I DETERMINATION OF AN ACETYLENIC HYDROCARBON (3-Hexyne) IN CARBON TETRACHLORIDE AND IN AQUEOUS SOLUTION

II COMPLEX FORMATION BY THE CARBON-CARBON TRIPLE BOND

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W. Smith Dorsey

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ABSTRACT

Using3-hexyne, the method of Lucas and Pressman (1) for determining acetylenic hydrocarbons by bromination with a mercuric salt catalyst in the absence of light and oxygen was studied in detail. Determinations of 3-hexyne in carbon tetrachloride solution yielded a two-phase system of considerable complexity, the rate of bromination being dependent upon several factors. From 99 to 102% of the 3-hexyne taken was found in numerous runs, the average deviation being usually less than 1%. Determination of 3-hexyne in aqueous solutions yielded a more simple system but gave the same results if oxygen was excluded from the solutions. The nature of the oxygen interference was not established. Some evidence indicates that the process involved is not true bromination, but rather some more complicated reaction.

It was found by a distribution method that 3-hexyne complexes with silver ion in aqueous solutions, but does not complex with bipositive cadmium, copper, nickel, cobalt, or zinc ions. A rapid reaction with mercuric salts precluded any conclusion about complexing. The evidence for cuprous chloride or for cuprous ion is inconclusive, but no complexing is indicated. Two silver ions complex stepwise with one molecule of 3-hexyne, the argentation constants being 19.1 and 0.22 respectively. The interaction is much weaker than that of olefins, but several times stronger than that of the aromatic hydrocarbons.

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INTRODUCTORY REMARKS

The research reported in this thesis is recorded in Work Books No.'s 174, 256, 207, 232 and 333 of the Gates and Crellin Laboratories of Chemistry, California Institute of Technology. The work book pages were numbered serially through the sequence of books given above. Experiment numbers are the number of the first page on which any data for that experiment is recorded.

Attention is invited to the assumptions made in calculating the nominal total volumes in Part I, and to the definition of "oxygen-free" as used in Parts I and II.

PART I

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DETERMINATION OF AN ACETYLENIC HYDROCARBON (3-Hexyne) IN CARBON TETRACHLORIDE AND IN AQUEOUS SOLUTION

A. HISTORICAL. SURVEY OF POSSIBLE NETHODS.

In distribution studies of 3-hexyne (see Part II) it was necessary to determine the concentrations present in both carbon tetrachloride and aqueous phases. The study of the analytical method divides itself into two sections according to the medium in which the 3-hexyne was dissolved. The following general considerations apply to both sections:

As a method for the determination of 3-hexyne, the use of the spectrophotometer was considered, but was not attempted because the very low wave length at which the carbon-carbon triple bond frequency occurs, about 1700 Å, was below the range of the available instrument. Among the chemical methods considered were bromination, ketal formation, the Karl Fischer reagent, dinitrogen tetroxide addition and thiocyanogen addition. The bromination had previously been studied in some detail (1) and appeared to be the quickest method. The formation of ketals, using a methanolic solution and a mercuric oxide-boron trifluoride catalyst has been described by Wagner, Goldstein and Peters (2) and offers advantages where mixtures of olefinic and acetylenic compounds are involved, but requires more time and offers no particular advantage where a single alkyne is being determined. The various methods based on the precipitation of copper or silver acetylides were not applicable here because a disubstituted acetylene was involved. Dinitrogen tetroxide (3, 4) and the Karl Fischer reagent (5) and thiocyanogen (6, 7, 8) have been used in quantitative determinations of olefins but are untried with acetylenic compounds and involve longer times to complete determinations. The addition reaction of nitryl chloride NO_2Cl , (9) might offer a possible method of analysis but would require much development. It was therefore decided to continue the use of the bromination procedure which was already available.

B. BROMINATION OF THE CARBON-CARBON TRIPLE BOND.

The generalization is frequently made that the carbon-carbon triple bond adds two moles of bromine, but it is the experience of several authors (summarized by Lucas and Pressman(1)) that under non-catalytic analytical conditions the reaction does not go to completion, or goes only very slowly. Indeed a search of the literature showed that only a limited number of the isomeric tetrabromo compounds derived by addition of bromine to acetylenic compounds have been prepared and studied, and in many reports the details of preparation are very scanty so that it is impossible to evaluate the ease or difficulty of preparation. The well known 1,1,2,2-tetrabromoethane and 1,1,2,2-tetrabromopropane (10), 1,1,2,2- and 2,2,3,3-tetrabromobutane and 1,1,2,2-

-3-

tetrabromopentane (11, 12) are reported, but none of the corresponding tetrabromohexanes are reported. Attempts to prepare 1,1,2,2-tetrabromohexane from 1-hexyne failed (13), and attempts in this laboratory (14) have also been unsuccessful; this study is being pursued further. A literature search for higher homologs was not made.

Except for a comparison by de la Mare (15)[#] of a relatively limited number of olefin and acetylene homologs, and some work on the stereochemical course of the reaction (16, 17, 18, 19) very little attention has been given the mechanism of saturating the carbon-carbon triple bond with halogens. It seems well established, however, that the reaction is stepwise.

 $-C \exists C - \frac{Br_2}{rapidly} - CBr = CBr - \frac{Br_2}{slowly if} - CBr_2 - CBr_2 - (1)$

The difficulty in achieving complete bromination might be logically explained by the lower reactivity of the dibromoolefin. In fact, Lucas and Pressman (1) in no instance observed less than 50% bromination of acetylenic hydrocarbons without catalysts, but did observe incomplete bromination of the olefinic compounds: dichloroethylene, fumaric acid and maleic acid under equivalent conditions and times. Davis et al (20) report results which show the same, and Mulliken *Given in a review article. Since it is not credited to any other source, it is apparently some of de la Mare's work.

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and Wakeman (21) found in 5 instances out of 8 that more than one mole of bromine was absorbed per original triple bond.

The unreactivity of dihalogenated olefins towards bromine addition is well known qualitatively, and has been the subject of some kinetic studies which are partially reproduced in Table 1.

Table 1

Relative Reactivities of Dihalogenated Olefins towards Bromine Addition

Compound	Relative Rate	s of Addition	Resonance
	Swedlund and	Anantakrishnan	Energies
	Robertson (22)	and Ingold (23)	kcal/mole
	ж Ж. 4		(24)
CH2=CH2	1	1	-
CH2=CHBr	3 x 10-4	Small	19 ²
£			
CHC1=CHC1	7		
$(\underline{cis})^{\perp}$	1×10^{-7}	-	28
CHCl=CCl2	3×10^{-10}	CD	42
6			,

1. It is of interest to note that Swedlund and Robertson (22) found addition faster to the <u>cis</u> compound than the <u>trans</u>, whereas <u>Chavanne</u> (25) and Verhoogen (26) report the opposite sequence. Isomerization is observed during bromination. It should also be noted that Swedlund and Robertson apparently quote Chavanne incorrectly since they indicate that he studied chlorine addition, whereas <u>Chemical Abstracts 9</u> 2898 (1915) and <u>Chem. Centr.</u>, 1914, II, 1144 report that he studied bromine addition. Unfortunately the original article was not available to check this point.

2. For vinyl chloride.

Various discussions have been given of reactivity and double bond character or bond order (27, 28), the most specific suggestions perhaps being those of Pullman (29) and Gold (30). No assignments of bond order of the carbon-carbon bond for the compounds in Table 1 (except ethylene) were found, but the resonance energies calculated by Ketelaar (24) are given for comparison. It would seem reasonable that the well established increase in double bond character of the carbonbromine bond in vinyl bromide (as compared with ethyl bromide) (27, 31) would be accompanied by a corresponding and critical decrease in the double bond character of the carbon-carbon double bond, even though the change in the carbon-carbon distance is small." A critical examination of this point appears to be desirable, although not directly pertinent to this analytical method for alkynes since the intermediate here is presumably always of the formula RCBr=CBrR where the bond order of the carbon-carbon bond will be quite similar as long as the R groups are ethyl, propyl, etc.

The possibility of a mechanism for the bromination of the triple bond other than Equation 1 is raised by the studies of a group of Russian authors (32), concerned primarily with the addition of mercuric halides to the carboncarbon triple bond, but including some work with mercuric nitrate (33). The results reported in this thesis show that

*Actually, this distance has been assumed constant in the studies of molecules such as vinyl bromide (31).

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mercuric chloride is not an effective catalyst for obtaining complete bromination of 3-hexyne. In this study no ready criterion was found to determine whether the catalysis observed involves the initial addition to the triple bond or the subsequent addition to the dibromoolefin. From the preceding paragraphs, it would appear that the latter phase of the reaction is the one which goes only with a catalyst.

Indeed, there are some considerations which indicate that it is not a case of catalysis, but one where stoichiometric amounts of mercury are required. This will be discussed further.

C. DETERMINATION OF 3-HEXYNE IN CARBON TETRACHLORIDE SOLUTION

In one phase of the work, the amounts of hexyne to be determined were 0.02 to 0.2 milliequivalents (0.005 to 0.05 millimoles), about one one hundredth to one tenth the amounts previously analyzed (1), and initial attempts to adjust the method to these reduced amounts failed to produce satisfactory results. The following study was therefore undertaken to define more accurately the variables involved. Later work required the determination of amounts of hexyne up to 2.0 milliequivalents, but using a smaller total volume of carbon tetrachloride phase and a large volume of aqueous phase. For the latter, a briefer study was made which sufficed to develop adequate conditions, but which was not extended to define minimal conditions.

It was found in some of the experiments with 3-

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hexyne in aqueous solutions that oxygen interfered with the analysis. No such interference was observed with solutions of 3-hexyne in carbon tetrachloride, and no precautions against oxygen were taken in any of the experiments on such solutions.

MATERIALS AND SOLUTIONS

Since the materials for Part I coincide largely with those of Part II, this section will serve for both Parts. Only such items as are peculiar to Part II will be discussed there.

<u>3-Hexyne</u>. The 3-hexyne was in part furnished by Dr. H. Lemaire of this Laboratory (synthesized by the method of Bried and Hennion (34)) and in part purchased from the Farchan Research Laboratories. When freshly distilled in an atmosphere of nitrogen the value's shown in Table 2 were obtained.

Table 2

Properties of 3-Hexyne

Source of 3-Hexyne	n ²⁵	n20	b.p., ⁰ C	
Lemaire	1.4087	- "	80.0-80	.6 (746mm)
Farchan	1.4089	-	80.0-80	•3 (744)mm)
Literature Henne and Green-			Ŷ	
lee (35)	1.4089ª	1.4115	81	(760mm)
Campbell and Eby (36)	1.4084ª	1.4110	-	
a. Calculated, using	n_{D}^{20} and	dn/dt = 0.0	005237	(37).

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The agreement of our observed values with that calculated from $n_D^{20} = 1.4115$ would appear to support the contention of Henne and Greenlee (35) that their value is a better one than that previously reported (36). A portion of the 3-hexyne which had been stored for several weeks in contact with air and which presumably contained appreciable amounts of oxidation products gave $n_D^{25} = 1.4282$.

Immediately after distillation under nitrogen the 3-hexyne was introduced by hypodermic syringe into previously weighed glass ampoules, 0.05 to 0.3 gm per ampoule, and the ampoule sealed and weighed. Identification was made positive by including inside the ampoule glass threads of various colors in recorded combinations. The weights were checked before using each ampoule. The free air space was about 1.5 ml per ampoule and never exceeded 3 ml. Assuming 0.1 gm hexyne present, 3 ml of air and absorption of 2 atoms of oxygen per molecule of hexyne, only 0.2% of the hexyne would be transformed into peroxide. Actually, no peroxide effects were observed in any titrations, even when the carbon tetrachloride solutions of hexyne had stood in contact with air for several days after preparation.

<u>2-Pentanone</u>. (Diethylketone). Eastman Kodak Company White Label grade was redistilled, a cut boiling at 99-101°C (751 mm) being collected. This was immediately introduced into glass ampoules and sealed, as described for 3-hexyne.

<u>2-Butanone</u>. (Methyl ethyl ketone). Eastman Kodak Company White Label grade was redistilled through a 2 cm

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inside diameter column with a 36 mm length packed with 0.5 cm of 6mm tubing. Using a reflux ratio of 8 to 1, a cut was collected at $78.3 - 78.5^{\circ}$ C (749mm).

Nitrogen. Compressed nitrogen derived from liquefied air and rated as 99.7% nitrogen by the vendor was used in experiments up to and including Expt. 622. It was passed through three absorption bottles, the first two containing copper turnings and aqueous ammonia and the last sulfuric acid. After Expt. 622, dry, high purity nitrogen claimed to be 99.99% pure by the vendor was used.

Carbon Tetrachloride. All carbon tetrachloride used was purified as previously described (1, 38).

Potassium Iodide. U.S.P. grade was found satisfactory. At first fresh solutions were prepared daily, but later the method of Stansby (39) was applied and solutions were made up to contain 2 to 4% (by weight of total solids content) of sodium carbonate. Such solutions were stable over the two or three week period required to consume them.

Other Reagents. Potassium bromide, potassium bromate, mercuric sulfate, mercuric oxide and mercuric nitrate were reagent grade. Mercuric nitrate was dried in a desiccator containing phosphorous pentoxide before weighing out. Other reagents were C.F. grade.

Forms for Analytical Data. The many factors which had to be recorded to keep a complete record of an analysis led to the adoption of a mimeographed form which was pasted in the notebook where desired. The form was revised several times and a copy of the last format is included as page 11.

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II- Date Analyses Performed IN CCl₄ AQUEOUS PHASE (of CCl₄-aqueous solution distribution). ANALYSES OF

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Deter	mination No.		10. 18				ļ
Proce	edure No.	20			1.3	á	
VOLUM	IES, ml CCl ₄ Ph.						
bro	mination Aq. Ph.					ester Salar	
Br03	-KBr,N (a)						~
Disti	lled H ₂ 0					5. g	
3 N H	1 ₂ 50	10 m 10					
Sampl	.6				а. -	2	
lesh	CCl4			•			1
Catal	yst Soln.		-	*** ±	ş.,	Ξ×.	
laci	al Acetic Acid						
Nash	H ₂ 0						
Shaki	ng Time, minutes						
Time	Bromin. Begun			· ·	1	100 100 100	
Elaps	sed Time (b)						
CI So	Jn.		5				
Disti	lled H ₂ 0		•				
Shaki	ng Time, minutes				. 6		-
Indic	eator (c)		ан) Ац				+
Va.	Final Rdg.						
Sn.	Initial Rdg.	-					
) _a	Used	1. S. S.		1.			1
0	Plus blank						1.7 200
· · ·	Corrected			x *			
AT.C			3		2		
Vol 1	(N) (N)						
Vol 1	$Na_{2}S_{2}O_{3}$ (N)						a a
orr.	meq. (d) KBr03-KBr						
om.	of alkyne = <u>Corr. meq.</u> Vol Sample						
Four	nd of Alkyne Taken		2				
	(a) Mole ratio KBr/KBrO3.	k					4
	 (b) From prepm. of known to water, hours (c) 1% aqueous soln of so (d) milliequivalents 	soln o: luble	r exp	osure h, pr	of a epare	lkyne d thi /dat	to .s

[/]date.

Stopcock Lubricant. A lubricant which did not interfere significantly with analyses was made by melting together 40 g stearic acid, treated as described below, 20 g #7 mineral oil and 1.0 g zinc oxide (Baker's CP Analyzed). On cooling, a smooth, faintly yellow, moderately stiff paste resulted. The stearic acid prior to mixing had stood for 24 hours in the dark with acidified bromide-bromate solution, then melted and, while molten, washed well with water. The treated stearic acid absorbed bromine, 0.0082 meq per gram. The mineral oil absorbed 0.0038 meq per ml.

The lubricant was quite satisfactory even though inferior as a lubricant to some commercial preparations which were unsuitable because they absorbed appreciable amounts of bromine. Assuming 0.017 meq of 3-hexyne and that as much as 0.05 g of lubricant would be dissolved into the analysis, the maximum error would be 2.4%. This is believed to represent the extreme condition.

Later a sample of Fluorolube Light Grease, a polymer of trifluorochloroethylene, was kindly supplied by the Hooker Electrochemical Company. This was very satisfactory as a lubricant*, although, as before, the solvents leached the grease to such an extent that relubrication was necessary after each use of the stopcock-stoppers. Blanks showed that 1 gm of Fluorolube Light Grease absorbed 0.0051 to 0.0081 M

*This was also used very satisfactorily on other experiments with fuming sulfuric acid and dinitrogen tetroxide vapors.

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of bromine under conditions of the analysis. This represented a maximum error of 2.6 per cent, calculated on the same basis as above.

PROCEDURE FOR ANALYSIS

<u>Known Solution of 3-Hexyne in Carbon Tetrachloride</u>. An ampoule of 3-hexyne was broken under the surface of carbon tetrachloride in a nearly-filled volumetric flask, the breaking rod washed down and withdrawn, and the solution diluted to volume. The resulting solution was approximately 0.005 M. Because of the high coefficient of expansion of carbon tetrachloride the temperature was closely observed and corrections applied when necessary. Corrections were also applied for the volume of glass from the ampoule.

It will be noted in some instances that the maximum analyses obtained were as much as 2.5% below the theoretical. Since the values always lay below 100.0% and since any one solution of hexyne gave consistent maximum analyses which would differ slightly from the maximum analyses for another solution of hexyne, it is considered that the errors were due at least in part to losses of hexyne in preparing the solutions.

The possibility of polymerization, oxidation or loss of hexyne from the known solutions was checked by analyzing the same solution under the same conditions (which gave maximum analysis) over a period of 12 days. On the lst, 2nd, 3rd, 5th and 12th days after preparing the solution, 97.6,

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97.5, 97.5, 97.5 and 97.5 per cent of the calculated amount of hexyne was found. The excellent agreement is considered to be partially fortuitous since in general the reproducibility of results was not this good. It shows, however, that the strength of the solution did not alter appreciably.

Samples for Analysis. Two methods were employed. In Method A, a portion of the known solution was taken in an Eberz pipette (38) and washed through the pipette into a glass-stoppered mixing cylinder, then diluted to 40 ml with carbon tetrachloride. This procedure was followed so that, from a given known solution of 3-hexyne, a series of samples of the same total volume but of different hexyne content could be prepared.

In Method B, the sample was taken in an Eberz pipette, then sucked directly into the bromination flask and washed through the pipette with enough carbon tetrachloride to make the desired total volume, or with the acetic acid if the total volume of carbon tetrachloride was insufficient.

<u>Procedure F-03</u>. For <u>Determination of 3-Hexyne in</u> <u>Carbon Tetrachloride</u>. This procedure is modified from that of Lucas and Pressman (1). It should be noted that the bromination is conducted in the absence of light and under low pressure (little oxygen). The <u>nominal total volumes</u> are calculated on the admittedly approximate assumption that all aqueous solutions and acetic acid remain in the aqueous phase.

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and that all carbon tetrachloride remains in the carbon tetrachloride phase.

An excess of 25 to 100%, the higher figure being used with smallest amounts of hexyne, of the standard potassium bromide-bromate solution (mole ratio bromide/bromate = 5.00/1.00) was measured into a 250 or 300 ml 24/40 standard taper Erlenmeyer flask. The flask was (a) fitted with a 24/40 standard taper stopper bearing a sealed-in stopcock; (b) covered with a black cloth bag and (c) evacuated to a pressure of 12 to 50 mm of mercury. Into the flask were sucked the sulfuric acid and the mixture allowed to generate bromine for at least 15 minutes.

When Method A was used, the sample was transferred to the reaction flask by suction through a U-shaped capillary tube and the mixing cylinder washed down (without removing the capillary) with enough carbon tetrachloride to bring the nominal total volume of carbon tetrachloride to the desired Similarly, the catalyst solution, glacial acetic acid value. and sufficient wash water to bring the nominal total volume of the aqueous phase to the desired value were successively added to the mixing cylinder, each reagent being sucked into the flask before adding the next reagent. The capillary was removed and the flask mounted in a clamp on a Boerner oscillating platform shaker and shaken for 15 minutes \pm 1 minute. (A reasonable over-run of shaking time was probably not serious, but since the shaker employed had a built-in timer, the above limits were maintained.) When Method B was used

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for sampling, the catalyst solution, acetic acid (if not used for washing sample through special pipette) and wash water were added after the sample through a special funnel (a test tube of suitable size with a delivery tube sealed in the bottom).

The desired volume of potassium iodide solution and 50 ml of water were sucked into the flask at the end of the shaking period and the shaking resumed for 3 minutes. The cloth bag was then removed, vacuum broken and the flask washed down. The free iodine was titrated with standardized sodium thiosulfate. Starch solution was used as an indicator (1).

Blanks were run using 50 ml of carbon tetrachloride for a sample and about 1/3 the amount of bromide-bromate used for determinations. During exploratory work, the volumes of all reagents were recorded. Under routine conditions this would be unnecessary, but the volumes of reagents should be controlled to minimize variation in the blank. The amounts of reagents taken were:

Sulfuric acid: 6.0 ml of 6.0 N.

Catalyst: 5.0 ml of solution 0.20 M in mercuric sul-

fate and 1.0 N in sulfuric acid.

Glacial acetic acid: 10 ml

Nominal total volumes:

Carbon tetrachloride phase: 50 ml

Aqueous phase: 37 ml

Potassium iodide solution: 7.0 ml of 1.00 N.

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Table 2

Effect of Varying Catalyst Salt

C Cata	lyst Solu	tion	Hg	Vol	Vol	Percent
Salt	Salt Conc. <u>M</u> .	Solvent	Taken mmol	Acid ^a Taken ml	Glacial Acetic Acid Taken ml	Found of Hexyne Taken
HgCl ₂	0.030	Water	0.0 0.12 0.12	6.0 6.0 6.0	0 0 5•0	35 38 63
HgCl ₂	Sat.	Water	4.4	6.0	0	58
HgCl ₂	0.810	0.99 <u>M</u> aq. Na Cl	12 .1 12 .1	3.0 2.0	0 0	83 83
HgCl ₂	1.217	1.5 <u>M</u> aq. NaCl	12.2 12.2	6.0 2.0	5.0 0	80 82
HgSO4	0.10	0.96 <u>N</u> H ₂ SO4	0.12 0.50	6.0 6.0 ^b	0 5.0	44 97.5°
нg(ClO ₄)) ₂ 0.20	0.414 <u>N</u> HC104	0 0.16 1.0 1.0 2.0 1.0	6.0 ^d 6.0 ^d 6.0 ^d 6.0 ^d 6.0 ^d 6.0 ^d	0 0 0 5•0	9 35 89 91 88 99•2°

Notes

a. 6.0 <u>N</u> HCl except as noted.
b. 6.0 <u>N</u> H₂SO₄.
c. The known solution of 3-hexyne used for these runs was not the same solution as used for all other runs.

d. 6.0 <u>N</u> HClO4.

DETERMINATION OF 3-HEXYNE IN AQUEOUS SOLUTION

To exclude air from the solution, water was boiled under reduced pressure (about 20 mm.) until small bubble evolution ceased and bumping began, with the formation of very large bubbles of vapor. This behavior was taken as a criterion of "oxygen-free" conditions and, within the limits of these experiments, was entirely satisfactory. The bottle was disconnected from the aspirator line and connected to a nitrogen supply. The time interval during which the water was exposed to the air was in general less than 15 seconds and never exceeded 45 seconds. When first connected, the nitrogen stream was run for a few minutes before the stopper was firmly seated so as to flush out the air in the neck of the bottle. The bottle was allowed to cool to room temperature.

It was found that dissolving 3-hexyne in water did not give satisfactory solutions, apparently because the hexyne (Sp.G. about 0.8) floated on the water and did not dissolve readily. To achieve complete solution of the hexyne, the apparatus shown in Figure 6 was set up and the following procedure adopted.

Procedure S-Ol. Preparation of Known Solutions of 3-Hexyne in Oxygen-Free Aqueous Acetic Acid. The ampoule was broken under 50 ml. of glacial acetic acid in a centrifuge bottle (Figure 6) and 5 ml. of acetic acid used for washing down. The stopper assembly was put in place and the whole moved so as to introduce the discharge end of the sample delivery tube into a small opening in the stopper of the bottle containing oxygen-free water. The stopcock of the separatory funnel was left open and unlubricated

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<u>Procedure F-04</u>. This procedure was the same as Procedure F-03 insofar as sequence of actions is concerned, but the following amounts of reagents were taken:

Sulfuric acid: 6.0 ml of 18 N.

Catalyst: 10.0 ml of solution 1.00 M in mercuric

sulfate and 3.00 N in sulfuric acid.

Glacial acetic acid: 10 ml

Nominal total volumes:

CCl, phase: 11 ml

Aqueous phase: 45 to 48 ml

Potassium iodide solution: 20 ml 3.00 N.

<u>Nitrogen System</u>. The nitrogen system used for the experiments on aqueous solutions of 3-hexyne and later in distribution experiments (Part II) evolved from a very simple beginning into the arrangement shown in Fig. 1. This was used for all experiments from No. 510 onward.

A "high" pressure line, usually operated at about 5 to 7 psi gauge, was used for displacing solutions and filling burettes. The "low" pressure line, usually operated at about 1 to 2 psi, was used to provide the atmosphere for storage of solutions. The reducing valve between the high and low pressure lines was built for higher pressures and greater differentials, and did not function too well. As a result of the low flow rates and low differential, it functioned primarily as a controllable leak. If the consumption of low pressure g_{BS} was small, the pressure in the low side



gradually built up to a point near that in the high side. Thus, if no gas had been drawn for a time, it was necessary to vent the low side before filling a burette.

While only one burette and one bottle are shown in Fig 1, actually three burettes were so equipped for sulfuric acid, acetic acid and catalyst solution. The burettes were used for dispensing without calibration, the manufacturer's graduations being accepted. The overflow connections at the top of the burettes were initially connected to the low pressure vent lines, but one or two flooding accidents made it desirable to run the overflow lines into a trap bottle large enough to hold the contents of the largest bottle on which any burette was mounted. The trap bottle was then connected to the low pressure line.

RESULTS OF DETERMINATION 0.02 to 0.2 MILLIEQUIVALENTS OF 3-HEXYNE

A detailed study was made of the effect of varying one factor after another, usually under conditions which would not give quantitative results, so as to emphasize the effect of the variable.

Standard Conditions. These are, as outlined in Procedure F-03: nominal total volume of aqueous phase, 37 ml; nominal total volume of carbon tetrachloride phase, 50 ml; mole ratio of bromide to bromate, 5.00 to 1.00; bromination time, 15 minutes. These are the conditions prevailing in the experiments depicted in the figures, except as otherwise noted.

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Effect of Time of Bromination. As previously shown (1) and as borne out by experiments in this study, increasing the time of bromination causes the analysis to approach 100%more closely when catalyst is present but in insufficient amounts to give 100% analysis in a short time. A bromination time of 15 minutes, ± 1 minute, was arbitrarily selected as convenient and easily reproduced, and was used for all runs unless otherwise indicated.

Effect of Bromide/Bromate Mole Ratio and of Addition of Chloride Ion. While the reaction

 $\operatorname{Bro}_3^- + 5 \operatorname{Br}^- + 6 \operatorname{H}^+ \longrightarrow 3 \operatorname{Br}_2^- + 3 \operatorname{H}_2^0$ requires a mole ratio of bromide/bromate of 5/1, a ratio of 10/1 was used by Lucas and Pressman (1; this fact was not stated in the original paper) to speed up the generation of free bromine. Since enough mercuric ion must be provided to complex all excess bromide as HgBr_4^- , plus additional mercuric ion to provide catalytic action, the higher ratio requires use of more mercuric salt. Further, enough iodide ion must later be added to convert all HgBr_4^- and Hg^{++} to HgI_4^- . Sodium chloride had previously (40) been added after the bromination period to assist in complexing the mercury. The equilibrium constants for

 $\operatorname{Hg}^{++} + 4 x^{-} \Longrightarrow \operatorname{Hg}_{h}^{--}$

are given (41) as 1.2×10^{15} , 1.0×10^{21} and 6.8×10^{30} for chloride, bromide and iodide, respectively. These constants

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indicate that any moderate amount of chloride or bromide ion will not convert any appreciable fraction of HgI_{4}^{--} to $HgCI_{4}^{--}$ or $HgBr_{4}^{--}$. This was verified by taking all reagents (except bromate) in sequence as prescribed for satisfactory analysis. The potassium iodide solution (last reagent) was added by titrating until all the initially-formed orange mercuric iodide preciptate was redissolved. Using 1.00 mmol mercuric sulfate and 10.0 meq sodium chloride, 3.75 meq of potassium iodide (mean of 3) were required; using 1.00 mmol mercuric sulfate and no sodium chloride, 3.82 meq (mean of 3) were required. The difference of 0.07 meq is of doubtful significance and so small a saving of potassium iodide as not to justify the nuisance of the additional reagent and the accompanying build-up of ionic strength.

Considering the above, the bromide/bromate mole ratio was reduced to 5/1 and the use of sodium chloride solution was omitted in all experiments in this thesis unless otherwise noted. The rate of bromine generation and the complexing of mercury were satisfactory insofar as no detectable change in results was observed.

Effect of Acetic Acid. It was previously shown (1) that at a given mercury concentration the addition of acetic acid reduced the error of analysis from 10% or more to 3% or less, it being postulated that the effect was due to solvent action. It was found that in a system with no acetic acid present perfect analysis could be achieved by increasing the

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amount of mercuric salt used, as illustrated in Figure 2. An entirely analogous curve was obtained when 5.0 ml of glacial acetic acid were used in each run, except that a smaller amount of mercuric salt was required to achieve 100% analysis. It should be noted in examining the curves that they were obtained from two different known solutions of hexyne. The difference in maximum per cent found was attributed to errors in preparing the known solutions.

An attempt was made to determine the minimum amount of acetic acid required to give the maximum improvement when an amount of mercuric salt insufficient to give 100% analysis in 15 minutes was used. Figure 3 shows that using 0.10 mmols of mercuric sulfate, as little as 2.0 mmols of acetic acid gave as large an improvement as any amount up to 17.5 mmols. The beneficial effects of such small amounts of acetic acid indicate that the acid may enter into the reaction mechanism, although a simple solvent action is by no means excluded.

As a practical consideration, in the absence of acetic acid the two phases emulsified quite badly when shaken during the titration, making the end point difficult to determine exactly. Five ml of glacial acetic acid, even if added after the bromination period but before titration, greatly reduced the emulsification; 10 ml gave very rapid separation of the two phases. The addition of a suitable amount of acetic acid before the bromination period is therefore recommended, so as to take advantage of both effects.

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Figure 3. EFFECT OF ACETIC ACID ON ANALYSIS.

Effect of Excess of Bromine. While a large excess of bromine was undesirable because of possible substitution, the effect of bromine concentration upon the rate or extent of addition was not known. At two different mercury concentrations insufficient to give 100% analysis in 15 minutes with a 10 to 25% excess of bromine, it was found (Figure 4) that increasing concentration of bromine gave improved analysis. The values show that no appreciable substitution occurred under the conditions investigated.

Effect of Volume of Carbon Tetrachloride Phase during Bromination. Fixing all other conditions and taking an amount of mercuric sulfate insufficient to give 100% analysis in 15 minutes, it was found (Figure 5) that as the volume of the carbon tetrachloride decreased, the per cent of hexyne found also decreased. This suggests that an appreciable portion of the bromination may occur in the organic phase.

Effect of Volume of Aqueous Phase during Bromination. Fixing all other conditions except total volume of the aqueous phase, it was found (Figure 6) that an increase in the volume of the aqueous phase during bromination gave a rapid decrease in the per cent of hexyne found. This would be expected from kinetic considerations.

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Figure 4. EFFECT OF EXCESS OF BROMINE.

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Figure 6. EFFECT OF VOLUME OF AQUEOUS PHASE DURING BROMINATION.

Effect of Amount of Sulfuric Acid. Fixing all conditions except the amount of sulfuric acid taken and using an amount of mercuric sulfate insufficient to give 100% analysis in 15 minutes, it was found (Figure 7) that as the amount of acid decreased the per cent of hexyne found also decreased. (The amount of acid was at all times more than adequate to react with the bromide-bromate present.) The interpretation of these results is not known.

Effect of Varying Catalyst Salt. In an attempt to provide some further information on the catalytic mechanism a few experiments were performed with mercuric salts other than the sulfate. Inspection of Table 3 indicates that mercuric chloride or mercuric sulfate in the presence of chloride ion, is a much less effective catalyst, 15 meq of mercury as the chloride giving an analysis of only 80-83% in the presence of acetic acid. This low activity of mercuric chloride parallels the low activity of mercuric chloride as a catalyst for the hydration of acetylene (42).

It may also be seen that a mercuric perchlorateperchloric acid system will work satisfactorily, although the amount of mercury required to achieve 100% analysis in 15 minutes appears to be somewhat higher than when mercuric sulfate-sulfuric acid are used. Acetic acid also enhances the activity of the mercuric perchlorate.

An attempt to perform the analysis in a mercuric acetate-acetic acid system with the use of no other acid was a complete failure since the bromide-bromate did not react under these conditions.

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Figure 7. EFFECT OF AMOUNT OF SULFURIC ACID TAKEN.

-30-

Table 3

Effect of Varying Catalyst Salt

Catal	Catalyst Solution			Vol .	Vol	Per	
Salt	Salt Conc. M	Solvent	Hg taken	Acid ⁵ taken (ml)	Glacial Acetic Acid taken (ml)	Cent Found of Hexyne taken	
HgCl ₂	0.030	Water	0.0 0.12 0.12	6.0 6.0 6.0	0 0 5.0	35 38 63	
Hg012	Sat.	Water	4.4	6.0	0	58	
HgCl ₂	0.810	0.99 M aq NaC1	12.1 12.1	3.0	0 0	83 83	
HgCl 2	1.217	1.5 M aq NaCl	12.2 12.2	6.0	5.0	80 82	
HgSOL	0.10	0.96 N H2SOL	0.12	6.0 6.0°	0 5.0	44 97.5ª	
нg(с104) ₂	0.20	0.414 N HC104	0 0.16 1.0 1.0 2.0 1.0	6.0d 6.0d 6.0d 6.0d 6.0d 6.0d	0 0 0 5.0	9 35 89 91 88 99.2 ^a	

a. Different known solutions of 3-hexyne b. 6.0 N HCl except as noted c. 6.00 N H₂SO₄ d. 6.00 N HClO₄

RESULTS OF DETERMINATION OF 0.2 TO 1.5 MILLEQUIVALENTS OF 3-HEXYNE.

Procedure F-03 was used for analysis of the carbon tetrachloride phase in distribution experiments, Expts. 510 through 697, and gave consistent results within any experiment, but low material balances. It was first assumed that the low balances were to be attributed to manipulative losses, a new distribution technique being involved. Finally the failure to achieve consistent values for the distribution constant of 3-hexyne between carbon tetrachloride and 100 N aqueous potassium nitrate solution led to the suspicion that the extrapolated analytical conditions for the larger amounts of 3-hexyne were unsatisfactory. Experiments 708, 716, and 726 were undertaken to check this.

The conditions used in Expts. 510 through 697 are given in Table 4, together with material balances obtained. It is readily observed that even if the aqueous phase analysis had been several hundred per cent in error, perfect recovery of 3-hexyne would not have been attained. Therefore the most significant, if not the entire, error lay in the analyses of the carbon tetrachloride phase. It is to be noted that three different catalyst solutions were employed, namely Solutions 422-1, 525-1, and 651-1. All were supposed to be 0.25 M in mercuric sulfate, but 1.26, 1.57 and 1.28 N in sulfuric acid respectively. The results of the analyses are compared against the catalyst solution used in Table 5.

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It appears that there is some difference among these solutions, most probably in mercury content since the bromination is more sensitive to this factor than to acid concentration. Unfortunately, the solutions were made up by weight, no analysis being made to check the mercury content.

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TABLE	

Summary of Erroneous Analyses of Carbon Tetrachloride Phases, Expts. 510 to 697

Nominel Total Volume CCl₄ phase # 11 mL.; Nominal Total Volume Aqueous phase = 45 mL.; Mmols HgSO₄ takes = 1.25; Conc.^c of Hg = 0.028 M.; Bromination Time = 15 minutes; Conc.^c of H₂SO₄ =.080 N. (36.2 meq.) to.085 N. (38 meq.); Accetic Acid Täken, 10 ml. Conditions:

																				•	
					34	-									2			1	11 22	40 81	
rcent	Hexyne CC1 ₄	96	8	%	16	8	96	76	82	16	67	86	96	56	56	80	8	volumes	s Phase a	- 11936 -	
e.	of fa Phur																	total	noenby	moenbr	
Total	Hexyne Recovere (\$)	¢	Ę	78	78	100	68	61	69	63	61	8	68	8	65	61	61	nominal	Volume /	a anton	
	F															5		Is of	° 22 %	off IC	
ound	Total Sample (Meg.	0.917	0.816	0.478	067*0	0.376	0.829	0.979	1.019	866.0	0.698	0.357	0.785	0.783	1.053	0.638	1.017	d on bas	Hg = 0.0		
-Hextre 1	Aver. Dev. (%)	0.2	1.2	1.5	5.2	1.5	0.4	1.2	0.6	7*0	4.6	1.3	0.8		4.7	2.2	0.4	calculate	conc. of	conc. of	
	Meen Conc. (Meg/n	0.875	0.79	0.504	0.517	0.396	0.874	0.753	0.783	0.768	0.537	0.376	0°759	0.747	0.811	0.609	0.782	6	6	50	
5	0							ł.													
Excess	Bromin	7	47	39	58	210	133	31	34	*	52	8	67	85	32	65	28			HAGO.	BAAVIN N
	£																	puno		C C	
Meq.	Takei	ð	°.	8	8	%	R	8	38	38	33	36	38	8	8	38	33	lexyne i	<u>0</u>	nlns /	a state a
Salts in	Aq. Soln.	KIO,	MOS	KIO3	KN03	KNO3	KNO3	None	CuO1.	Cucl	Hg(Ac),	cuso, -	$2n(80_3)_2^{c}$	cd(NO ₃) ₂ e	N1(N05)50	AgN0.76 -	Co(N03)2	per cent of F	in both phese	A5 men HC101	Same think the
<u>د</u>						601	فنا											.	å .	5 %	
EXD	No	510	517	670	682	069	169	606	626	633	629	659	561	573	580	534	587				

Table 5

Comparison of Material Balances Against Catalyst Solution, Expts, 510 through 697

Jatalyst	Hexyne 1	Recovery, %	No. of	H2SOL
Solution Number	Mean	Aver. Dev.	Expts.	Conc.d N.
422-1 ^a	75	14.0	Se	1.13
525 -1 ^b	63	2.7	9 ^f	0.85
651-1°	86	8.1	Цв	0.80

a. 0.25 M HgSO_{μ} in 1.26 N H₂SO_{μ}.

- b. 0.25 M HgSOL in 1.57 N H2SOL.
- c. 0.25 M HgSO, in 1.28 N H2SO,

d. During bromination period.

- e. Expts. No.'s 510, 517.
- f. Expts. No.'s 534, 561, 573, 580, 587, 606, 626, 633, 639.

g. Expts. No.'s 670, 682, 690, 697.

-36-Table 6 Conditions for Determination of 3-Hexyne in Carbon Tetra-chloride. Experiments 708 - 716 - 1 706 chloride. Experiments 708, 716 and 726.

Conditions: Bromination Time, 15 minutes; Vol.ª CCl_l 18 ml.; Vol.^b Aqueous Phase, 35 or 45 ml.; Total Mercury Conc.^c 0.11 to 0.44 M.; Sulfuric Acid Conc. C 1.93 to 3.02 N.; Excess^d Bromine, 89 to 209%; Amount of 3-Hexyne in Sample formm 0.708 to 1.413 Milliequivalents.

10.0	ml glacial	acetic acid	no g	lacial ace	tic acid	
Detn No.	Per cent Found ^d	Known soln. used	Detn No.	Per cent Found d	Known soln. used.	
61 63	98.2 101.5	D D	60.	98.8 96.2	D D	
64 71	101.2 102.4	D P	67 68	102.8 95.6	D D	
84 8 7	99.8 97.9	G G	74	97.1	F F	
90 94	101.6 101.7	G G	78 80 _{* -}	95.0	F	
95 96	100.2	G G	82 85	97.9 95.2	\mathbf{F} G	
97 100	99.5 100.8	G C				
Mean c	of $12 = 100$.4%	Mean	of 10 = 9	6.8%	
Aver. Max. I	Dev. = 1.1	a	Aver. Max.	Dev. = 1 Dev. = 6.	• 9% 0%	
a. Nominal total volume, neglecting any CCl ₄ dissolved in water.						

b. Nominal total volume, assuming no water or acetic acid enters COll,, and that volumes of water, glacial acetic acid, sulfuric acid (18 N) and mercuric sulfate solution are addative.

c. Calculated on basis of b.

d. Based on amount of 3-hexyne taken.

Regardless of the differences in catalyst solutions it was evident that more vigorous conditions were necessary to achieve complete bromination of samples more rich in hexyne. Including a few determinations under the conditions used in Expts. 670, 682, 690 and 697, 43 analyses of known solutions of 3-hexyne in carbon tetrachloride included only two values (84.0, 86.0) of per cent found of hexyne taken below 87.8 and only two (100.8, 98.9) above 98.0. It is thus seen that the conditions were nearly adequate. However, satisfactory reproducible results were obtained only by rather radical increases in the amounts of mercuric sulfate and sulfuric acid used. The conditions found which did give satisfactory analysis are set forth in Table 6, as well as a second set of conditions which were not satisfactory. The latter set indicate that it is necessary to use acetic acid for perfect analysis, although the full 10 ml used is probably not required. This has previously been discussed (see Figure 2.).

The conditions, including the use of acetic acid, as summarized in Table 6, and incorporating a safety factor in the increase of the amount of mercuric sulfate were set up in Procedure F-04.

After performing the analyses of Expts. 708, 716 and 726, no further tests of known solutions were performed, but the recovery of 3-hexyne was always calculated in the distribution experiments. Table 7 shows the success of Procedure

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F-O4. In fact, when silver salts were present in the aqueous phase the material recovery observed was in excess of the theoretical 100%. No explanation is known for this, but it is evident that the phenomenon is reproducible as shown by the low average deviations.

Table 7

Results of Analyses Using Procedure F-04 as Shown in Recovery of 3-Hexyne

Salts in Aqueous	No. of	Recovery of	<u>3-Hexyne, %</u>
Soln. of Distri- bution	Expts.	Mean	Aver. Dev.
KNO3	4	99	3
AgNO3	5	1.04	2
KNO3, AGNO3	10	107	3

DETERMINATION OF 1,1,1,4,4,4-HEXAFLUOROBUTYNE-2.

The recent synthesis of 1,1,1-hexafluorobutyne-2 and report of its very low reactivity towards bromination and other reactions (43) made it of interest to test the analytical method on this compound. Dr. W. G. Finnegan of this Laboratory had prepared some of the compound in connection with another investigation and very kindly supplied two grams of the material.

The hexafluorobutyne was condensed into ampoules (44) at dry ice temperature and the ampoules sealed. To prepare a known solution, a 100 ml volumetric flask about 4/5 full of carbon tetrachloride was chilled in an ice-salt mixture. An ampoule containing 0.0695 gm of hexafluorobutyne was cooled to dry ice temperature (where the compound is liquid), grasped in a towel to avoid warming, cut open and as quickly as possible dropped into the volumetric flask. Estimated time the ampoule was open before being immersed was less than five seconds. The solution was allowed to warm to room temperature, diluted to volume and sampled. The semples were run by Procedure F-03. Instead of the calculated 0.3477 meq of bromine which should have been absorbed by each sample, the analyses indicated the absorption of 0.006 and 0.004 meq. The method is therefore useless for determination of hexafluorobutyne. This result was not surprising in consideration of the unreactivity of the compound.

D. DETERMINATION OF 3-HEXYNE IN AQUEOUS SOLUTION

Lucas and Pressman (1) worked with homogeneous systems containing acetylenic compounds only when the compounds have a solubilizing group such as the carboxyl group. Their results were satisfactory, except in some instances where the additional group apparently made the compound very sensitive to substitution.

In this study it was necessary to determine the concentrations of 3-hexyne in the aqueous phase of a two phase distribution system. Considering the difficulties described for the analysis of carbon tetrachloride solutions, it was

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deemed necessary to check the analysis of known solutions of 3-hexyne in water and in 1.00 N aqueous potassium nitrate solution.

PREPARATION OF KNOWN SOLUTIONS OF 3-HEXYNE IN AQUEOUS MEDIA, INCLUDING OXYGEN-FREE CONDITIONS.

The initial experiments were performed by breaking an ampoule at the bottom of a volumetric flask or bottle, using a glass rod with a slightly cupped end to hold the ampoule in place while it was being submerged". Later this rod was replaced by an assembly hereafter referred to as the "breaker". It is described in Figure 8. The stem of the ampoule was inserted through the end of the breaker and slipped into the rubber tubing which, together with the wire, held the ampoule in place at any angle. After lowering to the desired position, the rubber tubing was gently withdrawn so as to avoid any absorption of hexyne on the rubber or wire. The ampoule was broken by striking the end of the breaker smartly but lightly with a small wooden block. In general the procedure was very satisfactory, but on two or three occasions unusually heavily walled ampoules resisted the attack whereas the volumetric flask did not. It is recommended that the weight (including stem) of ampoules of 10 to 13 mm bulb diameter be held below 0.25 g to avoid this difficulty.

"Its apparent specific gravity was less than one and it floated unless forced beneath the surface.



Figure 8. BREAKER ASSEMBLY.

Later when it became necessary to exclude air from the solutions, the simple technique described above was insufficient. Use was then made of a bottle fitted as shown in Figure 9. In the bottle, water would be boiled under reduced pressure (water aspirator) until the cessation of small bubble evolution occurred and bumping began. At this point very large bubbles of vapor extending sometimes almost entirely across the bottle would form near the bottom and rise through the liquid. This behavior was taken as a criterion of "oxygen-free" conditions, and within limits of these experiments was entirely satisfactory. When the water was oxygenfree, the bottle was disconnected from the aspirator line and connected to a nitrogen supply. The time interval during which the water was exposed to the air was in general less than 15 seconds and never exceeded 45 seconds. When first connected, the nitrogen stream was run for a few minutes before the stopper was firmly seated so as to flush out the air in the neck of the bottle. After the water had cooled to room temperature, the ampoule and breaker were introduced through the small stopper opening, the nitrogen being allowed to flow so as to prevent the introduction of air, and the ampoule broken as previously described. It was found that this method did not give satisfactory results, apparently because the hexyne (Sp.G. about 0.8) floated on the water or aqueous solution, and did not dissolve readily. To achieve complete solution of the hexyne, the apparatus shown in Figure 10 was set up and the following procedure adopted.

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Figure 9. FITTINGS OF BOTTLE FOR OXYGEN-FREE SOLUTIONS.



Figure 10. APPARATUS FOR DISSOLVING HEXYNE.

Procedure S-OL. Preparation of Known Solutions of 3-Hexyne in Oxygen-Free Aqueous Acetic Acid. In the centrifuge bottle (see Fig. 10) 50 ml of acetic acid* were placed, the ampoule introduced and broken under the acetic acid, The breaker was removed, being washed down with acetic acid as it was withdrawn. The stopper assembly was put in position with the separatory funnel stopper in place."" The solution delivery tube discharge end was introduced into the small stopper opening (see Fig. 9) of the solution bottle, and the nitrogen supply to the centrifuge bottle turned on until all the solution was delivered to the solution bottle. Washing of the centrifuge bottle was achieved by proper control of the nitrogen flow and by introducing the appropriate amount of acetic acid through the separatory funnel.

The procedure proved very satisfactory and gave complete solution of the hexyne. It was also used once with butanone as a solvent. However, the butanone interfered with the starch iodine end point and made the analysis impossible.

^{*}All of the acetic acid used was stored under nitrogen until used. In a preliminary experiment, the acetic acid was boiled under reduced pressure without boiling aid; no small bubbles were evolved and the liquid bumped; this was taken to indicate that very little gas was dissolved in the acetic acid. No data could be found concerning the solubility of oxygen in acetic acid.

"" The stopcock of the funnel was left open and unlubricated, since all the lubricants tried dissolved sufficiently in the acetic acid to cause the cock to stick. When the acetic acid was diluted into the water, the lubricant then formed a colloidal suspension. PROCEDURE FOR ANALYSIS OF AQUEOUS SOLUTIONS OF 3-HEXYNE, PROCEDURE E-07.

The procedure for analysis was essentially that of Lucas and Pressman (1), but will be described, as modified, for the sake of completeness.

Procedure E-07. Analysis of Alkyne in Aqueous Solution (No Silver Ion Present), Into a 500 ml S Erlenmeyer flask was pipetted an amount of bromide-bromate solution (mole ratio of bromide/bromate = 5.00) to give an excess of bromine of 75 to 125 per cent over the amount of alkyne expected in the sample. The flask was fitted with a stopcock-stopper, covered with a black cloth, evacuated and the sulfuric acid added^a, The generation of bromine was allowed to proceed for at least five minutes, then the sample (not over 100 ml) was added by sucking into the flask from an Eberz pipette. The sample was washed through with water^b, the catalyst solution added^a, the flask shaken briefly^c to mix the contents thoroughly, then allowed to stand 15 minutes. Potassium iodided was allowed to react 3 to 4 minutes, and the vacuum was broken, the flask being refilled with nitrogen rather than air.

a. B:	sucking	into	flask	through	special	funnel.
-------	---------	------	-------	---------	---------	---------

b. Oxygen-free, distilled.

c. Frequently the determination was run the whole time on the shaker, since the shaker had a built-in timer.
d. Stabilized with sodium carbonate (39).

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The stopcock-stopper was removed, the flask washed down^e, and the mouth of the flask promptly covered with a rubber cap^f. Titration was with sodium thiosulfate solution, using starch solution for indicator. At least 10 seconds of swirling was allowed between each of the last few drops.

The titration box was merely a wooden or cardboard box painted a flat white inside, and of a size to accommodate a titration stand. A daylight tungsten lamp was mounted on the stand above the level of the flasks and the stopcocks of the burettes. A piece of foil-covered cloth was stretched across the box to shield the operator's eyes from the lamp.

Results. For the first attempt to check the analysis, a solution was prepared by breaking an ampoule in a volumetric flask filled with 1.00 N aqueous potassium nitrate solution. After standing four days, analysis was attempted under the following conditions:

> Total volume during bromination, 140 to 160 m. Meq of bromine taken, 2.695 Calculated amount of 3-hexyne content of sample, 1.072 meq. Sulfuric acid taken, 15 ml of 6.0 N = 90 meq.

The results are compared in Table 8.

e. Starch solution was frequently added at this point. The solutions were so dilute in iodine that no trouble with coagulation was experienced. This eliminated the necessity of uncapping to introduce the starch, which introduced some air into the flask. Also, the yellow color of (presumably) the HgI complex which persisted after the end point was reached, made it difficult to determine when the end point was being approached.

f. The cap had a small slit in it, through which the burette tip could be introduced.

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Table 8

Results of Analysis of 3-Hexyne in 1.00 N Aqueous Potassium Nitrate. Experiment 262. No Precautions Taken Against Oxygen

Detn. No.	Bromin- ation Time (hours)	Mmols HgSO ₄ taken	Meq H ₂ SO ₄ takena	Acetic Acid taken (ml)	CCl ₄ taken (ml)	Per Cent Found of 3-Hexyne taken
1 2 4.	0.25 0.50 4.87	2.0 2.0 2.0	100 100 100	0	0 0 0	11.7 14.7 18.5
35	0.25	6.0	118 118	15 0	0	33.6 34.0
6 1	0.25	2.0	100 100	15 0	0	16.8 11.7
95	0.25	6.0	118 118	5	5	25.4

a. Including acid from catalyst solution

It may be seen that: Lengthening the bromination time by a factor of 19.5 increased the per cent found only from 11.7 to 18.5. Adding acetic acid did not significantly increase the per cent found, although tripling the amount of mercuric sulfate approximately doubled that value. The addition of carbon tetrachloride did not produce any beneficial results.

At this point it was mistakenly concluded that insufficient amounts of mercury selts were the cause of low analysis, and attempts were made to improve the situation by adding more mercury. This led to a number of difficulties

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which will be summarized only briefly.

To increase the amount of mercury salts, solutions as concentrated as 2.00 M. mercuric nitrate in 1.1 N nitric acid were used. This, plus the large amount of potassium nitrate in the samples and other reagents, produced very high ionic strengths of 2.0 or higher during the titration period. This, as is well known but frequently not stated, causes the starch-icdine end point to degenerate from a sharp blue-tocolorless change to a gradual blue-to-red-brown-to-orange-to yellow change. The final color was presumably due to some species remaining at the end of the titration, possibly the HgI, complex. Since the bromide-bromate and thiosulfate solutions were about 0.004 N, the end points were difficult to reproduce, especially since the next-to-the-last color matched quite closely the reflection of the incandescent lights in the room. The use of the titration box as described above was of great assistance in overcoming this trouble, and with the use of a comparison flask it was found possible to reproduce end points within the limits of the other variables. Later work, where the ionic strength was less, gave end points which were easier to detect. although not appreciably more reproducible.

Initially, the end points were found to be somewhat erratic at high ionic strength when the titration was conducted in the air, even though oxygen-free solutions had been used throughout. It has been reported ($l\mu l$) that the oxidation of the iodide ion by air is catalyzed by various heavy metal

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ions. The practice was therefore adopted, as incorporated in Procedure E-07, of bleeding the flask back to atmospheric pressure after the bromination period with nitrogen rather than air, and of keeping a rubber cap over the top of the flask during titration. The improvement which this effected is shown in Table 9.

Table 9

Effect on Blank Titrations of Conducting Titrations under Nitrogen^b

		Me an Blank (ml) ^a	N	o. of Detn.	Aver. Dev. (ml)a	Max. Dev. (ml) ^a
Under	Nitrogen	-0.87	1 10 11	4	0.03	0.07
Under	Air	-1.00		4	0.15	0.19

a. of 0.005095 N Na25,03

b. Ionic strength estimated as 2. or greater.

While attempting to decrease the ionic strength during the titration by diluting the mixture after bromination, some evidence (Table 10) was found that the reaction of excess bromine and iodide ion to form iodine was finite at these concentrations.

Table 10

Effect of Volume during Titration^C upon Blank for All Aqueous Analysis

Expt. No.	Detn. No.	Total Volume during Titration (ml)	Timea (minutes)	Blank (ml) ^b
288	10 9	250	1 2	1.97 1.30
s • • •	4 3 1 2	350	1 2 3 5	1.32 1.32 1.32 1.32
ж н к	567	400	3 10 15	3.11 1.61 1.34
292	6 531	400	1.5 2 5 5	2.12 1.50 1.28 1.38

a. From addition of potassium iodide solution to addition of starch solution and beginning of titration.

b. Of 0.005620 N sodium thiosulfate.

c. Ionic strength estimated as 1.3 (for 400 ml) or greater.

While the values are somewhat erratic, it was adopted as practice and incorporated in Procedure E-07 to allow three full minutes for reaction after the addition of potassium iodide solution when the lower concentrations of bromine were involved. Whether the apparent time effect was caused by the kinetics of the oxidation or merely by the slowness of mixing of the larger volumes is unknown. It was noted that the mixing and/or reaction of each additional drop of thiosulfate solution required a finite time, so that at least ten seconds were allowed between each of the last few drops of the titration.

The stability of an aqueous solution of 3-hexyne was tested in Experiment 322, the results of which appear in Table 11.

Table 11

Stability of Solution of 3-Hexyne in 1.00 N Aqueous Potassium Nitrate. Expt. 322^b

Detn. NO.	Elapsed ^a Time (minutes)	Per Cent Found of Hexyne taken
1 2 3 4	6 33 57 128	69.5 69.0 74.2 65.5
5678	204 1401 1418 2753	70.3 59.4 60.2 57.6
9	2776	61.2

a. From breaking of ampoule under solution.b. No precautions taken against oxygen.

The results are somewhat erratic but do show a definite decrease with time.

To determine whether the repeated failure to achieve 100% analysis were caused by failure of the analysis or by some defect of preparation of the solutions, some runs were made extracting the 3-hexyne from the aqueous solution with carbon tetrachloride, then analyzing the extract by the methods which previously had been shown reliable. Special care was taken to avoid losing any hexyne during the preparation of the solutions by holding the volumetric flasks in a special rack inclined at such an angle that any hexyne rising to the top when the ampoule was broken rose, not to an air-water interface in the neck of the flask, but to a closed, water-filled part of the flask. While still in the inclined position, the flask was rotated until no liquid hexyne was visible. The results are indicated in Table 12.

Table 12

Determination of 3-Hexyne in Aqueous Solutions by an Extraction Method. No precautions taken against oxygen.

Expt.	Solvent	Per Ce	Per Cent Found of Hexyne Tak			
No.		Mean	Aver. Dev.	Max. Dev.	No. of Detn's.	
336	1.00 N KNO3	75.2	0.6	1.0	4	
344	Water	75.2	3.3	5.7	5	
348	Water	41.9	4.0	7.9	5	

The loss of hexyne was for a time considered as being due to hydration of the 3-hexyne to 3-hexanone. To determine whether this compound would be brominated, ampoules of 3-pentanone (the nearest homolog readily available) were prepared and a solution of 3-pentanone in carbon tetrachloride prepared. The solution was "analyzed" by the procedure used successfully for carbon tetrachloride solutions of 3-hexyne. Under identical conditions, except the amount of 3-pentanone in the sample, the following ratios of meq of bromine taken up per mmol of pentanone were observed: 0.046, 0.60, 0.88, 0.54, 0.066. These values correspond to 0.0014, 0.0037, 0.0054, 0.0033, and 0.0020 meq of bromine absorbed. It is seen that the amount of bromine is essentially constant and apparently a function of conditions" rather than of the amount of pentanone. Hence any hexyne which has been converted to hexanone would not be detected in the analysis.

At this point it was noticed that the greatest per cent losses were experienced in those experiments where the hexyne concentration was lowest. The comparison shown in Table 13 was made.

²Dr. H. Lemaire has found (46) that it is possible to achieve a considerably higher degree of bromination of 3-pentanone under somewhat different conditions.

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Table 13

Comparison of Losses of 3-Hexyne in Various Aqueous Solutions

Expt. Solvent No.	Per Cent Hexyne Found ^a ,b	Per Cent Hexyne Lost	Calculated Conc. of Hexyne ^C meq/ml	Hexyne Lost meq/ml
322 1.00 N KNO3	70	30	0.00299	0.00090
336 ^d 1.00 N KNO3	75	25	0.00272	0.00068
344 Water	75	25	0.00302	0.00075
348 ^d Water	42	58	0.00129	0.00075
			Mean =	0.00077
			Aver. Dev. =	0.000065
		×.	=	8%
			Max. Dev. =	0.00013
			=	17%

a. Within a short time after breaking ampoule. b. Mean value

c. All solution prepared at about 22 to 25°C.

d. Extraction method used for analyses.

The agreement of the concentrations of hexyne lost is good, considering that two different solvents and two different methods of determination were used. In particular, the two values for solutions in water using the same method of determination agree very well. The constancy of the amount of loss, regardless of the amount of hexyne initially taken, suggested that the hexyne was reacting with some substance dissolved in the water. The only likely possibility is oxygen, although carbon dioxide is not excluded by this evidence.

The solubility of oxygen in water and in 1.00 N aqueous potassium nitrate under air at atmospheric pressure is given by MacArthur (47) as 5.78 and 4.61 ml per liter, respectively. These figures correspond to 0.000258 and 0.000206 mmol/ml, respectively. This gives a ratio of $\frac{0.000258}{(0.00075)(0.25)} = 1.38$ moles of oxygen per mole of hexyne lost in water, or $\frac{0.000206}{(0.00079)(0.25)} = 1.04$ moles per mole in 1.00 N aqueous potassium nitrate. The relatively good agreement here points strongly to the conclusion that oxygen is the material which destroys the hexyne. This limited evidence is not complete proof, nor does it establish whether 2 or 3 atoms of oxygen react with one molecule of hexyne.

The exact nature of the reaction of 3-hexyne with (presumably) oxygen in water is unknown. A ratio of 3 atoms of oxygen per mole of hexyne may be satisfied by both of the following equations which are purely speculative:

 $\begin{array}{c} \text{CH}_{3}\text{CH}_{2}\text{C} \equiv \text{CCH}_{2}\text{CH}_{3} + \text{H}_{2}\text{O} + 3 | \text{O} | \xrightarrow{??} 2\text{CH}_{3}\text{CH}_{2}\text{COOH} \\ \xrightarrow{??} \text{CH}_{3} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{2} - \text{CH}_{3} \\ \xrightarrow{\text{OOH}} 0\text{OH} \end{array}$

This very interesting problem was not pursued further.**

"Recent studies in this laboratory to explore this reaction further fail to show any appreciable uptake of oxygen by 3hexyne in the presence of water. Oxygen is, however, taken up when mercury salts and acid are present. It may be that the oxygen present did not react with the hexyne until after the sample was in contact with the catalyst solution.

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However, the apparent effect of oxygen or some other material led to the attempt to prepare solutions under what will be called "oxygen-free" conditions. "Oxygen-free" will be defined, for the purposes of this thesis, as meaning that water was freed of dissolved gases by boiling, then protected from all other gases except nitrogen (and such argon or other inert gases as may have been in the nitrogen). Table 14 shows the results of these attempts.

Table 14

Analyses of Freliminary Solutions Prepared by Oxygen-Free Techniques

Expt. No.	Method by which Solution Prep'd.	No. of Detn's.	Per Cent Found of Hexyne Taken			
	~		Mean	Aver.Dev.	Max.Dev.	
358	Ampoule under water	4	90.6	0.3	0.6	
367	Ampoule under water	5	57.1	1.1	2.4	
377	Procedure S-01	Ц.	101.3	1.8	3.7	
382	Procedure S-01	5	97.3	2.6	5.1	

The success of Expt. 358 in achieving a recovery of hexyne of 90.6%, some 15% higher than the best previous value, was very encouraging, but the mediocre results of Expt. 367 made it evident that an improved method of solution preparation was necessary. As discussed under Preparation of Known Solutions, Procedure S-Ol was evolved and tried. The immediate improvement of results to 97-101% of theoretical is evident. The analyses of Expts. 322 through 382 (except for Expts. 336, 344 and 348, by extraction methods) had been performed under essentially the same conditions. Experiment 406 was therefore undertaken to obtain information concerning the required amount of catalyst. The following "standard conditions" were taken:

Total volume during bromination, 70 ml

Meg bromine taken, 0.0535

Mmols mercuric sulfate taken, 5.0

Meq sulfuric acid, including catalyst solution taken, 42 Meq 3-hexyne in sample, 0.02222. (This was smaller than amount of 3-hexyne encountered in any actual distribution run by a factor of about 2.)

These were used for analyses of approximately three out of four samples, and the composition of the solution followed over a period of six days. Modifications were made for the analyses of the other samples. Blanks were determined for various amounts of catalyst solution taken, the results plotted in Fig. 11, and the desired blank interpolated from from the resulting straight line. All analyses are shown in Table 15. Those results obtained under standard conditions were plotted in Fig. 12. The zero time per cent found of hexyne taken is extrapolated as 99.8%; the average deviation of 25 points from the line fitted by inspection is 2.3%, the maximum deviation 5.0%. For "non-standard" analyses, a percent-found value was interpelated from Fig.12, and the ratio,

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Figure 11. BLANKS FOR EXPT. 406.

TABLE 15

Results of Experiment 406

Detn. Elaps		sed	Per Cent Found			Mmols	R°	
NO.	LLL TION	ac l	Standand	1 1.5	SAYNG LAK	Tritor	4	
	(mou)	.01	Conditio	ns	Standard	polate	1	
1	0.00	n den fordelige van de	98.5		and the second	and the second secon	n fan in fersen fan de ferste fers	- (B (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) - (-) -
2	0.60		98.0					
3	1.10		98.5					
4	1.52		98.5					
8	3.42		88.5					
9	5.82				91.8	96.3	2.5	0.953
10	4.23				94.0	95.8	1.5	0.982
11	4-67				79.1	95.3	0.0	0.831
							~	
12	5.08		e1.3		ĝ*			
TA.	23.55		76.4					
16	93 07		2 .		72 7	70 0	0.0	1 053
16	91 00		A 10		1.42.0.1	10.0	0.00	1
40	as an a trade		Andre 🔹 😒					
7 77	07 00		On E	÷ .				iy t
17	01.00		00.0		5 0 0	F7 # 13	A. E	7 000
10	60.66 00 05				70.6	74.0	0.0	1.047
7.2	20.00		13.05 W		11.0	14.0	U.L.	1.038
24	30.00		40.*T	2		<i></i>		
m#7	174 AM		F7 F7 F7					
27	31.08		77.0					
~~			المجنى بينمود بنجو	÷ .		4		
28	47.87		58.5					
29	49.25		61.6					
30	49,70		58.5	1		.*		1 2.
32	50.40		(30 mi	n)	60.6		, ⁹	*
36	53.55		56.2					
37	53.95		60.6					
39	54.40		59.8					
41	71.18		51.7					
-3. 1980	T CAN OF MANY NOT		~~****					6
49	71 65		51.7					
AS	79 08		EA O					
4A	00 06		20 17					
大 な 大 天	00 00		100.01 AS A	1		· · · ·		* <i>10</i>
***V	50.10		10 × 0					
18	00 14		15 0	3				
10 AFI	140 00 UV		20.0					
10	LAN AT		06.0					
40	147.01		64.0					
4.W	147.92		20.0					
Notes	8.	Fro	n breakin	<i>a</i> a	mpoule. 1	b. 5.0 (except a	s noted.
16	C.	R =	5 found	as	observed		• · · · ·	
			% found	88	interpola	ted from	Fig.	



R, of the observed value to interpolated value was calculated. The values of R are plotted against the amount of catalyst in Fig. 13. For more than 0.5 mmol mercuric sulfate, the mean of four values of R is 1.005, with an average deviation of 0.038. The apparent upward trend of R as the amount of mercury decreases is considered of doubtful significance; it may be partially due to errors in locating the curve of Fig. 12 by inspection. Note that in all instances the ratio of moles of mercury to moles of hexyne was 0.5/ 0.00555 = 9, or greater. The exact lower limit to which the amount of mercuric sulfate might be reduced and still give good analysis was not determined.

The kinetics of the disappearance of hexyne were examined, but no definite conclusions were possible. It appears to be first order in hexyne through the first fifty hours. It was initially believed that the disappearance of hexyne under these "oxygen-free" conditions was caused by hydration, but the results of later experiments where high purity nitrogen was used, indicated that the hydration was extremely slow. It seems likely, therefore, that the slow disappearance of hexyne might be due to small amounts of oxygen introduced with the less pure nitrogen, unless the hydrogen ions provided by the acetic acid (but not present in the distributions) catalyzed the hydration.

In consideration of Expt. 406, Procedure E-07 and the following conditions were set up:

Known solution prepared by Procedure S-01

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Figure 13. EFFECT UPON R OF MERCURIC SULFATE TAKEN. EXPERIMENT 406.
Total volume during bromination, 165 ml (It was anticipated that 100 ml samples would be required during distribution runs.)

Mercuric sulfate taken, 2.5 mmols. (Concentration
 of mercury = 0.015 M, compared to 0.5/70 = 0.0071 M
 in Expt. 406.)

Sulfuric acid taken, including catalyst solution, 42 meq

Three experiments were then performed using four different sample sizes from the same known solution (but diluting to the specified total volume during bromination), and analyzing at least four samples of a given size. The first experiment (No. 433) gave erratic results for reasons unknown.

The results of the next two experiments (No,'s 441 and 460) are shown in Fig.'s 14 and 15. In Fig. 14 it is evident that while the analyses of the two largest sample sizes are reasonably accurate and consistent, those for the two smallest sample sizes are erratic and unacceptable.

The absolute excess of bromine in the latter samples was somewhat smaller than in the former, and it seemed that this, together with the low concentrations of hexyne, lowered the rate of bromination to an unsatisfactory point. In Expt. 460 the excess of bromine was increased to 100% and the other conditions held constant. The results in Fig. 15 and Table 16. The points for 20.94 ml samples are not shown in the figure; as shown in the table they give a line of somewhat different



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TABLE 16

Analyses of Known Solutions of 3-Hexyne in Aqueous Acetic Acid Under Oxygen-free Conditions Experiment 460

Points Used	No. of Points	Per Cent Found at Zero Time	Best Line ^{2,b} Aver. Dev%
л. ж. т.			y = mx + B
All except 20.94	17	100.7	y = 100.7-3.83x 0.90
All 102.3 and 50.76	12	100.7	y = 100.7-3.83x 0.72
All 10.61	5	101.0	y = 101.0-4.31x 0.66
11 20.04	5	98.4	$v = 98.4 - 8.70 \times 1.0$

Sample Size (ml)	3-Hexyne Content ^d (meq)	Per Cent Excess Bronine
102.3	0.5491	46
50.76	0.2721	38
20.94	0.1122	124
10.61	0.05691	165

Notes: a. Fitted by inspection.

b. y = per cent found of hexyne taken.

x = time from breaking of ampoule, hours

B = Per cent found of hexyne taken at zero time.

c. Based on Zero time hexyne content.

d. Calculated from weights taken.

slope. The reason for this is unknown. Table 16 shows that all zero time values agree quite well, however.

E. RECOVERY OF PRODUCTS OF BROMINATION OF 3-HEXYNE IN CARBON TETRACHLORIDE SOLUTION

In an effort to gain some insight into the mechanism of bromination, the carbon tetrachloride phases of the analysis of several experiments were saved. Those from Expts. 708, 716 and 726 were combined, washed with dilute aqueous sodium thiosulfate to remove the faint iodine color which had appeared in them while standing, and dried over calcium sulfate. The total volume of dried solution was about 1.2 liters. This was distilled through a column in portions of about 250 ml each at a pressure of 110 mm and a reflux ratio of 2 to 1. The still pot was kept in a water bath which was maintained at less than $\mu 0^{\circ}$ at all times. The distillate was collected from 24.8 to 25.4° (110mm; uncorrected). (At these temperatures the vapor pressure of carbon tetrachloride is 113 to 118 mm; the solution contained some acetic acid.) The resulting concentrate of about 320 ml was then stripped in a smaller column, using portions of about 60 ml each time, at pressures from 110 to 113 mm with a reflux ratio of 5 to The pot temperature was controlled not to exceed 42°. A 1. final concentrate was produced with a total volume of 7.5 ml.

A few drops of the concentrate, after warming for several minutes with aqueous hydrochloric acid, gave no

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precipitate of mercuric sulfide while standing 24 hours with a solution of aqueous sodium sulfide.

The concentrate appeared to contain more than one compound, and possibly three or four. None was readily separated by the crystallization techniques attempted.

One fraction crystallized from the original concentrate and recrystallized from hexane with a white solid with a melting point range from 104 to 160° . Another cut produced by dropping some of the concentrate into 98% ethanol, then recrystallizing from 98% ethanol, was a soft, smeary white solid which melted from 60 to 91°. This portion contained bromine but gave a negative test for iodine and mercury. An analysis gave C, 20.38%; H, 0.41%, Br, 0.39%. These figures shed little light on the nature of the mixture.

The products of the "bromination" process remain unidentified, and the reaction schemes in Section G must be considered as tentative.

F. SOLUBILITY OF 3-HEXYNE IN WATER AND IN 1.00 N AQUEOUS

POTASSIUM NITRATE

To be sure that the failure to achieve good analyses was not caused by working at concentrations greater than the solubility of 3-hexyne and because it was desirable not to approach the solubility limit too closely in distribution experiments, the determination of the solubility was undertaken.

The procedure was to equilibrate the aqueous phase * By Dr. Adalbert Elek.

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by stirring with enough 3-hexyne to provide a visible second phase, allowing the phases to separate, and then taking samples of the aqueous phase. The results are shown in Table 17.

Table 17

Solubility of 3-Hexyne in Aqueous Media

at Room Temperature (20-25°) and Atmospheric Pressure .

Expt.	Solvent	Gas in	-			
No.		Contact with Solution	meq/ Mean	ml Aver. Dev.	No. of Detn b	mol liter (mean)
326	1.00 N eq. KN03	Air ^a	97.9 x 10-4	4.4 x10-4 (4.5%)	4	0.00245
677	Water	Nitro- gen	122 x10-4	3.0 x10-4 (2.4%)	6	0.00305

a. The results here are considered reliable, since the amounts of hexyne in the sample were moderately large compared to the amount of oxygen. Even though some hexyne may have been consumed, the solution remained in contact with liquid hexyne. The probability that the oxidation products seriously influenced the solubility seems slight.

b. Samples taken for analysis, not equilibrations.

The highest concentration of 3-hexyne in water solution ever used was $52 \ge 10^{-4} \mod/ml$ (Expt. 460; some acetic acid present in solution), or less than half-saturated. In 1.00 N aqueous potassium nitrate solution, the highest concentration of hexyne used was 30 $\ge 10^{-4} \mod/ml$, or less than one third saturated.

It is to be noted that the potassium nitrate salts

out the 3-hexyne somewhat, the solubility in water being about 1.24 times the solubility in 1.00 N aqueous potassium nitrate.

G. DISCUSSION OF RESULTS

APPLICABILITY OF METHOD

In view of the results of Lucas and Pressman (1) it is presumed that the considerations outlined here apply to other alkynes and to dihalogenolefins unless other functional groups interfere. The failure of the method for 1,1,1,4,4,4-hexafluorobutyne-2 is presumably due to the effect of the trifluoromethyl groups on the carbon-carbon triple bond. Any extrapolation of the method as used here should be tested on known solutions.

REACTIONS INVOLVED

As previously discussed, the principal difficulty is indicated but not definitely proven to be the conversion of a readily formed intermediate dibromo compound into a final product which has absorbed four equivalents of bromine. The finding of several products in the "bromination" mixture is not surprising since Francis (49), Ushakov and Tchistow (50) and others have shown that addition reactions carried out in media containing negative ions will produce a mixture of products where a negative ion has added in place of a bromide ion. The situation in this analysis might be repre-

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sented by the following scheme:



X is most probably the acetate ion, OH_3COO^{-1} , or less probably $SO_{14}H^{-1}$, OH^{-1} , or some more complex ion involving mercury. It should be noted that where the carbon atoms are marked with an asterisk, a pair of optical isomers are produced (unless some unknown consideration of mechanism prevents it). The above scheme shows that seven distinct compounds are possibly produced, namely: IV, v-d-configuration, V-1-configuration, V-1-configuration, VI-d-configuration, VI-d-configu

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the number of possible products mounts rapidly, and if an X^{*} rather than a Br^{*} adds to I, the same is true.

The reason for the difficulty in progressing from the olefinic intermediate to the saturated final product(s) is not known. It may merely be that the rate is quite slow or negligible, or it may be that there is an equilibrium position between the two states of saturation. If the mercury enters as a catalyst under the former, some type of reactive intermediate might be formed of the type

$$\left[RCX = CXR \cdot Hg\right]^{++}$$

Such are well known for ordinary olefins (40). This speculation might offer a profitable point of attack for further study of the mechanism.

If the mercury serves to displace an equilibrium between the olefinic intermediates and the final products, some new products must be involved for which the equilibrium lies much farther to the right.

FACTORS INFLUENCING ANALYSES OF SAMPLES IN CARBON TETRA-CHLORIDE SOLUTION

Such solutions produce a two phase system when the sample is added to the aqueous reagents used. As is readily evident, the situation is quite complex when two phases are present, whereas it appears to be much more simple when the system is homogeneous. Consideration should be given in any further studies to the use of a system which would be homogeneous even when carbon tetrachloride is added, as was done by Johnson and Clark (51) by using an acetic acid medium. Solubility data for the acetic acid-water-carbon tetrachloride system is available (52) which would be of considerable help with such work.

The work, done with Procedure F-03 and illustrated in Figures 2 to 7 and Table 3 shows that in a sulfuric acidmercuric sulfate-bromine-water-carbon tetrachloride system, the rate of bromination is: (a) highly dependent upon the amount of mercuric salt present, the rate increasing as the concentration of mercury increases: ionized salts (mercuric sulfate, mercuric perchlorate) are much more active than unionized salts (mercuric chloride); (b) only slightly dependent upon the concentration of bromine present, the rate increasing slightly as the concentration increases; (c) apparently independent of the presence or absence of bromide ions, except as such ions reduce the concentration of uncomplexed mercury present: the theoretical bromide/bromate mole ratio of 5/1 should be used; (d) dependent on the amount of acetic acid present, up to a small but definite value; the rate increases as the amount of acetic acid increases, reaching a maximum value; (e) slightly dependent upon the volume of the carbon tetrachloride phase, the rate decreasing as the volume of carbon tetrachloride decreases; (f) markedly dependent upon the volume of aqueous phase, the rate decreasing as the concentration of reagents decreases;

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(g) dependent upon the kind and amount of acid in the system, the rate decreasing slightly as the amount of acid decreases.

The rate of bromination is sufficiently rapid to give a good analysis in a sulfuric acid-bromine-carbontetrachloride-water system if sufficient mercuric salt is present. Less mercury is required if a small amount of acetic acid is added. Perchloric acid may be substituted for sulfuric acid, but a greater amount of mercuric salt is required.

The rate of bromination is not sufficiently rapid to give satisfactory analysis in a hydrochloric acid-brominewater-carbon-tetrachloride system using mercuric chloride as a catalyst, either with or without acetic acid.

Addition of sodium chloride after the bromination period may be omitted without affecting results.

The above result were determined using amounts of hexyne from 0.02 to 0.2 meq. When larger amounts were to be determined, further work was necessary to achieve satisfactory results. The various conditions of analysis and the results they produced are summarized in Table 18. In addition to the considerations previous mentioned, it seems indicated that only mercury-to-hexyne mole ratios greater than unity are satisfactory, and that as the volume of the carbon tetrachloride phase diminishes, higher ratios are necessary. The implication is that the mercury enters the reaction stoichiometrically, as would be the case of the formation of a

-71-Table 18

Comparison of the Conditions^e of Analysis for 3-Hexyne in Carbon Tetrachloride Solution

	Proc. F-03	Table 4	Lucas & P.	Table 6	Table 7
Analysis Satisfactory	Tes	No	Yes	Yes	Yes
Volumes ^b CCl ₄ Phase, ml	50	11	21	18	11
Aqueous Phase, ml	37	40-50	70	35-45	45-48
Excess Bromine ¹	50 to 100	39 to 210	10 to 15	89 to 209	75 to 125
Meq of 3-hexyne in sample ^a	0.02 to 0.2	0.376 to 1.019	2.0	0.708 to 1.413	0.226 to 1.211
Conc. ^c of Hg, M	0.027	0.025 to 0.031	0.027	0.11 to 0.44	0.21 to 0.22
Conc. ^c of H ₂ SO ₄ ,N	1.11	0.80 to 0.85	2.14	1.93 to 3.02	2.88 to 3.06
Conc. ^C of Acetic Acid, N	4.7	3.5 to 4.3	5.0	3.4 to 5.0	3.6 to 3.9
Bromination Time, Minutes	15	15	7	15	15
M Moles Hg Taken	1.0	1.25	4.0	4.45 to 21.2	10.0
Ratio, M Moles Hg Naximum M Moles Hexy	ne 5.0	1.22	2.0	3.50	8.25

Notes:

a. No precautions were taken against oxygen in any of these experiments. It is to be noted that if the same amounts of hexyne were lost as in aqueous solutions (Table 13), the loss would not be noticable.

b. Nominal total volumes

c. Calculated on same assumptions as nominal total volumes.

mercury-containing compound was the factor which shifted the equilibrium (see above). However, the exact species as which the mercury is present is unknown; probably it is distributed among Hg^{++} , $HgSO_{14}$, $Hg(HSO_{14})_2$, $Hg(HSO_{14})^+$, $Hg(OCOCH_3)_2$, $Hg(OCOCH_3)^+$, or others, some of which might complex ions carrying a negative charge. There has been reported some evidence for complexes between bromine and mercury compounds of the type $HgX_2 \cdot Br_2$ where X is bromine or chlorine (53). The complexes of olefins and mercuric ions have previously been mentioned.

The distribution of three and perhaps more solutes appears to be of importance in the two phase system. The three essential solutes are hexyne, bromine and some mercury compound. The improvement of analysis as the volume of the carbon tetrachloride is increased, all other factors being equal, suggests than an appreciable fraction of the bromination takes place in that phase. Since the bromination at least of 1-hexyne (13) does not go to completion in carbon tetrachloride in the absence of a catalyst, it appears that some mercury species is in the carbon tetrachloride phase. This might explain the beneficial effect of acetic acid if mercuric acetate is more soluble in carbon tetrachloride than is mercuric sulfate or mercuric bisulfate.

Inspection of Table 18 elso indicates that possibly more sulfuric acid is required as the volume of the carbon tetrachloride phase is decreased. The reason for this, if it is true, is not evident. It may be necessary to distribute

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more sulfuric acid into the non-aqueous phase, or to convert the mercury into some species such as $Hg(SO_{l_1})_2^{-1}$.

FACTORS INFLUENCING THE ANALYSES OF SAMPLES IN AQUEOUS SOLUTION

The analysis of 3-hexyne in a single phase all-aqueous system appears to be much less complicated than in a two phase system, providing that no loss of hexyne occurs in preparation of the sample solution. Sulfuric acid concentrations of 0.26 N, mercury concentrations of 0.0303 M and 100% excess of bromine proved to be adequate. Aside from the less readily detectable and more slowly functioning end point found when high ionic strengths occur during the titration, the procedure is satisfactory.

The question of what destroys or converts the 3hexyne in aqueous solution remains somewhat in doubt. The results of this work were satisfactory only if all gases except nitrogen (and concomitant inert gases) were excluded. Other evidence (48) suggests that the hexyne does not react with oxygen until mercuric salts and acid are present as catalysts.

ACCURACY AND PRECISION OF METHOD

Tables 6, 7, 14 and 16 have shown achievement of analyses indicating values of per cent found of hexyne taken of 97.3 to 102.4, with practically all results lying between

99 and 102. Table 19 details the information noted during the distribution experiments described in Part II (as summarized in Table 7). The material balances tended to exceed 100% when the aqueous phase contained silver ion. The cause of this is unknown. It is believed not to be absorption of bromine in the silver bromide precipitate, since blanks were run and were reproducible under identical conditions. It seems doubtful that it was due to substitution, unless the silver ion somehow catalyzes substitution, for no substitution was indicated at any time in dealing with solution in either carbon tetrachloride or in water so long as the flasks were kept covered during the bromination time. It is of interest that under different conditions, results in the determination of 3-hexyne which were some 2 to 7% greater than theoretical were observed (46).

The average deviations experienced within sets of determinations are indicated in Tables 4, 6, 14, 16 and 19. Caution should be exercised, however, since low average deviations are encountered even when the analysis is inaccurate (Table 4).

It is concluded that, under the conditions described here, accuracy of 99 to 102% with an average deviation of 1% may be obtained in the determination of 3-hexyne for amounts of from 0.02 to 0.52 meq in aqueous solution and from 0.02 to 1.41 meq in carbon tetrachloride solution. Extrapolations of the conditions should be tested upon known solutions.

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TABLE	19

Summary of Analyses Performed in Distribution Experiments

Expt.		CC1, Phase				Aqueous Phase				% of	Total
No.		No. of Detn's	Mean Conc. Heryne Found	Devia % of Hexyn Found	tion e	No. of Detn's	Mean Conc. Hexyne Found (meg) (10 ⁴)	Deviations % of Hexyne Found		Total Hexyne in CCl4 Phase	Hexyne Recov- ered
		meq/ml	Aver.	Max		Aver.		Max			
0	748	8	0.794	3.6	5.9	7	3.33	0.3	0.8	97.4	181
N	758	7	1.012	1.5	2.0	8	4.35	2.6	4.6	96.8	95
A I	764	6	0.585	3.4	5.6	4	2.36	0.1	0.3	98.5	103
0 T	768	5	1.279	1.4	2.2	5	5.84	-	-	96.4	95
	778	3	0.472	0.1	0.2	4	49.1	0.2	0.3	79.6	104
6	783	3	0.735	0.1	0.3	3	77.7	0.1	0.2	69.4	108
"B"	787	4	0.191	1.1	2.0	4	24.1	1.3	2.6	75.7	82
NA	793	5	0.276	0.7	1.0	5	29.3	2.3	3.9	80.0	109
8.	798	4	0.253	0.6	0.6	3	26.9	0.8	1.2	77.3	110
4	802	4	0.226	0.5	1.4	3	27.0	2.0	3.0	73.1	112
6											
B	516	4	0.826	0.4	0.7	3	21.6	0.8	1.1	91.1	109
Harr I	820	3	0.230	0.5	0.8	3	5.94	0.9	1.3	96.5	107
2	826	2	0.208	-		4	5.30	0.7	0.9	92.4	110
750	832	4	0.171	0.6	1.0	3	1.15	0.8	1.2	97.9	107
9	835	3	0.567	0.4	0.6	3	15.3	0.2	0.3	80.1	108
m	835	3	0.300	0.7	1.0	2	10.5	0.2	ant	-	100
B	844	3	0.372	0.5	1.2	3	9.82	0.6	0.0	06.8	107
NA	848	3	0.401	0.7	1.0	3	13.1	1.7	2.6	92.9	87
20	852	3	0.414	0.4	0.7	3	10.2	0.6	0.9	97.3	104
	856	3	0.388	0.7	1.4	3	10.0	1.1	1.7	97.1	102
	860	2	0.527	-	-	3	14.0	1.9	2.0	477	•••
sales.	806	3	0.779	0.2	0.3	4	25.8	1.4	2.8	88.6	108
0	811	4	0.815	1.3	2.8	4	40.4	1.4	1.9	82.9	107
MIS	841	2	0.840	-	-	3	4.96	1.4	2.1	96.8	104

Notes:

Amount of 3-Hexyne in samples ranged from 0.483 to 1.212 meq when the solvent was carbon tetrachloride and from 0.0241 to 0.249 meq when the solvent was an aqueous solution. CG1₄ Phase analyses performed by Procedure F-04. Aqueous Phase analyses performed by Procedure E-07. H. REFERENCES

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PART II

COMPLEX FORMATION BY THE CARBON-CARBON TRIPLE BOND

A. INTRODUCTION

It has been postulated that the carbon-carbon triple bond should show complex formation with metallic ions in aqueous solution as does the carbon-carbon double bond, yet a search for this effect was unsuccessful where the influence of an acidic acetylenic hydrogen was absent. The tremendous development of acetylene, olefin, and carbon monoxide chemistry in Germany in the years 1939 to 1945, involving in many instances the catalytic effect of copper or silver compounds, raised again the question of a triple bond-metallic ion interaction. This work was undertaken to re-examine the problem.

B. HISTORICAL. OLEFIN COMPLEXES.

The work in this field prior to 1940 has been reviewed by Keller (54). Comparatively little has been done since that time except for the papers by Andrews, Keefer and Kepner (55, 56, 57, 58, 59), of Gilliland, Bliss and Kip (60a), and of Ward and Makin (60b). With the exceptions

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which will be specifically noted later, all the work summarized by Keller was of a synthetic nature. A very considerable number of different olefins were tested up to and including seven-carbon compounds and some terpenes. Table 20 shows some typical examples for each metal reported to complex, and draws some comparisons. It does not, however, include samples of all the various types. The principal feature which may be noted is that, for the compounds which are the best defined, the metals have linear (copper, silver, mercury) configurations or square planar (platinum, palladium) configurations. Inspection of a table of ionic radii (especially the picture by Campbell (61)) suggests that the complex-forming ability of the metals falls in the area of minimum size change in going from neutral atom to charged ion. Whether or not this has any significance is not appar-Bailar (60c) has discussed the coordinating tendencies ent. of metal ions with various reagents.

The equilibria existing in the formation of olefinmetallic ion complexes were unstudied until the work of Eberz, Welge, Yost and Lucas (62) and of Winstein and Lucas (63) who investigated the interaction of silver ions with various olefins. Since then papers by Lucas and collaborators (64a, b), Lucas, Hepner and Winstein (65) and a series by Andrews, Keefer and Kepner (55, 56, 57, 58, 59) have studied the equilibria for silver, mercuric and cuprous ion complexes. The latter group introduced (56) a two-phase liquid-solid equilibration method which appears to be

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-82-Table 20

Some Typical Solid Metallic Salt - Olefin Complexes

Metal	Olefin	Reported Formula	Che	racteristic	SK
(a)	(a)	(a)	Group (j)	Co-ordin- ation Number	Config- uration (27)
Ag	c	AgN03.C10H12 (54)	Ib	2	Linear
	C	$AgC10_4.C_{10}H_{12}(54)$			
Cu-I	Ъ	CuCl.C2H4	Ib	2	Linear
	đ	Cu2Cl2.C4H6			
Hg-II	e,f		IIb		
Zn	g	ZnCl ₂ .C ₅ H ₁₀			
Pt	b,h	PtCl ₂ .Un	VIII	4	Square
	b	KC1,.PtCl2.C2H4.H	I ₂ 0		▲ ader \. As & As & Sole Le
Pd	b,f,i,	h[Paci2.Un] 2	•	4	Square Planar
Fe II	Ъ	$\mathrm{FeBr}_{2}\text{-}\mathrm{C}_{2}\mathrm{H}_{4}\ \mathrm{12H}_{2}\mathrm{O}$	ج ب	6	Octa- hedral
Fe III		$\texttt{FeCl}_{3} \textbf{.} \texttt{C}_5 \texttt{H}_{10} \texttt{CH}_3 \texttt{OH}$		6	Octa- hedral
Ir	b	Ircl ₂ .c ₂ H ₄		6	Octa- hedral
Al	b	$A1C1_{3} \cdot C_{2}H_{4} \cdot 2C_{2}H_{5}O$	H III		
Notes:	 E. Fr b. Et c. di d. l, e. pr f. is g. an h. st i. cy 	om Keller (54) unl hylene cyclopentadiene 3-butadiene opylene obutylene ylene yrene clohexene Periodic Table in	ess othe	erwise noted	•

k. as usually reported for inorganic compounds

superior for work where the solubility of the inorganic salt is very limited, whereas Lucas and his collaborators had used a two-phase liquid-liquid equilibration with inorganic salts of moderate solubility. The available data is still somewhat scanty, but Table 21 makes such comparison as is possible for the different metals. Only those olefins are included with which more than one metal has been studied; constants with one metal are available for many more olefins. It is evident that the equilibrium lies much further to the right for complexes containing the cuprous ion or the mercuric ion than for the silver ion.

The bond formed in an olefin-metallic ion complex has been much discussed (54, 63, 66, 67, 68). It appears that the bond is formed by the interaction of the electrons in the pi molecular orbital of the double bond with the metallic ion, the exact nature of both having considerable effect on the strength of the bond. The various studies give insight into the influence of the hydrocarbon structure, but no work is reported on the characteristics of the metal.

AROMATIC COMPLEXES

The first investigation of the complexes formed by aromatic compounds appears to be the work of Winstein and Lucas (63) with phenol. The first aromatic hydrocarbons were studied by Andrews and Keefer (69). The affinity is much less pronounced than that of the olefins or even of 3-hexyne (see Table 30). Subsequently a study of the Henry's

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TABLE 21

Relative Complexing Powers^a of Various Metals with Olefins

Olefin	Cur	prous lon	Silver ion	Me	Mercuric ion	
	KC	ĸđ	K ₁	E1	кb	
Cyclo hexene,25°c			79.5 (63)	8.2x10 ⁴ (65)	5.0x104 (65)	
Ethyl vinyl carbinol	59,x10 ⁴ (59)	15x10 ⁵ (59)	14 (59)			
Methyl vinyl carbinol	3.3x10 ⁴ (59)	17x10 ⁵ (59)	14 (59)			
r,r-dimethyl allyl alcohol	1.1x10 ⁴ (59)	7.0x10 ⁵ (59)	2 (59)			
b-methyl allyl alcohol	0.92x10 (59)	⁴ 4.2x10 ⁵ (59)	11 (59)			
2-methyl- 2-butene-1-01	0.35x10 (59)	⁴ 5.9x10 ⁵ (59)	5 (59)			
b-chloro allyl alcohol	0.022x1((59)	0.35x10 ⁵ (59)	0 (59)			
crotyl alcohol	4.0x10 ⁴ (59)		3 .9 (63)			
Allyl alcohol	5.2x10 ⁴ (59)		14 (59)			

Notes: a. See section on "Notation" for symbols.

b.
$$K = (HH_{COH}^{+})(H^{+})$$

(B) $(Hg^{++})^{-}$
(C. $K = (BCu^{++})^{-}$
(B) $(Cu^{+})^{-}$
(C. $K = (BCuC1)$
(B) $(Cu^{+})(C1^{-})^{-}$

Law constants for hydrogen chloride in various aromatic hydrocarbons was reported by Brown and Brady (70), while Benesi and Hildebrand (71) studied the complex formation of iodine with benzene and mesitylene. The latter was continued and discussed by Mulliken (72). Rundle and Holman (73) have studied a tetramethyl-platinum-benzene complex of the formula $(CH_3)_{16}Pt_4 \cdot 2C_6H_6$. Uemura <u>et al</u> (74) are reported to have studied the complexes of substituted triazenes with unspecified metals.

ALKYNE COMPLEXES

The earliest evidence of complexing of acetylene or acetylenic compounds is contained in the work on cuprous and silver acetylides of complex composition. This has been reviewed by Nieuwland and Vogt (42). Even today some of the phenomena observed there are not completely understood, although in recent years Vestin and co-workers have resumed the study of such compounds (76, 77, 78); they described a compound with the formula C2(CuCl)8K2, and several others. Shaw and Fisher (79) have described Ag2C2.6AgNO3 and Ag₂C₂.AgNO₂, and Shaw (80) has been issued a British patent forthe preparation of Ag2C2.6AgNO3 and HgC2.3AgNO3. The exact structure of these compounds does not appear to have been elucidated. The formulae, however, suggest that the C_2 group may coordinate with up to 6 or 8 other groups such as AgNOg or CuCl. The crystal structure of these compounds would be of interest.

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Taufen, Murray and Cleveland (81) examined the effect upon the Raman specta of various acetylenic compounds of dissolving them in aqueous solutions of silver nitrate or silver perchlorate. For cis- and trans-2-butene, cyclopentene, hexene-1 and cyclohexene and for ethyl-, propyl- amyland phenylacetylene they observed" an appreciable increase . in solubility (as compared with the solubility in water) and a shift in the double or triple bond frequencies. No solubility increase was noted"" with diamylacetylere, ethylbutylacetylene and diethylacetylene. They did not, or at least do not state in their paper that they did, examine the spectra of any solution of a disubstituted acetylene. It is believed that this is the evidence on which they reported that the disubstituted acetylenes did not complex with silver ions.

With olefins, Taufen <u>et al</u> observed that complex formation lowered the double bond frequency of 1600 to 1700 cm⁻¹ by 60 or 70 cm⁻¹. In mono-substituted acetylenes the complexing split the triple bond frequency of 2110 or 2120 cm⁻¹ into three lines which had frequencies of approximately 15, 45 and 65 cm⁻¹ lower than the original line. No precau-

"Presumably by visual estimate, although not specifically so stated.

This is not surprising, considering the approximate visual method used to estimate solubilities. The results obtained in the present study by analyses show only a ten-fold or less increase of a very small original solubility.

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tions were taken against oxygen, but the amounts of alkyne were so large that the amount which might have been consumed by any oxygen originally present in the aqueous solution would be small and unnoticed.

The above work by Taufen <u>et al</u> and of Vestin and of Shaw indicates that when an acetylenic hydrogen is present or, more accurately, has been replaced by a metal ion, the carbon-carbon triple bond is able to interact or complex with metallic ions or compounds. The evidence does not disprove, however, the ability of the carbon-carbon triple bond to complex with groups other than hydrogen or metal attached to complex.

No reference to any study of acetylene complexes was found in the reports of the German work on acetylene chemistry.

Lemaire (46^{*}) has used an indicator method to investigate the 3-hexyne-mercuric acetate-perchloric acid complex in a non-aqueous medium, which appears to be the first report of complexing of the carbon-carbon triple bond when no acidic hydrogens are present.

C. PRELIMINARY CONSIDERATIONS

The study of the alkyne-metallic ion complexes reported here was pursued in the light of the above considerations.

"Lemaire's work was done while this work was in progress.

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To be free of any complications arising from the presence of a =CH group, the simplest symmetrical liquid alkyne was chosen, namely 3-hexyne. Its properties have been described in Table 1. The two-phase liquid-liquid equilibration method of Eberz, Welge, Yost and Lucas (62) and of Winstein and Lucas (63) was adopted, since it permitted calculation of the equilibrium constants involved. The twophase liquid-solid equilibration method of Keefer and Andrews (56) was published while this work was in progress; it did not offer any advantages where adequately soluble metal salts such as silver nitrate were available. Following Winstein and Lucas, the ionic strength of the aqueous phase was maintained constant at μ = 1.00 by using the proper quantities of potassium nitrate in solution with whichever other salt was in solution. This minimized any salting-in or salting-out effects, although other considerations occasionally necessitated deviation from the practice.

The choice of metals to be studied was guided by the considerations already discussed for the olefin complexes. Although the ions of ruthenium, rhodium, osmium, iridium, palladium and platinum demonstrate marked complex forming ability, they were not investigated here because of considerations of cost, side reactions, solubility characteristics unfavorable to liquid-liquid distribution methods, and possible interferences with analyses. It would be of much interest to try these metals, either by the synthetic method of Kharasch and Ashford (82) or by the liquid-solid method of Keefer and Andrews. Gallium, indium and thallium were not tried because of theirfailure to complex the olefins.

Some consideration was given to the possibility of a non-aqueous distribution system, particularly one using tetrahydrofuran, the solvent used so widely by the German chemists in their acetylene studies. The liquid-solid equilibration method might be more successful here since the solubilities of inorganic salts in organic liquids are very small.

D. EXPERIMENTAL

The chronological development of the distribution studies closely paralleled the development of the analytical method, in that as the interference of oxygen became evident, the distribution technique was modified accordingly.

MATERIALS

Most of the materials used in this Part are identical with those used in Part I and will not be described again here. The following exceptions are noted:

Zine nitrate hexahydrate, cadmium nitrate tetrahydrate, nickel nitrate hexahydrate, cobalt nitrate hexahydrate and cupric sulfate pentahydrate were all reagent grade. Solutions of these for blanks and for distributions were made up by weight; this procedure probably introduced some error for those salts which are hygroscopic, but since

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no appreciable complexing was indicated and no calculations involving the exact concentration of metallic ion were performed such errors did not affect the results.

<u>Cuprous chloride</u> was prepared by the method of Henderson and Fernelius (83). It was stored in small amounts of a gram or less in small test tubes sealed by paraffincoated cork stoppers. Over the four month period when the material was used, no deterioration was perceptible by color.

<u>Cyclohexene</u>, Eastman Kodak Company White Label grade, was distilled, a cut boiling $81.1-81.5^{\circ}$ (uncorrected) being taken. When some was required for a run, the amount needed was redistilled from sodium immediately before use. The redistilled material gave $\underline{n}_D^{25} = 1.4437$. Egloff (37) gives $\underline{n}_D^{25} = 1.4437$. Since all likely contaminants such as cyclohexanol and cyclohexane had \underline{n}_D^{25} values which differ by at least 0.016, it was considered that the cyclohexene was sufficiently pure for the preliminary studies in which it was utilized.

NOTATION

The notation is that of Eberz, Welge, Yost and Lucas (62) and was also used by Winstein and Lucas (63).

B = unsaturated substance

(Bt) = total concentration of unsaturated substance in aqueous phase, moles/liter

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- (B) = concentration of uncomplexed unsaturated material in aqueous phase, moles/liter
- (BAg) = concentration of species (B.Ag) in aqueous phase, moles/liter
- (BAg₂) = concentration of species (Ag·B·Ag)⁺⁺ in aqueous phase, moles/liter
 - (Ag⁺) = concentration of free silver ion in aqueous phase, moles/liter
 - (Agt) = total silver concentration in aqueous phase, moles/liter
 - (B)_c = concentration of unsaturated material in carbon tetrachloride phase, moles/liter

$$\mu$$
 = ionic strength

 $K_D = (B)_c/(B) =$ distribution coefficient of the unsaturated material between carbon tetrachloride and the aqueous phase

K = evaluated complexing constant $\frac{(BAg)}{(B)(Ag^+)}$

$$= \frac{K_{\rm D} [(Bt) - (B)]}{(B)_{\rm c} [(Agt) - (Bt) + (B)]}$$

$$= \frac{K_{\rm D} |(Bt) - (B)_{\rm c}/K_{\rm D}|}{(B)_{\rm c} [(Agt) - (Bt) + (B)_{\rm c}/K_{\rm D}]}$$
(2)

Note that these expressions are based on the assumption that no (BAg₂) is present. See discussion on evaluation of K_1 and K_2 .

$$K_{1} = (BAg)/(B)(Ag^{+}) = \text{first argentation constant}$$

$$K_{2} = \frac{(BAg_{2})}{(BAg)(Ag^{+})} = \text{second argentation constant}$$

$$K_{0} = K_{1}/K_{D}$$

$$Z = \frac{K_{D}}{K_{D}} \text{ observed for some aqueous solution}$$

$$Z = \frac{K_{D}}{K_{D}} \text{ interpolated for potassium nitrate solution}$$

The following abbreviations are also used: meq = milliequivalent(s). Most of the concentrations were expressed in this unit for ease of calculation of analyses. On the basis that four atoms of bromine add to one molecule, for hexyne, 4 meq = 1 millimole. Note that all symbols preceding this are expressed in moles/liter.

PRELIMINARY DISTRIBUTIONS

The first exploratory distributions were undertaken in the simplest apparatus considered adequate for the purpose: a flask which was stoppered and shaken by hand. The aqueous phase was decanted from the carbon tetrachloride phase, and both phases sampled and analysed for 3-hexyne content. In some of these experiments, the aqueous phase was centrifuged before sampling so as to insure complete settling out of any carbon tetrachloride droplets. This method was used for the distributions of cyclohexene and for the preliminary distributions of 3-hexyne. A simple water bath without automatic control provided temperature control at $25^{\circ}\pm1^{\circ}$.

APPARATUS FOR OXYGEN-FREE DISTRIBUTIONS

When study of the analytical method for 3-hexyne indicated the interference of oxygen, the procedure and apparatus were devised to carry out the distributions under oxygen-free conditions. Two discreet steps were necessary: the preparation of the oxygen-free aqueous solution, and the oxygen-free distribution. The apparatus is shown in the following figures:

Fig. 16 Special Mixing Cylinder, Head and Delivery Tube Fig. 17 Equilibration Flask

- Fig. 18 Gadget Mark 78 Mod 3.
- Fig. 19 Sample Removal Tube
- Fig. 20 Storage Cylinder for Carbon Tetrachloride Phase
- Fig. 21 Schematic Nitrogen Connections to Distribution Apparatus.

The Nitrogen Inlet Tube is not shown. It consisted of a stopcock sealed on one end to a male $\frac{12}{40}$ joint, and on the other to a $\frac{12}{5}$ socket joint to give as compact an assembly as possible.

The assembly of the special mixing cylinder for preparing solutions is evident from Fig. 16.

The distribution apparatus was mounted on a special stand made of aluminum plate (21 x $15 \times \frac{1}{2}$ inches) drilled for rods and equipped with feet. The entire assembly was thus a unit which could be moved out of the way when desired simply by disconnecting the electricity, nitrogen and com-



Figure 16. SPECIAL MIXING CYLINDER, HEAD, AND DELIVERY TUBE.



Plan View



Figure 17. EQUILIBRATION FLASK (1 liter).


Figure 18. GADGET, MARK 78 MOD 3.







Figure 20. STORAGE CYLINDER

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pressed air supply lines. The total height of the assembly was 30 inches.

The equilibrium flask was mounted in a thermostat (a glass jar) equipped with a stirrer, a 100 watt immersion heater, a Central Scientific Co. "Cenco-de Khotinsky" thermoregulator (Catelog No. 99005A), and a thermometer (15 to 33° C., division 0.1°). The thermometer was compared with a thermometer certified by the United States Bureau of Standards and was found to agree within 0.1°. The temperature regulation obtained was +0.1° of the set point, except when the equilibration stirrer was operating. The vibration of the latter caused the thermoregulator contacts to stick and cause overheating. This was avoided by keeping close watch during the comparatively brief equilibration period and shutting off the heater when the temperature went over 25.0°. On two or three other occasions the contacts also stuck and caused the temperature to rise. For future apparatus, a reverse acting circuit is recommended where a sticking of the contacts in the closed position would turn the heater off. Since the room temperature was never observed below.18° and usually between 21 and 24°, the errors introduced by thermoregulator failure would thus be much more restricted. Use of some other type of thermoregulator, such as a mercury-filled model or the "Thermocap" electronic controller, would be preferred. When room temperature rose above 25°, sufficient cooling was obtained by directing a jet of compressed air against the surface of the water bath.

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The equilibration flask was fitted with a conventional mercury seal and a Patterson (84) upflow stirrer driven by a Palo-Meyers variable speed motor. The stirrer gave results which can only be described as excellent. Considerable care was taken to get smooth-running bearings by sizing of the glass shaft and the metal sleeves. Moderate care in having the stirrer shaft straight produced a minimum of vibration. In a 1-liter equilibration flask (Fig. 17), a distance of 8 to 10 cm from the wings of the stirrer to the tip of the hollow shaft gave some vortex formation and consequent introduction of gas bubbles at the speeds necessary to give good pick-up and droplet formation. Reduction of this dimension to about 3 cm, as was possible because of the small volumes of the carbon tetrachloride phase, gave equally good drop formation, adequate pick-up at lower speeds and no vortex formation. The whole body of liquid in the flask rotated at a slow speed, and the baffle effect produced by the sample removal tube projected the carbon tetrachloride droplets toward the upper part of the Thorough contact was thus assured. aqueous phase. Bv using a stirrer speed not higher than that necessary to produce an opaque suspension, the formation of very small droplets was minimized" and the settling after equilibration

[&]quot;At high stirrer speeds the aqueous solution took on a misty or foggy appearance as very small carbon tetrachloride droplets were produced, whereas at lower speeds the droplets were for the most part individually visible, yet the suspension contained so many droplets as to be opaque.

rendered more rapid than when very small droplets were present. It is also recommended that, if possible a stirrer motor be used where the resistor or variable transformer used for speed control is separate and independent of the motor; the controller may then be mounted so that any adjustment made will not tend to misalign the motor and stirrer.

PROCEDURE S-02. PREPARATION OF OXYGEN-FREE AQUEOUS SOLUTIONS

The desired weighed amount of solid chemicals was placed in the special mixing cylinder and the head put in place, using a \$ 14/35 stopper rather than the delivery tube. The vacuum line (from a water aspirator) was connected to one of the lines on the head, and the high pressure nitrogen line to the other. The mixing cylinder was evacuated, bled black to the pressure of the nitrogen line with nitrogen, and the cycle repeated. Oxygen-free water was added through the delivery tube opening to approach the desired final level, all solids dissolved by swirling the mixing cylinder, then water added to the calibration mark. The cylinder was restoppered, the stopcock on the head closed and the cylinder inverted several times to obtain complete mixing. After this the nitrogen was turned on again to maintain the solution under positive pressure of nitrogen until used. Immediately before delivery of the solution, the stopper was removed and the delivery tube inserted, nitrogen being allowed to stream in such a manner as to flush out the delivery tube and to

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prevent entry of air into the cylinder. The nitrogen was shut off, the delivery tube seated in the head, and the nitrogen turned on again and the solution blown out of the cylinder into the equilibration flask. The volume remaining in the cylinder was measured and subtracted from the total volume of solution made, so that an accurate value was obtained for the amount of solution used for distribution.

PROCEDURE G-O1. DISTRIBUTION OF AN ALKYNE BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SOLUTION UNDER OXYGEN-FREE CONDITIONS

The apparatus was assembled and flushed thoroughly with nitrogen, and the water bath brought to temperature (25.0°) . About 5 ml of carbon tetrachloride were placed in the Gadget Mark 78 Mod 3 (Fig. 18) and the ampoule and breaker rod introduced, taking care not to trap air bubbles in the dome. The ampoule was broken by supporting the end of the gadget with a block of wood, then striking the end lightly but smartly with another block. When the ampoule was broken, any air and undissolved hexyne were trapped in the dome, rather than rising to the surface. The breaker was removed and washed down with carbon tetrachloride. The solution was drained into the flask, after the flask had been vented to atmospheric pressure. The solution was washed through the gadget with more carbon tetrachloride, the total volume of this reagent being recorded. The gadget was removed and replaced by a stopper to minimize danger of breaking the gadget,

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a positive pressure of nitrogen being maintained in the equilibration flask at all times. The aqueous solution. previously prepared by Procedure S-02, and at a temperature as close to 25° as practicable, was then added. The stirrer was started and operated for the desired equilibration time (30 minutes in the later experiments). When the stirrer was stopped, that time was recorded as "zero time". After most of the carbon tetrachloride phase had settled, it was blown out through the sample removal tube into the storage cylinder. As soon as possible, two samples of the carbon tetrachloride phase were analyzed in succession. The half hour which this consumed was usually sufficient for all droplets of carbon tetrachloride to settle out of the aqueous phase, and a sample of the aqueous phase was then taken and analyzed. Samples were taken alternately from each phase until the desired number had been obtained. The time of beginning bromination of each sample was recorded, so that if any trend with time were noted in the results, the hexyne concentration could be extrapolated to zero time. Procedures F-04 and E-07 were used for the analyses of the later experiments.

E. RESULTS

PRELIMINARY DISTRIBUTIONS OF 3-HEXYNE

The values of K_D obtained from the preliminary distributions of 3-hexyne are of doubtful value except to define the order of magnitude of distribution coefficients and

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concentrations involved. To illustrate the variations encountered, the results are summarized in Table 22. It is easily seen that the scatter is quite large, although some downward drift of $K_{\rm D}$ is indicated as (B)_c increases.

TABLE 22

DISTRIBUTION CONSTANTS FOR 3-HEXYNE, PRELIMINARY EXPERIMENTS^a

Expt. No.	Conc. ^b of	<u>3-Hexyne</u>	K	Material	
	Aqueous Phase	CC1/4 Phase	U	Balanced	
56	0.000351	0.793	2230	34	
90	0.00048	1.19	2480	57	
129	0.000187	0.530	2830	24	
140	0.000656	1.15	1770	47	
152	0.000416	0.669	1680	39	

a. No precautions taken against oxygen.

b. Mean values; meq/ml.

c. 1.00 N aqueous potassium nitrate.

d. Percent found of hexyne taken.

An attempted calculation of K_D from material balances and the assumption that the analyses of one or the other phases were correct gave equally erratic results. It was evident, therefore, that some major error was being made, most probably in the analyses of both phases, or in the material balance, or in all three.

Note that all distributions except those summarized in Table 22 were conducted under oxygen-free conditions. DISTRIBUTION OF 3-HEXYNE UNDER OXYGEN-FREE CONDITIONS

The discovery, mentioned in Part I, that oxygen somehow interfered, either in the analysis itself or with the hexyne in aqueous solution prior to analysis, made it apparent that a simple distribution as described in the preliminary experiments would not be adequate. Procedures G-Ol and S-O2 were therefore evolved to provide the following features:

- 1. Complete exclusion of oxygen from the apparatus or solutions, by working under nitrogen.
- 2. Complete solution of the 3-hexyne by first dissolving it in the carbon tetrachloride.

The procedures worked with gratifying smoothness. The results will be discussed in two sections, the first of which contains results up to 40% in error because of errors in the carbon tetrachloride phase analyses, and the second where results are believed to be correct within 5%. During the first group of experiments, the low material balances were at first attributed to manipulative losses of 3-hexyne, the distribution technique being a new one, and it was only gradually realized that the analyses were in error. Fortunately, the errors do not invalidate the conclusions drawn from this data.

<u>Distributions Where Analyses of Carbon Tetrachloride</u> <u>Phase Were Imperfect</u>. The results here are given in Table 23. In most instances both phases were stable over the

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periods of time during which the hexyne concentration was followed, but in some the hexyne content decreases with time and in a few the hexyne content showed a small increase with time. The latter effect is unexplained, but is believed to be attributable to some systematic error in the succeeding analyses. The loss of hexyne was at first thought to be caused by hydration, but since no such losses were observed when high purity nitrogen was used (Expt. 626 and higher), it is believed that the losses were due to small amounts of oxygen not removed by the purifying train and introduced into the aqueous phases as the distribution progressed. Where any drift in concentration was noted, the values were extrapolated back to zero time at the cessation of equilibration stirring. In general, such plots fitted straight lines quite well.

Limiting values of $K_{\rm D}$ were calculated on the assumption that all error in the observed values was in the analyses of the carbon tetrachloride phases. These values are shown in Table 23; in Fig. 22 the limiting $K_{\rm D}$ values for 1.00 N aqueous potassium nitrate-carbon tetrachloride distributions of 3-hexyne are plotted against the concentration of 3-hexyne. The line shown is the least squares line obtained in later experiments and represents the best known values of $K_{\rm D}$ from Fig. 23. It is evident that the calculated $K_{\rm D}$ values are in reasonably good agreement with the line, substantiating the assumption on which the calculations were

TABLE 23

Summary of Distributions with Imperfect Analyses of Carbon Tetrachloride Phase

lase No.of Points	5 10 W IN	4	-108 5 5-	5 M M M	to o to	4 ~†	
eous P Max. Dev.	20000 110	0.6	4.7 3.9	0°4 12°4 0°8	11.0 20.0	0.6 11.1	oted 03
Aque Aque Aver 5 Dev.	0.0 0.7 0.5	0°5	500	0.420 0.420	5°6	0.3	laleul. Bases.
Anal 136 No.of Points	9220	9	50	30150	N 09 09	40	ten. (
11, Phe Mex. Dev.	50000 5000	J.0	3.0	3.44 N.	2002	0.9	ne tak bility i H25
e Aver. Dev.	0 4 4 4 0 6 4 4 6	Ŷ*0	7.27 1.27	0.8 0.8 0	3.0	0.6 0.4	f hexy 1 solu 0.01 N
Cele'd Limit of Kp	2080 2440 2402	2540	1920 1680	420 1840 2280	1970 2230 2560	700 2390	found o g mutua -4) M; dded. ure F-0
eterial slance ^f	\$ F \$ 01	68	19	3285	339	S S S	r cent glectin 31)(10 proced
R C	1640 1560 2400	2260	1170	255 2170 2170 1530	1180 1425 1560	481	Post in the second
Time Conc. Followed (Hours)	6 4 4 4 4	5	50 50	พิ๊งตั้ง	to the	nn	1 KI103
of Mqueous Phase	5.30d 4.99d 2.72 1.65	3.86	6.43 3.84	23.87d 6.62 1.73 4.96	5.69 5.69 5.03	16.26 5.10	1.00 vith of observe
Conc. <u>3-Hex</u> cc14 Phase	0.871d 0.779 0.517 0.396	0.874d	0.753	0.609 0.93 0.759	0.747 ^d 0.811 0.782	0.783 0.768	ooted. a up to ime. error o
quili- retion ime Minutes)	4555	15	13	7207	222	ជន	ept as () mad sero t hat all
a cho							to to
Aqueous b Solution ^b b T	.00 N, KNO3	x	iter c	20 N.AENO3 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 Cuso4 C	20 M.Cd(N03)2 20 M.N1(N03)2 01 M.Co(N03)2	0:01 ¹ 0:01 ¹	Mean values exc Ionic strength except as noted = 0.00 Extrepolated to On assumption t



 $4(B)_{c}$ = Concentration of 3-Hexyne, meq/ml Figure 22. LIMIT OF K_D FOR DISTRIBUTIONS WHERE ANALYSES OF CARBON TETRACHLORIDE PHASE WERE IMPERFECT.

made. The data on the analytical method also bears out this assumption (see Part I).

For those experiments where metallic salts other than potassium nitrate were present, Table 23 shows that the deviations of the analyses were much higher than the deviations encountered when only potassium nitrate was present. For the cobalt, nickel and copper experiments, this is partly because of the additional uncertainty introduced in the aqueous phase analysis end points by the color of the solutions. This explanation is not valid for the runs with cadmium and zinc nitrate, however.

Table 24 shows the ratio, Z, of the calculated Kn for various metals to the interpolated K_D for 1.00 N aqueous potassium nitrate solution at the same concentration of 3hexyne in the carbon tetrachloride phase. It is seen that for aqueous solutions of zinc, cadmium, nickel and cobalt nitrates and of cupric sulfate, the values of Z lie between 0.91 and 1.25. This indicates, ignoring the variations of ionic strength and of concentration of salts, that no appreciable change in the distribution of 3-hexyne has occurred. That is, Zn⁺⁺, Cd⁺⁺, Ni⁺⁺, Co⁺⁺, and Cu⁺⁺ ions do not complex with 3-hexyne in aqueous solution. The values for cuprous chloride of Z = 3.24 and Z = 0.98 and Z = 1.28 are conflicting, the first showing complexing and the last two showing no appreciable complexing. No conclusion is possible here, but it is indicated that cuprous chloride does not complex. Silver nitrate shows definite evidence for com-

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TABLE 24

Comparison of Distribution Coefficients of 3-Hexyne Between Solutions of Various Metal Salts and Carbon tetrachloxide.

Expt. No.	Metal Salt	Observed ^b ^K D	Calculated ^b Kp	Interpolated ^C K _D for KNO ₃ (= 1.00)	Za
534	AgN03	255	420	2390	5.70
561	Zn(N03)2	1530	2280	2350	1.03
573	Cd(NO3)2	1180	1970	2350	1.19
580	Ni(NO3)2	1425	2230	2330	1.04
587	co(NO3)2	1560	2560	2340	0.91
626	CuCl	481	700	2340	3.24
633	CuCl	1507	2390	2340	0.98
659	CuS04	2170		2460	1.13
646	CuS04	1400	1840	2300	1,25
864	CuCl [.]	1830 ^d		2340	1.28

a. Z = <u>interpolated Kp for KNO₃ (μ = 1.00</u>)
b. See Table 23 for conditions
c. At same conc. of 3-hexyne in CCl₄ phase as observed in distributions from Fig. 23.
d. Material balance 100.7%; (β)_c = 0.791; μ= 0.0189

plexing. The above conclusions are considered valid in spite of the errors in the carbon tetrachloride phase analyses.

Distributions with Satisfactory Material Balance. After detecting the error in the analyses of the carbon tetrachloride phases in Experiments 510 through 697, and revising the analytical procedure to give satisfactory results, the distribution studies were resumed. Again, Procedures S-02 and G-01 were used. Table 25 and Fig. 23 show the K_D for 3-hexyne between 1.00 N aqueous potassium nitrate and carbon tetrachloride under oxygen-free conditions at 25°C. The straight line shown was fitted by the method of least squares. The trend of KD with change in hexyne concentration is easily noticed. The average deviation of 6 points from the line is 1.9% (of 2400). While it is not included here, a straight line of similar slope is also obtained if K_{D} is plotted against the concentration of hexyne in the aqueous phases. The reason for the trend is unknown. It is to be noted that the saturation concentration of 3-hexyne in the aqueous phase (See Table 17) is more than 15 times as large as the maximum concentration observed here.

The results of distributions for aqueous solutions containing silver nitrate are summarized in Table 26. Except in Expts 806 to 841, the ionic strength is made up to 1.00 with potassium nitrate.

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TABLE 25

Expt. No.	Time ^a	3-Hexy CC14 Phase ^e (mec) (m1)	ne Conc. ^b Aqueous Phase (<u>mec</u>) (ml) (10	M.B.C 0 ⁴)	K d
690	15	0.396	1,65	100.1	2400
697	15	0.874	3.86	89.3	2260
748	30	0.794	5.33	100.7	2380
758.	30	1.002	4.35	95.3	2300
764	30	0.585	2.36	102.9	2480
768	20	1.279	5.84	95.5	2190

Distribution Coefficient of 3-Hexyne Between Carbon Tetrachloride and 1.00 N Aqueous Potassium Runs with Satisfactory Material Balance

Notes:

For equiliboration, minutes. a.

Mean values, or zero time values. Deviations of analyses are shown in Table 17. b.

Per cent recovered of hexyne taken. Calculated C. neglecting mutual solubility of phases. At 25° and 1 atm.; oxygen-free conditions. Ionic

đ. strength = 1.00.

By procedure F-05 for Expts 690 and 697; procedure F-04 for all others. e .



Table 26

DISTRIBUTION EXPERIMENTS WITH SOLUTIONS CONTAINING SILVER NITRATE. OXYGEN-FREE CONDITIONS. IONIC STRENGTH = 1.00

Expt. No.a	Conc. ^b of	M.B. ^C	3-He Conc	xyne d	K _D ^f	ĸ .
	AgNO3 N.		CCl _l Phase ^e meq ml	Aqueous Phase <u>moq</u> x10 ⁴	, .	
778 783 787 793	1.000 1.000 1.000 1.000	10/4 108 82 109	0.472 0.735 0.191 0.276	49.1 77.7 24.1 29.3	2430 2360 2500 2480	24.2 24.0 30.5 25.3
798 802 811 816	1.000 1.000 0.500 0.250	110 112 107 109	0.253 0.226 0.815 0.826	26.9 27.0 40.4 21.6	2480 2485 2340 2330	25.4 26.5 21.3 20.4
820 826 832 835	0.250 0.250 0.250 0.250	107 110 107 108	0.230 0.208 0.171 0.567	5.94 5.30 1.15 -15.3	2490 2490 2510 2400	21.7 21.5 23.1 22.0 ^g
-835 -844 -848 -852	0.250 0.250 0.250 0.250	107 87 104	0.390 0.372 0.401 0.414	10.5 9.82 13.1 10.2	2450 2460 2450 2440	22.58 22.08 28.15 20.0
856 860 806 841	0.250 0.250 0.250h 0.000i	102 108 104	0.388 0.527 0.779 0.840	10.0 14.0 25.8 4.96	2450 2420 1690k	21.4 21.7 (20.0) j

a. The deviations of the anlyses have been summarized in Table 19.

b. Ionic strength, μ , made up to 1.00 by potassium nitrate.

- c. Material balance, per cent found of hexyne taken. These values are calculated neglecting the solubility of carbon tetrachloride in the aqueous phase, and vice versa.
- d. Note that these values of meq/ml must be divided by 4 to give (B), and (Bt), in moles/liter.
- e. By Procedure F-Ol.
- f. Interpolated from Fig. 24 to correspond to observed concentration of 3-hexyne in carbon tetrachloride layer. Used in calculation of K.

5.3/4 = 1.4 molal.

e E-Oh.

- g. See special discussion in text regarding nitrogen tanks used in these experiments.
- h. No potassium nitrate added; $\mu = 0.250$.
- i. No salt present; $\mu = 0.000$
- j. This value is somewhat uncertain since no appropriate K_D values for $\mu = 0.250$ where known. This value is calculated on the basis of a K_D of 1850, the linearly interpolated value between K_D 1690 at $\mu = 0.00$ and K_D = 2340 at $\mu = 1.00$.

k. Observed.

Fig. 24 shows a plot of the K values versus (B) ... The points for 1.00 N silver nitrate define a curve with good fit. However, the points for 0.250 N silver nitrate-0.750 N potassium. Litrate are more scattered. If we follow the experiments in sequence, starting at Expt. 816, it is seen that the points following Expt. 832 and preceding Expt. 852 lie above the curve defined by all other points for this silver nitrate concentration. After Expt. 848 and before beginning Expt. 852, the tank (called Tank A) of high purity nitrogen was replaced by a new tank (called Tank B) of the same grade. It is known that the tank (called Tank C) in use prior to Tank A was replaced about the time of Expt. 832. but the exact date was not recorded and is not known with certainty. Whether Tank A was contaminated in some manner so as to cause the K values of Expt.'s 835, 844, and 848 to fall above the other values is not known, nor can any conjecture be offered as to the nature of a contaminant which would produce such a change. A search of the data recorded disclosed no other change of reagents or conditions which might account for the discrepancy.



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The curve for the 0.250 N silver nitrate-0.750 N potassium nitrate distributions has been drawn on the basis of the exclusion of the values for Expts. 835, 844 and 848. It can be seen that even if a straight line had been drawn based on all points, the values of K_1 and K_2 which are calculated would be little affected.

FIRST AND SECOND ARGENTATION CONSTANTS OF 3-HEXYNE

The shift of the K values with a shift in silver concentration indicates that more than one silver ion coordinates with the molecule of 3-hexyne. On the assumption that no more than two silver ions coordinate, the values of K_1 and K_2 have been calculated following the method of Winstein and Lucas (63). Since K is a function of (B)_c, it was necessary to use K values for values of (B)_c as close together as possible. This was done by employing the K's of Expts. 816, 811 and 783. There is some uncertainty that these results are free of deviations such as those affecting other points (Expts. 835, 844 and 848). However, a plot of K versus silver nitrate concentration, Fig. 25, shows that they lie close to a straight line, which indicates that no major deviations are present.

It has been mentioned (see Notation, page 91) that the evaluated argentation constant, K, was calculated on the assumption that no complex species other than (BAg) was present. On the assumption given above that no more than two silver ions can coordinate, i.e. that only (BAg) and



(BAg₂) are formed, and making material balances of B and of silver, K may be written accurately as

$$K = \frac{K_{\rm D} [(Bt) - (B)]}{(B)_{\rm c} [(Agt) - (Bt) + (B)]}$$

$$= \frac{(BAg) + (BAg_2)}{(B) [(Ag^+) + 2(BAg_2)]} \neq \frac{(BAg)}{(B) (Ag^-)}$$

$$= \frac{\frac{(BAg) + (BAg_2)}{(B)}}{(Ag^+) + 2(BAg_2)} = \frac{K_1 (Ag^+) + \frac{K_2(BAg)(Ag^-)}{(B)}}{(Ag^+) + 2(BAg_2)}$$

$$= \frac{K_1 + \frac{K_2(BAg)}{(B)}}{1 + \frac{2(BAg_2)}{(Ag^+)}} = \frac{K_1 + K_1K_2(Ag^-)}{1 + 2K_1K_2(B)(Ag^-)} (3)^{**}$$

As a first approximation, it was assumed that the term $2K_1K_2(B)(Ag^+)$ could be neglected when added to 1.000. This reduced Eq. 3 to

$$K = K_1 + K_1 K_2 (Ag^{\tau})$$
 (4)

Using the additional approximation that $(Ag^{+}) = (Agt)$, the use of the K values from a pair of experiments permitted a first approximation of K_1 and K_2 , giving 18.6 and 0.290, respectively. With these values, the minor terms of Eq. 3 were evaluated, and a second set of values of K_1 and K_2 were calculated. Inspection of the numbers showed that a ^{*}Note that an error in the paper of Winstein and Lucas omits the factor of 2 from the second term of the denominator. further recalculation would not significantly alter the values. Table 27 shows the results when K1 and K2 are calculated from different pairs of experiments.

Table 27

FIRST AND SECOND ARGENTATION CONSTANTS OF 3-HEXYNE

Expts on which	K-	Ka
Ki and K2 are		۲
based	· · · · · · · · · · · · · · · · · · ·	
2. E		

783 1	8:	811	18.8			0.218
816	80	783	19.2	× *		0.251
811 8	8	816	19.4		÷	0.205

It is seen that the calculated constants agree quite well with the extrapolated zero-silver-concentration values of 19.7 (see Fig. 25) as should be the case. The values of K_1 and K_2 are taken to be 19.1 ± 0.5 and 0.22 ± 0.05 , respectively, under the following conditions:

(B)_c = approximately 0.20 moles/liter

Temperature = $25.0^{\circ}C$.

Total pressure, 1 atm. (nitrogem)

Solvents: Carbon tetrachloride and

aqueous silver nitrate-potassium nitrate;

Ionic strength = 1.00.

These values will shift somewhat as $(B)_c$ varies. The shape of the K curves (Fig. 24) indicates that K₁ and K₂ will not vary greatly as $(B)_c$ increases over 0.2, but that they may vary considerably as (B), decreases, particularly below 0.1.

The possibility that more than two silver ions complexed with one molecule of 3-hexyne was examined, using a derivation similar to that for Eq. 3. The results were erratic and unreasonable. It seems indicated but not proven definitely that not more than two silver ions complex, the limited accuracy of the data here precluding any final decision.

REVERSIBILITY OF COMPLEXING

In all save one of the experiments in Tables 25 and 26, the 3-hexyne was dissolved first in the carbon tetrachloride and this solution equilibrated with the aqueous solution (Procedure G-Ol). In order to test the reversibility of the equilibrium obtained, Expt. 835 was performed by a modification of Procedure G-Ol. The first portion of the experiment was performed as usual and the two phases analysed for more 3-hexyne, so as to establish a value of K. More carbon tetrachloride was then added to the flask and a second equilibration carried out. In this equilibration, the transfer of 3-hexyne was from the aqueous phase back into the carbon tetrachloride, the reverse of the process in the first portion of the experiment. Table 28 shows the results.

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Table 28

REVERSIBILITY OF 3-HEXYNE COMPLEX FORMATION WITH SILVER ION. EXPERIMENT 835ª

Equilibration Number	Direction of 3-Hexyne Transfer	3-Hexyne Conc. ^b <u>meq</u> ml	K
1	CCl ₄ to Aqueous	0.567	22.0
2	Aqueous to CCl ₄	0.390	22.5

a. See special comment in text concerning the K values and nitrogen tank used in this experiment.

b. In CCl, phase.

It is seen that the two values of K agree within 2.3 per cent, with the lower value being at the higher hexyne concentration, which is in agreement with the trend shown by other experiments. While Expt. 835 is one of the three which apparently suffered some slight interference of unknown origin, it was concluded that the complexing reaction is reversible, even though the absolute K values may be somewhat in error.

The short equilibration times required, 15 to 30 minutes, show that the complexing reaction is rather rapid. Probably the governing factor in achieving equilibrium is the rate of mass transfer of 3-hexyne from one phase to the other.

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EFFECT OF IONIC STRENGTH UPON THE DISTRIBUTION COEFFICIENT AND THE ARGENTATION CONSTANT

The two values of $K_{\rm D}$ for water-carbon tetrachloride in Expts. 606" and 670" (Table 23) of 1920 (calculated limit) and 1680 (calculated limit) are in moderate agreement with the value from Expt. 841 (Table 26) which gives $K_{\rm D}$ = 1690 for a hexyne concentration of 0.840 meq/ml. This last value is considered reliable. Unfortunately, not enough points are available to determine whether $K_{\rm D}$ drops as the hexyne concentration increases. The $K_{\rm D}$ value of 1.00 N aqueous potassium nitrate-carbon tetrachloride at a hexyne concentration of 0.840 meq/ml is interpolated as 2330.

The ratio of
$$\frac{K_D - aq. KNO3}{K_D - water} = \frac{\frac{C_{CCl_4}}{C_{aq. KNO_3}}}{\frac{C_{CCl_4}}{C_{water}}} = \frac{C_{water}}{C_{aq. KNO_3}}$$

= $\frac{2330}{1690} = 1.38$

This may be compared against the ratio of solubilities (Table 17) of 3-hexyne in water and in 1.00 N aqueous potassium nitrate, which is:

$$\frac{122 \times 10^{-4}}{97.9 \times 10^{-4}} = 1.25$$

* Note that these experiments were among those which had imperfect analyses of carbon tetrachloride phase.

To consider the effect of ionic strength upon the argentation constant, comparison is made of Expt. 806 where $\mu = 0.250$, (B)_c= 0.779 and K = 20.0 against Expt. 816 where $\mu = 1.00$, (B)_c = 0.826 and K = 20.4. The former value of K is dependent upon the estimated value of K_D for $\mu = 0.250$ (Table 26) used in its calculation. If the estimate is valid, the agreement of the two K values indicates that the ionic strength has very little effect upon the argentation reaction, although it has an appreciable effect on the distribution coefficient.

ATTEMPTED DISTRIBUTIONS WITH MERCURIC SALTS

With the series of experiments listed in Table 23, an attempt was made to perform distributions where the aqueous phase contained mercuric salts.

For the first attempt, Expt. 546, a solution which was 0.20 M in mercuric nitrate, 0.20 N in nitric acid and 0.20 N in potassium nitrate was employed. This gave an ionic strength of 1.00, the acid being employed to prevent hydrolysis of the mercuric nitrate. During the equilibration period of 15 minutes the carbon tetrachloride phase became distinctly yellow. Analyses were performed on both phases as usual. Those for the carbon tetrachloride phase proceeded without difficulty, although there is some doubt that the results actually express hexyne concentraion. When titration of the aqueous phases analyses was undertaken, the end point drifted quite rapidly. It was found possible to follow the drift, however,

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and this was done for several samples. By recording the volume of thiosulfate solution required to cause the disappearance of the starch-iodine color and the elapsed time from the addition of the potassium iodide solution, it was found possible to obtain smooth curves despite the rapidity with which the titrations were carried out. It was also possible to extrapolate to volumes of thiosulfate solution required at zero and at infinite time after the addition of the potassium iodide solution. A typical curve is shown in Fig. 26, and a set of superimposed curves in Fig. 27. The latter include all but two samples and are reduced to the same zero time and zero-time volume of thiosulfate. The marked similarity of the curves is evident, suggesting that the same phenomenon is causing the drift of all end points. The two values of thiosulfate volume permitted the calculation of two sets of hexyne concentration values. These are shown with other values in Table 29.

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Figure 26. TYPICAL TITRATION CURVE FOR EXPERIMENT 546

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Table 29

RESULTS OF ANALYSES OF AQUEOUS PHASE OF DISTRIBUTION EMPLOYING MERCURIC NITRATE. EXPERIMENT 546.

Detn. No.	12	13	14	15	16	18	19
Elapsed ^a time, hours	1.12	1.82	2.50	3.12	3.82	5.63	6.07
Conc. of 3-hexyne (meg/ml)(104)	ay e						
Zerob _{Time}	39.8		38.2	40.7	lt0.9	40.1	37.8
Trade as the Drive and	20.0	22 0	20.2	28 6	20 8	28.6	07 1

InfiniteTime30.233.929.228.628.828.627.4 Y^{C} 0.759-0.7640.7020.7050.7130.725

a.	From	stopping	of equil	ibration	stiri	er.
b.	After	• adding j	potassium	lodide	soluti	lon.
c.	Y =	Conc. of	3-hexyne	at infi	niteb	time

Conc. of 3-hexyne at zero^D time

The concentrations at both times are quite consistent, although a plot (not shown) against time elapsed after stopping the equilibration shows a small decrease in concentration at the time increased. The ratio, Y, of infinitetime concentration to zero-time concentration is remarkably constant, the mean of six values being 0.728, with an average deviation of 0.022 or 3.0 per cent. The X value is quite close to 0.75, and may indicate that one quarter of the total oxidizing equivalents taken up by hexyne (or some product from hexyne) is slowly released. No mechanism which appears likely has yet been postulated for this, however. The hexyne recovery, assuming that the analyses indicate hexyne, is 23.4 and 19.4 per cent at zero time and at infinite time, respectively. This suggests, together with the constancy of the concentrations over several hours, that the hexyne was transformed completely during the equilibration period, and that it was the transformation product which exhibited the anomalous behavior toward bromination. This does not account for the difference in behavior of the analyses of the carbon tetrachloride and aqueous phases.

A portion of the carbon tetrachloride phase containing the yellow color was examined⁴⁵ with the Beckman spectrophotometer. A very broad peak of optical density was observed, extending from 410 to 443 millimicrons, with the maximum falling at a wave length between 430 and 435 millicrons. On the postulate that the color might be caused by bipropionyl (3,4-hexanedione), a solution of biacetyl, the closest analog which was available, was prepared. The shape of the two curves differed considerably and it was concluded that the unknown compound was probably not bipropionyl. The curve observed here does not correspond to any of those observed by H. Lemaire (46) in his studies of the 3-hexyne-mercuric acetate-perchloric acid complex.

To investigate whether the rapid reaction of 3hexyne in the distribution system would be slowed down by increasing the hydrogen ion and mercuric ion concentrations, another distribution was undertaken. Expt. 653 showed that

"With the kind assistance of H. Lemaire.

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in a 0.01 M solution of mercuric acetate, an acetic acid concentration of 0.01 M was sufficient to prevent hydrolysis, at least over periods up to 24 hours. In Expt. 639, a distribution of 3-hexyne was made between carbon tetrachloride and a solution 0.01 M in mercuric acetate and 0.05 M in acetic acid. The ionic strength was 0.08. The results paralleled those of Expt. 546 described above, except that no yellow color developed in the carbon tetrachloride phase and the material balance at infinite time was 61 per cent. The apparent K_D values (at infinite time) were 189 and 189 for the two experiments. The agreement appears to be fortuitous.

In view of the complexities of the reactions, the study of mercuric compounds was not continued further.

F. DISCUSSION OF RESULTS

COMPLEX FORMATION OF THE CARBON-CARBON TRIPLE BOND WITH SILVER IONS

In aqueous solution of silver nitrate, two silver ions complex with one molecule of 3-hexyne, the argentation equilibrium constants, K_1 and K_2 , for the first and second ions being 19.1 0.5 and 0.22 0.05, respectively. The complexing undergoes an unexplained deviation as the concentration level of 3-hexyne goes toward zero, but appears to be essentially described by the values above where the concentration is 0.20 moles/liter or greater in the carbon tetra-

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chloride phase. 3-hexyne complexes more strongly than the aromatic hydrocarbons but less strongly than the <u>cis</u>- and <u>trans-2-pentenes</u>, as can be seen in Table 30.

Table 30

COMPARISON OF THE COMPLEXING OF ALKENES, ALKYNES AND AROMATIC HYDROCARBONS^a

Hydrocarbon	Kl	K ₂	Ko	Source
cis-2-pentene	112.5	-	0.0312	(64a)
trans-2-pentene	62.2	-	0.0111	(64a)
benzene	2.41 ^b	0.212	đ	(69)
biphenyl	3.94°	1.01	đ	(69)
3-hexyne	19.1	0.22	0.00787	This study

a. See Table 21 for other comparisons.
b. Smallest K₁ observed in the compounds tried (69).
c. Largest K₁ observed in the compounds tried (69).
d. No K_p values available (69) to calculate K_p.

Winstein and Lucas (63) and Anderson (85) came to the conclusion that the steric effects of structure played a very considerable part in determining the complex forming ability of an unsaturated organic compound. In 3-hexyne where the second, third, fourth and fifth carbon atoms are presumably in a linear structure, one would expect the steric hindrance to the approach of a silver ion to be at a minimum, with the exceptions of acetylene, the butynes and the pentynes. The low complexing ability observed suggests that the electrons of the triple bond are less mobile and less available for complexing than those of the double bond. Bergmann (86) reached such a conclusion from consideration of the ultraviolet spectra of the two bond types. These phenomena indicate that the highly symmetrical triple bond is less polarizable than the less symmetrical double bond.

The capability of the triple bond to complex with two silver ions is in distinct contrast with the failure of the double bond to do so. It is perhaps made possible by the establishment of a highly symmetrical structure such as might be formed by two silver ions on opposite sides of a triple bond, as

R C Ag⁺ Ⅲ Ag⁺ C

Any such stabilization might help to provide the energy required to bring the two positive charges into such close proximity. Three or four silver ions could also form very symmetrical structures about the axis of the $C \equiv C$ bond, but presumably too much energy is required to bring the positive charges together.

The bond structure of the silver ion-triple-bond bond seems likely to be very similar to that of the silver iondouble-bond bond. Perhaps the best mathematical description of the interactions which go to form the bond would be that which included resonance forms such as:

In any event, the bond appears to result from the electronic interactions of the triple bond and the silver ion. The notation of Dewar (28, p 157) may well offer the most concise means to express the situation, and might be modified to



It is assumed that considerations evolved here from a study of the triple bond in 3-hexyne are applicable to other compounds containing a triple bond, although no evidence for or against this assumption was obtained in this study.

INTERACTION OF OTHER METALLIC IONS WITH THE CARBON-CARBON TRIPLE BOND

Under the aqueous conditions employed in this study, the bipositive nickel, cobalt, zinc, cadmium and copper ions did not show any significant tendency to coordinate with the triple bond. This is the same situation which Winstein and Lucas (63) found for the olefins. It seems quite likely that the coordination of these ions with water is so strong as to suppress the complex formation with 3-hexyne to the vanishing point. In non-aqueous media complex formation might be possible. The two-phase liquid-solid method of Keefer and Andrews (56) might be applicable here.

The limited evidence afford by this study indicates that in aqueous solution, the cuprous ion or unionized cuprous chloride does not complex strongly with the triple bond, if at all. This is the reverse of the situation found for olefins where the complexing constant for cuprous materials is several powers of ten larger than that for silver ion. This point should be further investigated, perhaps by other methods.

The interaction of mercuric compounds has been shown to be very rapid and quite complex, with indications that the complex, if any, rapidly is transformed into some reaction product. The method of this study appears to be unsuited to further study of mercuric complexes with alkynes, but other methods might be applicable (46, 56).

It should be recalled that all experiments discussed here were carried out in the absence of oxygen to avoid its interference. The nature of the interference remains unknown but is being studied (48).

FUTURE STUDY

As has been mentioned above, further studies of various metals with 3-hexyne would be of interest. The complexing of other alkynes, and the effect of structure upon complexing properties should be investigated. The indications of this research and of the experience of Reppe

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et al (87) are that non-aqueous systems might be the best in which to conduct the investigations. The Raman spectra of silver ion-alkyne complexes where no acetylenic hydrogens are involved should be studied, since Taufen <u>et al</u> (81) did not make any such observations.

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PROPOSITIONS

1. The unit process of nitrosation of aromatic compounds has been very little studied, aqueous nitrous acid attacking only those compounds which are exceptionally reactive toward substitution in the ring. In view of the recent studies of Seel and Bauer (Z. <u>Naturforsch.</u>, <u>26</u>, 397-440 (1947); <u>C.A.</u> <u>43</u>, 8935g) of the behavior of nitrosyl chloride and antimony pentachloride in liquid sulfur dioxide, and the successful use by Leiserson <u>et al</u> (<u>Ind. Eng. Ghem.</u>, 40, 508-10 (1948)) of liquid sulfur dioxide as a medium for sulfonation, I propose that nitrosation could be performed and studied for a much wider variety of compounds in a nitrosyl chloride-antimony pentachloride-liquid sulfur dioxide system.

2. I have observed that when an object is placed on the bottom of a container in which a liquid is being boiled, the vapor bubbles form between the bottom of the object and the container, even when the object has a glazed surface of the type usually considered of very little value as a boiling aid. This suggests that the heat transfer is better at the point where the object touches or is near the container wall than at a point where the container wall is covered by a thick layer of liquid. I propose that this phenomenon be systematically studied. (This is to be distinguished from previously studied treatments of the container wall, such as roughing or grooving.)

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3. The particle size-frequency distribution of many powders may be represented by an equation of the type

$$\frac{dC}{dD} = e^{-\left[\frac{K}{B}\ln\left(\frac{D}{D_{0}}\right)\right]^{2}} = e^{-\left[\frac{1}{B}\ln\left(\frac{D}{D_{0}}\right)^{K}\right]^{2}}$$

where C is the number of particles, D is diameter, B is a uniformity coefficient, K is a shape coefficient and D_0 is the diameter of the most frequent size of particle. I propose that the flow characteristics of fluids through beds of such powders may be described by using B, K and D_0 in place of an "average diameter" in such conventional dimensionless groups as Reynold's number.

4. The pyridine-nitrogen dioxide complex is a stable but little studied substance (Spencer, J. F.; <u>Proc. Chem.</u>
<u>Soc.</u>, <u>19</u>, 79-80 (1903)). I propose that it be studied:
a. As a reagent for the nitration of aromatic substances

- which are highly reactive toward substitution but which are acid sensitive; e.g. pyrrole.
- b. As a source of nitrogen dioxide for the determination of olefines (Bond, G. R.; <u>Ind. Eng. Chem.</u>, <u>Anal. Ed.</u>, 18, 692-6 (1946)).

5. I propose that the cyclic fixed-bed method of utilizing oxygen-bearing chelate compounds (Folger, B. B.; <u>Ind. En.</u>. <u>Chem.</u>, <u>39</u>, 1353-60 (1947)) is markedly inferior to a continuous fluidized solid process, and that the latter should be given consideration as a source of tonnage oxygen. 6. Despite the tremendous amount of study devoted to the Grignard reagent, no report is found for the reaction of the reagent with sulfur trioxide or nitrosyl chloride. I propose that these reactions be attempted as possible syntheses of sulfonic acids and nitroso compounds.

7. The manufacture of cyclooctatetraene by the catalytic polymerization of acetylene has several characteristics which are not well explained by the postulated mechanisms (Reppe, W., et al; Ann., 560, 1-116 (1949)). I propose a mechanism based upon the formation of a nickel-acetylene complex, which more satisfactorily explains these points.

8. In the treatment of salts of compounds containing a keto-enol system with alkyl halides or acyl halides, the sodium salts generallyproduce C-substituted products, the copper or silver salts O-substituted products (Lander, G. D.; J. Chem. Soc., 83, 414-23 (1903); Michael, A., et al; J. Am. Chem. Soc., 57, 165-74 (1935); <u>ibid.</u>, <u>58</u>, 353-64 (1936); Beilstein, System 280). I propose that this difference in the products formed may be attributed to a shift of the keto-enol equilibrium toward the enol form by complex formation between the copper or silver and the double bond (either carbon-carbon or carbon-nitrogen) of the enol form.

9. I have observed that the product of Hammett's ℓ and absolute temperature is a constant. (Hammett, L.P.; <u>Physical Organic Chemistry</u>), so far as the very limited data

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permits evaluation. I propose that this matter should be investigated, and that the theoretical basis of Q^{T} = a constant be studied.

9. I propose that the present usage of quoting both volume number and year in references is inefficient and essentially redundant, since it conveys only the trivial information of the total number of volumes published beyond the information conveyed by the usage of quoting the year.

10. I propose that the convenience of using the Precision Scientific Co. constant temperature water bath (Catalog No. 66600) could be greatly increased by incorporating one or two additional mercury-filled thermoregulators, plus a selector switch to choose the desired thermoregulator. This would permit accurate and permanent setting of the desired temperatures (usually 20° to 25°) for instruments such as a refractometer, yet would permit easy and rapid change from one temperature to the other.

12. The replacement of atoms or groups other than hydrogen from an aromatic ring by electrophilic substitution appears to be unknown. I propose that the attack of electrophilic reagents on hexasubstituted benzenes would be of considerable interest and might provide additional knowledge of the mechanism of substitutes.