.)

Propiolic Acid

The preparation from dibromosuccinic acid was attempted (f). Dibromosuccinic acid was made by the action of bromine on wet fumaric acid in sealed tubes at 120°. The dibromosuccinic acid was dehydrobromated by alcoholic potassium hydroxide to form the potassium salt of acetylene dicarboxylic acid. Upon controlled acidification, the acid salt precipitated. The solid potassium acid acetylene dicarboxylate was heated in water to form potassium propiolate and carbon dioxide. The solution was acidified and extracted with ether. The combined ether extracts were dried with anhydrous sodium sulfate. The ether was distilled off at atmospheric pressure and the residue was subjected to a vacuum distillation at 130 mm. There was collected about 4 cc. of a product boiling at 40°-83°. I believe the low boiling material contained water. The product was made up as an aqueous solution for analysis. The yield was very poor. It would have been much simpler to have prepared this acid by the action of carbon dioxide on sodium acetylide.

## 2 HEPTYNE

This was prepared by the method of Lebeau and Picon (c) where sodium hexynide is methylated by a methyl halide. The procedure used was modified to us dimethyl sulfate in place of the methyl halide.

$$BuC \equiv CNa + (CH_3)_2SO_4 \longrightarrow BuC \equiv CCH_3 + (CH_3)NaSO_4$$

1/3 mole of 1 hexyne and 1/3 mole of sodium were added in that order to 200 ml. of ammonia. The sodium was added until a blue color persisted. Next ½ mole of dimethyl sulfate was added. At first, there was a violent gas evolution which was most likely due to the excess sodium's reacting. The mixture was refluxed for ½ hour after which the ammonia was permitted to evaporate. Dimethyl sulfate was a poor methylating agent, since it reacts with ammonia. The reaction mixture was hydrolysed and the organic phase washed with water and dilute sulfuric acid. Then it was dried with anhydrous potassium carbonate and fractionated twice through an 18 inch column of glass spirals. The crude yield was 25%. A much larger excess of dimethyl sulfate would have improved the yield. The final yield was 2 ml. of 2 Heptyne boiling 109.3-109.9°.

$\frac{1.6}{108} = .0016$

$C_7H_{12} = 96$ 5%?

$.33 \times .05 = 0.165$ mols

## Trans-Dichloroethylene

Eastman's Practical Grade Dichloroethylene was fractionated through an 18 inch column of glass spirals. The collected fraction boiled 59° - 60° uncor. and was hence almost pure trans-dichloroethylene.

## Fumaric Acid

Eastman's Practical product was twice recrystallized from water, rinsed with alcohol and dried at 105° for 5 hours.

## Cyelohexene

The sample was obtained from Mr. S. Winstein. It was fractionated in a nitrogen atmosphere and the fraction boiling 81.0° - 81.1° uncor. was collected.

## 1 Hexene

A small amount of a solution of the compound in carbon tetrachloride was provided by Mr. S. Winstein.

## 2,3 Dimethyl Butadiene

This compound was also furnished by Mr. S. Winstein, and had been freshly fractionated by him.

## MALEIC ACID

The Phansteil product was twice crystalized from water and then dried in a vacuum desiccator over calcium chloride for 24 hours.

## CINNAMIC ACID

The material used was of unknown origin and was twice recrystalized from dilute alcohol. It was dried in a vacuum desiccator for 24 hours.

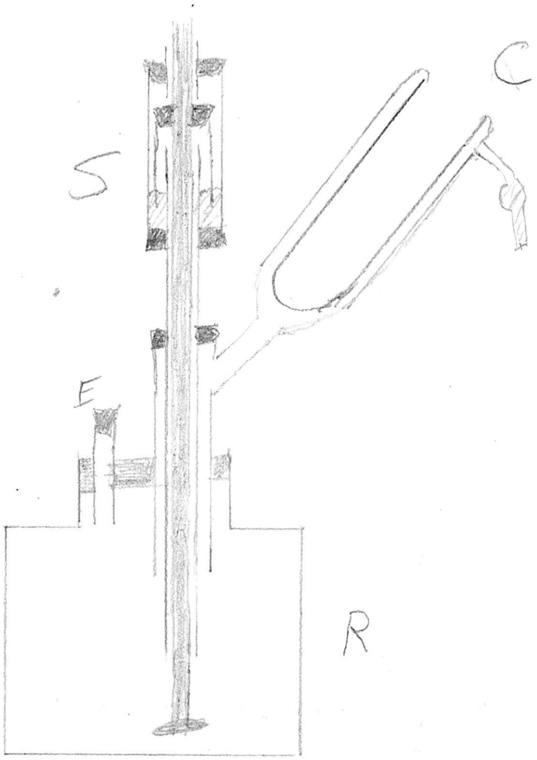
## Apparatus for Liquid Ammonia Technique

R is a 500 ml. bottle, the reaction flask. It is placed within an insulated container which can hold a carbondioxide alcohol bath.

C is a reflux condenser which holds a dry ice freezing mixture.

S is a stirrer equipped with a mercury seal and E is the addition tube.

In order to fill the chamber with ammonia, it is surrounded by a freezing bath and the ammonia vapor is admitted by a tube through E. Any ammonia that is not liquified in R is liquified at C.



# NOTE ON THE HYDRATION RATE OF 1 HEPTYNE

## Scheme of analysis.

100 cc. of the solution to be analyzed were run into a small amount of bromine solution to which had been added 5 ml. of mercuric sulfate solution. The flask was shaken for five minutes and then the contents were backtitrated with sodium thiosulfate solution. No exceptional precautions were taken.

## Hydration in the presence of mercury.

The solution was made up of 5 drops of 1 heptyne and 1½ ml. of .2 N. mercuric sulfate solution in 1 liter of 6 N. sulfuric acid solution. The resulting solution was very slightly turbid.

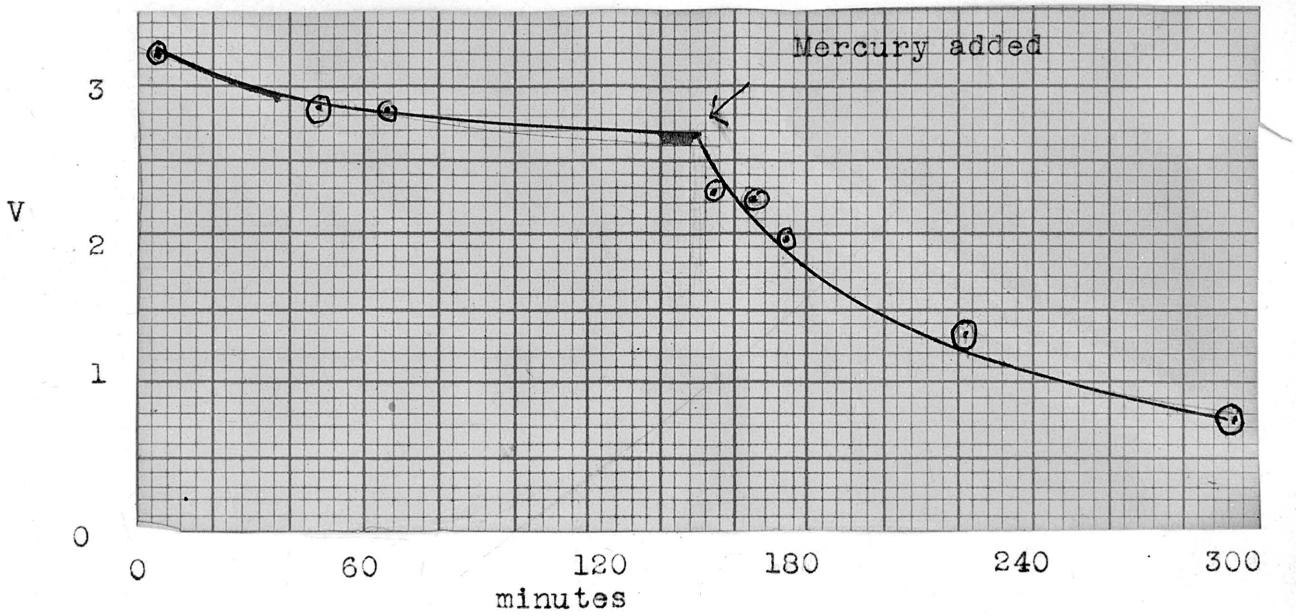
## Hydration without Mercury.

A solution was made up of 5 drops of 1 Heptyne in 1 liter of 6N sulfuric acid. The observed hydration was very slow. Then ½ ml. of .2 F mercuric sulfate was added to the heptyne solution in order to observe the effect of mercury.

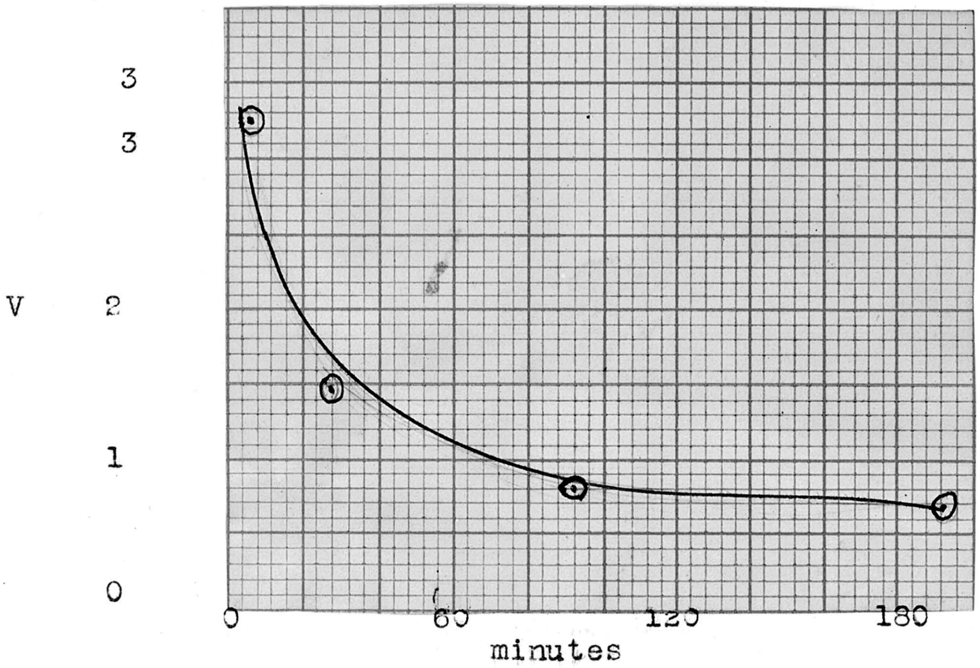
| Hydration with mercury | | Hydration without mercury | |
|---|---|---|---|
| Time Min. | Vol. of thiosulfate used up. ml. | Time Min. | Vol. of thiosulfate used up. ml. |
| 5 | 3.25 | 5 | 3.2 * |
| 28 | 1.46 | 48 | 2.84 |
| 94 | .80 | 65 | 2.83 |
| 194 | .70 | 154 | add mercury |
| | | 157 | 2.28 |
| | | 168 | 2.20 |
| | | 178 | 1.98 |
| | | 221 | 1.32 |
| | | 293 | .77 |

*May be off because large excess bromine was used.

# HYDRATION OF 1 HEPTYNE



Hydration, initially in the absence of mercury



Hydration in the presence of mercury

V is the volume of .025n thiosulfate solution equivalent to the remaining heptyne.

## Attempted Analysis of Hydration Product.

The hydrated solution had a sweet ketone-like odor and was fractionated to concentrate the ketone. About three ml were collected and about 3/4 drop of oil was observed as a second phase. A few drops of alcohol were added to cause complete solution of the ketone and the 2, 4 dinitrophenyl hydrazone was prepared by adding about 1 ml of a saturated solution of 2,4 dinitrophenyl hydrazine in concentrated sulfuric acid to it. The product was crystalized three times from alcohol. The product of the first crystallization melted 52-60° with fast heating. The final product melted 56° - 57°. The literature gives 89° and 106° respectively for amyl methyl ketone and Hemtaldehyde derivatives. (G ). According to Markonikov's rule, the product should be amyl methyl ketone. Perhaps the literature cited is in error. or a mixture formed.

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