ADDITION TO THE CARBON-CARBON TRIPLE BOND
THE REACTION OF ACETIC ACID WITH 3-HEXYNE

Thesis by

Henry Lemaire

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Abstract

The mechanism of the mercury-catalyzed addition to the carbon-carbon triple bond has been investigated. Acetic acid was used as the solvent and one reactant. The other reactant was 3-hexyne. The course of the reaction was followed by bromine titration and by a special indicator method. The addition was found to take place in two discrete steps, forming 3-acetoxyhexene-3 and 3-hexanone.

The rate of the initial reaction was determined for a range of initial concentrations of hexyne and the catalysts. When mercuric acetate and perchloric acid were used as the catalysts, the initial rates were found to be interpretable on the assumption that the reactive species was a 1 to 1 to 1 complex formed by the 3-hexyne, the mercuric acetate, and the perchloric acid. By means of indicator studies the existence of the 1 to 1 to 1 complex (probably a hexyne-mercuric monoacetate cation) was proved and its equilibrium constant measured.

The indicator studies were extended to the measurement of the basicities of weak bases in acetic acid. A simple relationship was found between the observed ionization constant and the thermodynamic activity constant. New values were found for the basic strengths of dioxane, acetonitrile, p-toluenesulfonamide, water, acetanilide, acetamide, and urea.

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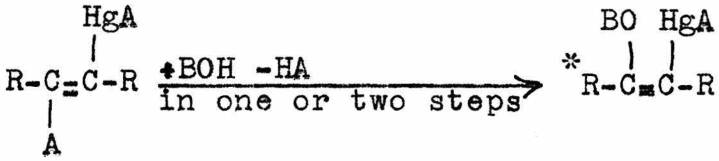
I. Historical Background and Discussion of Problem

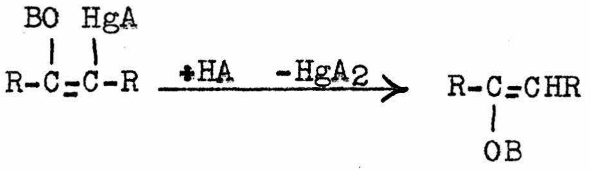
In 1936, Hennion, Vogt, and Nieuwland published "A Proposed Mechanism for Mercury Catalysis in Acetylene Addition Reactions"[1]. Actually, two different mechanisms were suggested for the reaction of hydroxyl compounds with alkynes. One proposal was that the mercuric salt reacted with the alkyne to form a metalated alkene and the other was that the mercuric salt reacted first with the hydroxyl compound. The first mechanism is shown in Equations 1, 2, and 3 and the second, in Equations 4 and 5.

A.

$$\mathrm{HgA_2 + R{-}C{\equiv}C{-}R \longrightarrow R\overset{*}{-}\underset{A}{C}{=}\overset{HgA}{C}{-}R} \qquad (1)$$

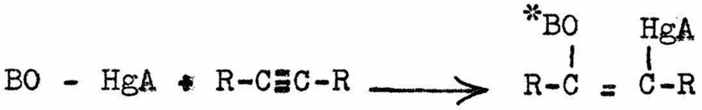


$$\mathrm{R{-}\underset{A}{C}{=}\overset{HgA}{C}{-}R \xrightarrow[\text{in one or two steps}]{+BOH\ \ -HA} {}^{*}R{-}\overset{BO}{C}{=}\overset{HgA}{C}{-}R} \qquad (2)$$



$$\mathrm{R{-}\overset{BO}{C}{=}\overset{HgA}{C}{-}R \xrightarrow{+HA\ \ -HgA_2} R{-}\underset{OB}{C}{=}CHR} \qquad (3)$$

$$\mathrm{HgA_2 + BOH \xrightarrow{-HA} BO - HgA} \qquad (4)$$



$$\mathrm{BO - HgA + R{-}C{\equiv}C{-}R \longrightarrow R{-}\overset{*BO}{C} = \overset{HgA}{C}{-}R} \qquad (5)$$

* *Cis* or *trans* compounds?

The product of Reactions 3 and 5 would either rearrange to form a ketone (if B was H) or would add another mole of BOH without specific catalysis (if B was an alkyl group).#

The next year Frieman, Kennedy, and Lucas published[3] the results of a study of "The Rate of Hydration of Acetylene in Aqueous Solution of Sulfuric acid and Mercuric Sulfate". They had studied the formation of acetaldehyde from acetylene and had found the initial rate to be proportional to the first power of the acetylene concentration and the second power of the mercuric sulfate concentration. The dependence of the rate upon the concentration of sulfuric acid was not determined.

Classical studies on the complexes formed between unsaturated organic compounds and mercuric salts were made by J. Sand and several collaborators. Sand and Breest[4] studied the equilibrium, which they wrote:

$$HgCl_2 + C_2H_4 + H_2O \rightleftharpoons HOCH_2CH_2HgCl + H^+ + Cl^- \qquad (6)$$

by measuring the conductivity of the aqueous solution. Hugel and Hibou[5] found that mercuric acetate formed complexes with olefins in glacial acid of the formula $C_nH_{2n} \cdot Hg(OAc)_2$. On the addition of water these complexes could be obtained as oils which crystallized rapidly. One of the acetate radicals

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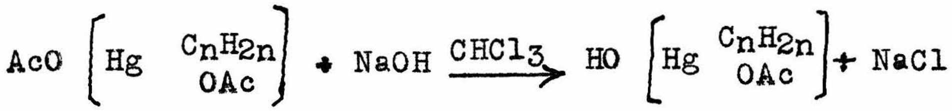
\# On the basis of experimental work, Wright[2] had concluded that reactions analogous to Equations 4 and 5 should be preferred in explaining the formation of olefin complexes.

was found to be very readily replaced by an hydroxyl radical on titration with alkali.



$$\mathrm{AcO}\left[\mathrm{Hg}\ \begin{matrix}\mathrm{C_nH_{2n}}\\ \mathrm{OAc}\end{matrix}\right] + \mathrm{NaOH} \xrightarrow{\mathrm{CHCl_3}} \mathrm{HO}\left[\mathrm{Hg}\ \begin{matrix}\mathrm{C_nH_{2n}}\\ \mathrm{OAc}\end{matrix}\right] + \mathrm{NaCl} \qquad (7)$$

In ether, the second acetate could be replaced slowly by alkali.

Much interest has been centered on the question of whether the products of the reactions between olefines and mercuric salts are loose complexes or saturated, mercurated compounds of a somewhat unstable nature[6]. For the purposes of this paper it is important to note that uponaddition of mineral acid (as in a bromide-bromate titration) the olefin is completely regenerated. Lucas, Hepner, and Winstein[7] measured the equilibrium of cyclohexene and mercuric nitrate in aqueous solution. Their data indicated the occurrence of two equilibria:

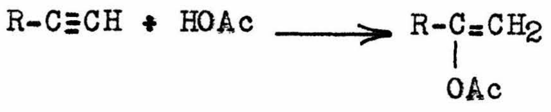
$$\frac{(\mathrm{B \cdot Hg^{+}})}{(\mathrm{B})(\mathrm{Hg^{++}})} = 2.2 \times 10^{4} \qquad (8)$$

$$\frac{(\mathrm{B \cdot HgOH^{+}})(\mathrm{H^{+}})}{(\mathrm{B})(\mathrm{Hg^{++}})} = 5.0 \times 10^{4} \qquad (9)$$

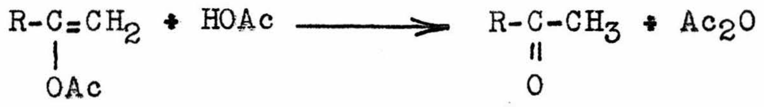
where B is cyclohexene.

The purpose of the work described in this thesis was to acquire new data on the mercury catalyzed addition to the carbon-carbon triple bond. In order to avoid any complications from the acidic nature of the hydrogen atoms of acetylene, diethylacetylene was chosen for investigation. After some preliminary work, acetic acid was chosen as solvent and second reactant. This decision was based on both theoretical and practical considerations. When water is added to the triple bond, the initial product, a vinyl alcohol, rearranges spontaneously to form an aldehyde or ketone. It is, therefore, not possible to study the addition reaction separately. Acetic acid, on the other hand, adds to alkynes to form stable derivatives of vinyl acetate. A second addition was believed to take place, but this reaction could be studied separately and its effect on the initial reaction determined. Acetic acid will dissolve hexyne, which is but sparingly soluble in water. Moreover, acetic acid has a high enough dielectric constant so that the mercuric salt catalysts were expected to be sufficiently soluble in it to make possible a homogeneous system. Finally, acetic acid was known to be stable to bromination, the analytical method which seemed best adapted for following the rate of reaction.

The course of the reaction between alkynes and acetic acid was investigated by Hennion and Nieuwland[8]. They reacted acetic acid with propyne, 1-hexyne and 1-heptyne. The catalyst was prepared by dissolving mercuric oxide in a mixture of methanol and ether-boron trifluoride and then in the acetic acid. The alkyne was added dropwise. Two products were isolated, the alkylvinyl acetate and the ketone.



$$R\text{-}C\equiv CH + HOAc \longrightarrow R\text{-}\underset{\underset{OAc}{|}}{C}=CH_2 \qquad (10)$$



$$\mathrm{R-\underset{\displaystyle OAc}{\underset{|}{C}}=CH_2 + HOAc \longrightarrow R-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3 + Ac_2O} \qquad (11)$$

The ester was obtained in 30% - 34% yield. It was not found possible to isolate a ketone diester, and the authors were not certain whether the ketone was formed by Reaction 11 or by hydrolysis of the mono-ester during isolation. 1-Hexenyl-acetate-2 boiled 74-47° at 39 mm. and had $\underline{n}_D^{26} = 1.4176$.

II. Preparation of Materials and Isolation of Products

3-Hexyne. A procedure published by Bried and Hennion[9] was adapted for the synthesis of 3-hexyne. Sodium acetylide is prepared and, in the presence of sodamide, reacted with ethyl bromide to form butyne-1. This alkyne is converted to its sodium salt by the sodamide and then reacts with a second mole of ethyl bromide to form 3-hexyne. The four successive steps are shown below.

$$\text{CH}\equiv\text{CH} + \text{Na} \longrightarrow \text{CH}\equiv\text{CNa} \tag{12}$$

$$\text{CH}\equiv\text{CNa} + \text{EtBr} \longrightarrow \text{CH}\equiv\text{C-Et} + \text{NaBr} \tag{13}$$

$$\text{CH}\equiv\text{C-Et} + \text{NaNH}_2 \longrightarrow \text{NaC}\equiv\text{C-Et} + \text{NH}_3 \tag{14}$$

$$\text{NaC}\equiv\text{C-Et} + \text{EtBr} \longrightarrow \text{Et-C}\equiv\text{C-Et} + \text{NaBr} \tag{15}$$

Sodium acetylide was prepared in liquid ammonia by adding to a reaction flask containing ammonia a stream of acetylene and a solution of sodium in ammonia. (The acetylene should be kept flowing continuously - a point on which the literature[10] is not clear - and should always be in excess over the sodium.) Three moles of sodium were dissolved in 1.5 liters of ammonia (which had to be replenished during the run) and forced over by the pressure of the ammonia into the 5-liter reaction flask. Ammonia causing excess pressure was allowed to escape from the sodium solution through an oil column. It was found that 6 mm. pyrex tubing and 3/16" rubber tubing became clogged with sodium during the periods when it was necessary to stop the flow of the sodium solution. Eight mm. pyrex tubing and 1/4" rubber tubing were satisfactory. Acetylene was led from a tank through aqueous sodium bisulfite, calcium chloride, and soda lime into the reaction flask, which was initially charged with about 2 liters of ammonia and fitted with a dry ice condenser. Vigorous stirring with a half-moon stirrer was employed and the proportion of entering acetylene and sodium solution so regulated that the entire reacting solution never became entirely blue. Under optimum conditions such a run could be completed intwo and a half hours.

Sodamide was prepared in liquid ammonia by dissolving about a tenth of a gram of ferric nitrate nonahydrate in a liter and a half of ammonia. When the entire solution had become orange about a gram of sodium was added and air, dried with potassium hydroxide, bubbled through until the blue color disappeared entirely, giving way to a black suspension. Four moles of sodium were then added and time allowed for the reaction to be completed (1 to 3 hours). Very little trouble was encountered in this preparation.

For the preparation of 3-hexyne the sodamide slurry had to be transferred to the 5-liter reaction flask. Considerable difficulty was encountered in effecting this transfer through glass and rubber tubing, and in the three most successful runs the slurry was simply poured. (It is notable that no great effort had to be taken in this series of preparations to keep out atmospheric moisture.) To the mixture of sodium acetylide and sodamide 5 moles of ethyl bromide (dried with calcium chloride and distilled) were added dropwise with vigorous stirring over a period of two to three hours and water was then added until the reaction flask contained clearly defined aqueous and organic phases. During the addition of water a copious stream of ammonia was evolved which was led over water in a filter flask, but in no run did a separate phase ever appear in this trap. The organic layer was washed thoroughly with water, dilute hydrochloric acid, water, dilute sodium carbonate, and water. The crude yields in four runs were 54 g., 135 g., 106 g., and 130 g. When these lots were combined and fractionated, a yield of 317 g. of pure 3-hexyne ($N_D^{25°} = 1.4082$) was obtained. The indicated yield on the best run was therefore, $\frac{135}{82.1} \times \frac{317}{425} = 1.2$ moles or 48%. Sodium acetylide is the limiting reagent.

Hexyne is unstable in air, reacting with oxygen to form peroxides. Some commercial 3-hexyne, purchased from Farchan, was found to have so much peroxide in it that the potassium thiocyanate - ferrous ammonium sulfate solution with which it was shaken became quite warm, and many extractions were necessary to remove the peroxide. On the other hand some hexyne which was rinsed out of a column with acetone and kept in this solvent for three years in a loosely corked flask was found to be nearly free of peroxides. Acetone is recommended for long storage of hexyne.

Three values for the melting point of 3-hexyne are available in recent literature, -51°[11], -101°[12], and -105.5°[13]. Several efforts to freeze the freshly distilled hexyne in an acetone bath at 78° were unsuccessful. The material froze in liquid air but melted again in the Dry Ice bath.

In the many distillations of 3-hexyne made during the course of this work, the major portion of the product always boiled between 79.9&80.2° at atmospheric pressure (about 745 mm.). Most of these distillations were made under nitrogen. In one such distillation (at 742.8 mm.) the main fraction almost all distilled at 80.0°. The same thermometer was then employed to measure the boiling point of C.P. benzene and was found to read 78.8°. If the stem and barometric corrections are assumed to be additive over the small range involved, the corrected boiling point of 3-hexyne is $80.0 + (80.1 - 78.8) = 81.3°$ at 760 mm. Campbell and Eby[12] give 81.2° - 81.3° at 747 mm., whereas the later paper of Henne and Greenlee[13], devoted exclusively to physical constants, gives merely 81° at 760 mm.

Acetic acid. Two methods were used for the preparation of anhydrous acetic acid: refluxing with acetic anhydride and fractional distillation. Fractional crystallization was attempted in a preliminary test but was found to be wasteful of acetic acid, and two recrystallizations raised the melting point only to 16.0°. Baker's Chemical Reagent acetic acid melts, usually, at 15.6° while pure acetic acid melts at 16.6°. Treatment with acetic anhydride was more efficaceous. The melting point of the reagent acid was taken and the amount of water present was calculated[14] on the assumption that the only impurity responsible for the freezing point depression was water. The calculated amount of acetic anhydride was then added and the liquid was refluxed for two to three hours. In this way various lots, melting from 16.2° to 16.5°, were obtained. Then it was found (the first time accidentally) that overnight refluxing gave a product with a melting point of 16.6°. Most of the early kinetic runs were made in acetic acid which had been refluxed overnight with about 0.05 M excess acetic anhydride. To some of the runs extra acetic anhydride was added. It was believed, and subsequent work clearly indicated, that small amounts of either water or acetic anhydride would not greatly effect the rate of the reaction, but that acetic anhydride was to be preferred to water.

The acetic acid for all indicator work and for the concluding and conclusive kinetic runs was prepared by fractionation through a 90 cm. column of glass helices fitted with an electrically heated jacket and a total-reflux partial-takeoff still head.[15] Batch lots of 2 1/2 liters were distilled and initial cuts of 500-700 ml. were discarded. The main product always melted at 16.6°. The various batches of purified acetic acid were kept in flasks fitted with a 24/40 standard-taper stopper. The acetic acid was found to be quite stable during continual use. In some cases melting points taken weeks apart showed no change whatever.

The thermometer used for taking these melting points was calibrated in 0.2°, and readings which coincided with a calibration were probably accurate to 0.02°. The melting point of one batch of acetic acid was taken with both the usual laboratory thermometer and with N.B.S. thermometer #42940, calibrated in 0.1°. Both thermometers read 16.60°. The Bureau of Standards certificate gave the following data.

Thermometer Reading	True Temperature
10.00°	10.03°
20.00°	19.98°

It is, therefore, concluded that the laboratory thermometer gives the true temperature to within 0.02° in the vicinity of 16.6°.

Cyclohexene. This alkene was prepared by fractionating 100 ml. of the Eastman product through 30 cm. of glass helices. A 20 ml. central portion was taken over a 0.2° range.

Carbon tetrachloride. This solvent was purified by saturating 2 1/2 liters of material with chlorine gas and exposing to sunlight for a week. The solution was then washed with aqueous sodium hydroxide, dried over calcium chloride for a day, and distilled through a Vigreux column. The first 200 ml. of distillate was cloudy. The main portion, more than 2 liters, was stored in glass stoppered bottles.

Diethyl carbitol (bis β-ethoxyethyl ether). Carbide and Carbon diethyl "cellosolve" solvent was stored for a week over potassium hydroxide and then distilled at 68-70 mm. The first 300 ml. were discarded and about 1 liter was collected and stored under nitrogen. A few ml. were heated in a test tube with potassium hydroxide. A second phase developed, but only a faint trace of color was visible. To another sample of the ether one drop of 2% aqueous potassium permanganate was added. There was no evidence of reaction. Finally, to an aqueous solution of ferrous ammonium sulfate and ammonium thiocyanate a small amount of the carbitol was added. No color developed. It is, therefore, concluded that the solvent was free of both aldehydes and peroxides.

Mercuric salts. General Chemical Company, C.P. mercuric acetate was used without purification. Its solubility in glacial acetic acid was found to be just short of 0.100 M. Such saturated solutions were made up as stock solutions but were always diluted to give an intermediate standard solution before being used in a kinetic or colorimetric determination.

Reagent grade mercuric sulfate was used in an attempt to make up a standard stock solution in acetic acid, but the salt was either so slightly or so slowly soluble that a solution 0.0002 M could not be obtained. Use was made of mercuric sulfate as a catalyst by mixing acetic acid solutions of mercuric acetate and sulfuric acid in the presence of hexyne. Although some trouble was experienced due to precipitation, much data was thus obtained.

Mercuric perchlorate was prepared by dissolving 0.46 mols of C.P. red mercuric oxide in 0.972 mols of $HClO_4$ in 60% aqueous

$HClO_4$. After several hours a still undissolved suspension was filtered off. After standing overnight at 5° in the cold room the crystals of mercuric perchlorate were filtered off with suction, bottled, and left in the cold room. They were deliquescent, however, and were not used. Mercuric perchlorate, like mercuric sulfate, was prepared in solution as needed by mixing acetic acid solutions of mercuric acetate and perchloric acid.

Strong Acids. Perchloric acid was prepared from a 60% aqueous solution of Baker's C.P. reagent. The normality of the aqueous solution was determined by diluting an aliquot from a total-delivery pipette[16] to provide about a 0.10 N aqueous solution, the strength of which was accurately determined by titration against an iodide-iodate solution[17]. The 60% solution was found to be 9.011 N in perchloric acid. A solution of this strength has 905.4 g. of acid per liter and a specific gravity of 1.529[18]. A ten-ml. volumetric pipette delivered 15.27 g. of the strong acid. Mr. Cunningham had found a specific gravity of 1.533 for the same solution. The value 1.530 was used to calculate that the solution was 59.16% $HClO_4$ and 40.84% H_2O. Baker's label gave an assay of 59.1% $HClO_4$.

Acetic acid solutions of perchloric acid were prepared in strengths ranging from 0.525 M to 0.0500 M by mixing in anhydrous acetic acid the appropriate quantities of acetic anhydride and aqueous perchloric acid. In the presence of the mineral acid the reaction between the water and acetic anhydride took place quite rapidly with the evolution of considerable heat. The solutions were adjusted to final volume with acetic acid after the mixtures had returned to room temperature. More dilute stock solutions of perchloric acid in acetic acid were prepared by diluting these solutions with glacial acetic acid. An 0.0500 M solution prepared according to these calculations was titrated with an acetic acid solution of freshly distilled aniline with crystal violet as indicator. The solution was found to be 0.0500 M in perchloric acid.

An acetic acid solution 0.0500 M in mercuric acetate and 0.200 M in perchloric acid was prepared by mixing the appropriate solutions. This solution was found to be quite stable. However, a solution prepared so as to be 0.100 M in mercuric acetate and 0.200 M in perchloric acid formed a precipitate, which was very slightly soluble even in water. An attempt to prepare a solution half this strength - 0.0500 M in mercuric acetate and 0.100 M in perchloric acid - also resulted in a water insoluble precipitate.

Boron trifluoride etherate, generously supplied by the General Chemical Company, was received as a black liquid which fumed vigorously in air. Distillation yielded a nearly colorless material, boiling point range 123.0° - 123.5°. A solution 0.200 M in boron trifluoride was prepared by making 25.0 ml. of the distillate up to a liter with acetic acid. The solution seemed to be fairly stable, but the unused distilled material became noticeably darker in one day.

An acetic acid solution 0.050 M in the hypothetical compound $Hg(OAc)_2 \cdot 2BF_3$ was found to yield a precipitate but solutions from 0.00100 M to 0.0100 M were stable. On another occasion a solution 0.0200 M in boron trifluoride and 0.00500 M in mercuric acetate gave a precipitate on standing for two days. The solid was not soluble in water, though it seemed to react with water to form a new precipitate. A precipitate was observed after three hours in a solution 0.0200 M in boron trifluoride and 0.00300 M in mercuric acetate. Precipitates, perhaps of a different nature, were also formed occasionally in the presence of hexyne.

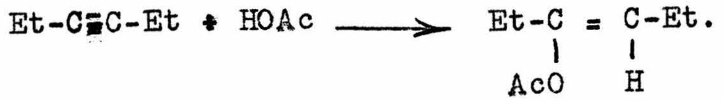
Sulfuric acid with a melting point of about 8° was prepared by mixing 50 ml. of 25% fuming C.P. sulfuric acid with 100 ml. of reagent grade (96%) sulfuric acid. Solutions in acetic acid were prepared from weighed amounts of this material.

3-Acetoxyhexene-3. Four attempts were made initially to prepare 3-acetoxyhexene-3 (also called hexenyl acetate and diethyl vinyl acetate) from hexyne with mercuric acetate and perchloric acid in acetic acid. The details of the runs are shown in Table 1. The synthesis being attempted is shown in Equation 16.

Table 1.

Attempted Preparation of Hexenyl Acetate.

Run	Hexyne moles/l.	$Hg(OAc)_2$ moles/l.	$HClO_4$ moles/l.
359	1.1	0.010	0.038
361	0.51	0.005	0.020
365	0.48	0.005	0.020
388	0.50	0.010	0.020



$$\text{Et-C}\equiv\text{C-Et} + \text{HOAc} \longrightarrow \underset{\text{AcO}}{\text{Et-C}} = \underset{\text{H}}{\text{C}}\text{-Et.} \qquad (16)$$

Unexpected colors appeared in these runs, ranging from pale yellow to deep red and brown. Precipitates were also formed in each. No hexenyl acetate could be isolated, and, in the case of the third and fourth runs, it was found that only a very small fraction of the unsaturation disappeared in 24 hours.

Since Hennion and Nieuwland accomplished the synthesis of 2-acetoxyhexene-1 from 1-hexyne with boron trifluoride, this acid was employed next. One hundred ml. of acetic acid solution 0.35 M in hexyne, (3.5 gm. of hexyne) 0.0200 M in boron trifluoride, and 0.00500 M in mercuric acetate (a similar run with 0.00100 M mercuric acetate gave no product) were allowed to stand at 25° for 24 hours. Titration then indicated the loss of half the original unsaturation and the 90 ml. of solution were steam distilled from 600 ml. of boiling water. The first 30 ml. of distillate included four ml. of an organic phase which was dried over calcium sulfate and distilled at 40 mm. A product weighing 2.4 g. was collected at 67-70°. Allowing for the aliquots taken for titration during the run, the yield was 55%. The steam distillation was continued until about 150 ml. of aqueous solution was collected. This material was neutralized with potassium carbonate and extracted with ether, which was then dried with calcium chloride. After stripping off the ether a residue of about 1/2 ml. was obtained.

Four such runs were made, two on a somewhat larger scale, with the products of each run being added to the crude material of the succeeding run for distillation. The final distillation was made at 40 mm. and six fractions collected as shown in Table 2.

Table 2.

Distillation of hexenyl acetate at 40 mm.

Fraction No.	Temp.	Weight (g.)	$\underline{n}_D$
1	69.5°-72.8°	1.9	1.4188
2	72.8°	2.4	1.4198
3	72.8°	2.1	1.4197
4	72.8°	2.6	1.4197
5	72.8°	2.4	1.4196
6	72.8°-72.9°	2.5	1.4196

The temperature control on the refractometer was inadequate when the readings were taken, the temperature varying 25° - 26°. Fraction 4 was submitted for a carbon hydrogen analysis. Calc'd. for $C_8H_{14}O_2$: C, 67.57%; H, 9.93%; found, C, 68.42%; H, 10.26%. Bromine titrations of aliquots containing 1.644 milliequivalents gave titers of 1.63, 1.648, and 1.653 milliequivalents.

Fraction No. 5 was used for a density determination. A pycnometer, kindly loaned by Dr. Harold Garner, with a volume of 1.6814 ml. at 25°, was found to hold 1.4924 g. of hexenyl acetate at 25°. Correction for the displaced air gives a calculated mass of 1.4942 g.[19] The specific gravity, d^{25}_{25} is, then, 0.888. The molar refraction was calculated from these data and found to be 40.49. The theoretical molar refraction for hexenyl acetate is 40.33.[20]

As in the runs with perchloric acid, the solutions of hexyne, boron trifluoride, and mercuric acetate gave colors and, usually, precipitates. The colors observed ranged from yellow through red to brown. In the absence of mercury, a boron trifluoride-hexyne solution became a quite pretty rose color without any appreciable loss of unsaturation.

A determined attack was then made on the problem of synthesizing hexenyl acetate with perchloric acid as the acid catalyst. Nineteen different solutions were prepared, as shown in Table 3, and tested at intervals for loss of unsaturation.

Table 3.

Attempted preparations of hexenyl acetate with perchloric acid.

Volumes 30 to 50 ml.

Run	Hexyne M	$Hg(OAc)_2$ M	$HClO_4$ M	
1a	0.34	0.0050	0.0200	
2a	0.42	0.0238	0.0485	
3a	0.29	0.0161	0.0323	
4a	0.29	0.0242	0.0161	
5a	0.25	0.0278	0.0139	
6a	0.22	0.0122	0.0244	
7a	0.25	0.0278	0.0139	
8a	0.02	0.0125	0.0050	G
9a	0.11	0.0125	0.0050	
11a	.04	0.0125	0.0050	
12a	.07	0.0125	0.0050	
13a	.09	0.0125	0.0050	
14a	0.11	0.0077	0.0077	
15a	0.35	0.0050	0.0200	
16a	0.35	0.0030	0.0200	
17a	0.18	0.0030	0.0200	
18a	0.11	0.0037	0.0250	G
19a	0.088	0.0050	0.0300	G

Runs 8, 18, and 19 were the only ones to show sufficient loss of unsaturation to give promise of yielding much hexenyl acetate.

A large scale run using the same concentrations of materials as were used in Run 19 was then made. Ten ml. of hexyne were dissolved in a liter of catalyst solution. After four and a half hours the unsaturation had dropped from 0.35 to 0.24 equivalent weights per liter. The one liter of solution was steam distilled from three liters of boiling water. The acetic acid was added gradually during the distillation, and it was noted that towards the end of the run, when the still pot residue was 15%-25% acetic acid, much less organic phase was distilled. (It should be noted that the ratio of water to acetic acid is less than half the corresponding value in the boron trifluoride runs. This fact has an important bearing on the lower yields obtained with perchloric acid.) About 250 ml. of distillate was collected and extracted with ether. The ether solution was dried (calcium chloride seemed to be better than calcium sulfate for this purpose) and the ether stripped off at atmospheric pressure.

The products from four such runs were combined and distilled at 41 mm. pressure. Six and a half ml. were collected from 68-78°. The dry ice trap contained water and about 8 ml. of organic material which smelled strongly of hexenyl acetate. The 6 1/2 ml. were combined with 1 1/2 ml. from a previous similar (single) run and 3 ml. from the boron trifluoride synthesis (Table 2) and redistilled. At 31 mm. 7 ml. distilled from 63°-69° and at 25 mm. 3 1/2 ml. distilled from 68°-71°. The indices, $\underline{n}_D^{25}$ were 1.4239 and 1.4231 respectively at 25.0. These products were recombined and fractionated through a semi-micro column with a coiled glass rod for packing. At 33-34 mm. four fractions were collected.

Table 4.

Distillation of hexenyl acetate at 33-34 mm.

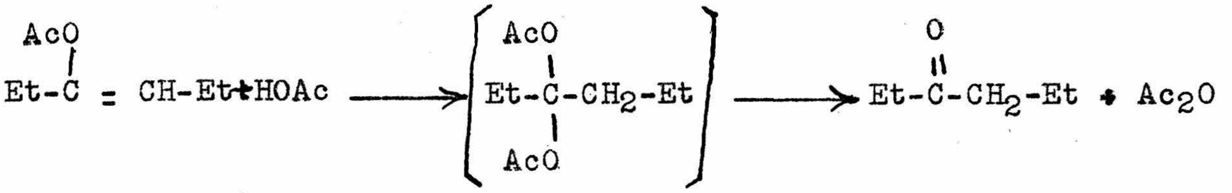
Fraction No.	Temp.	Volume (ml.)	$\underline{n}_D^{25.0°}$
A	52°-59°	0.6	1.4180
B	61.5°-66°	2.0	1.4260
C	69°-74°	5.5	1.4229
D	73°-75°	1.1	1.4212

Fraction B was later redistilled and collected in quite good yield with $\underline{n}_D^{25}$ equal to 1.4233, so it may be that the high reading for B above was due to impurity in the apparatus. It is apparent, however, both from the boiling point range and from the index of refraction that this product differs from that obtained with boron trifluoride. The best yield was probably about 15%. Bromine titration indicates a saturated impurity amounting to about 6%, and the analysis for carbon was low. Calculated for $C_8H_{14}O_2$: C, 67.6%; H, 9.9%; found: C, 65.9%; H, 9.9%.

<u>3-Hexanone</u>. 3-Hexanone was prepared from 3-hexyne in an acetic acid solution 0.25 $\underline{M}$ in hexyne and a little less than

0.020 M in boron trifluoride and 0.010 M in mercuric acetate. (The reaction mixture contained 20% of the supernatant liquid from a solution 0.050 M in mercuric acetate and 0.100 M in boron trifluoride. A slight precipitate had deposited in this solution.) After 29 hours 93% of the unsaturation had disappeared. The 80 ml. of reaction mixture was steam distilled from 200 ml. of water. About 1.9 ml. of organic layer were collected in 25 ml. of distillate. This layer was dried with calcium chloride and calcium sulfate and distilled with tert.-butylbenzene as a still base. About 0.3 g. of product distilled at 118°-124° and an equal amount was obtained at 124°-124.5°. The calculated yield was about 30%. The first cut had n_D^{25} equal to 1.4000. The literature gives a boiling point of 123°[21] and n_D^{22} equal to 1.3990[22]. The 2,4-dinitrophenylhydrazones of some ketones are di- or polymorphic[25]. The melting point of the hexanone-3 derivative has been reported as 130°[24] and 146.5°-148.5°[25]. The above two 0.3 g. cuts were mixed and used to make the derivative according to Allen's[24] directions. Recrystallization from ethyl alcohol and acetic acid gave a product melting 127°-129°.

The reaction between hexyne and acetic acid to yield 3-hexanone probably takes place in two steps. The hexyne reacts first with one molecule of acetic acid to give 3-acetoxyhexene-3 (Equation 16). A second molecule of acetic acid then adds to this ester to form an unstable intermediate which, as shown in Equation 17, breaks down to give 3-hexanone and acetic anhydride.



$$\overset{\text{AcO}}{\overset{|}{\text{Et-C}}} = \text{CH-Et} + \text{HOAc} \longrightarrow \left[\text{Et-}\underset{\underset{\text{AcO}}{|}}{\overset{\overset{\text{AcO}}{|}}{\text{C}}}\text{-CH}_2\text{-Et} \right] \longrightarrow \text{Et-}\overset{\overset{\text{O}}{\|}}{\text{C}}\text{-CH}_2\text{-Et} + \text{Ac}_2\text{O} \quad (17)$$

Because they were unable to isolate the ketone diester in certain analogous reactions, Hennion and Nieuwland[8] were uncertain whether Reaction 17 actually took place or whether the ketones they isolated were formed by hydrolysis of the substituted vinyl esters during the isolation. The nearly complete loss of unsaturation observed in the above synthesis of 3-hexanone shows that Reaction 17 actually took place. Tentative evidence will be presented later that the ketone diester is unstable, decomposing even in the anhydrous solution.

Analytical reagents. Merck reagent grade potassium bromate was used as the primary standard for the analytical determinations. It was dried in an oven at 110° for three days and thereafter stored in a vacuum desiccator over calcium chloride and phosphorus pentoxide. Two-liter batches of 0.1000 N bromide-bromate solution were made up with 5.568 g. (1/30 mole) of the potassium bromate. During the early part of the work 35 to 40 g. of sodium or potassium bromide (about 1/3 mole) were used in preparing the solutions, but later, at Mr. Dorsey's suggestion, the amount of bromide was reduced to 1/6 mole. Solutions of sodium thiosulfate (0.05 M) were prepared by dissolving 25 g. of Baker's C.P. pentahydrate and about two grams of sodium carbonate in 2 liters of water. This solution was standardized against the bromate solution with the same technique as was being employed for the hexyne determinations. The need for running blanks was thus avoided. Occasionally the thiosulfate solutions were also standardized with potassium dichromate[28] and the results always agreed well with the bromate standardizations. The thiosulfate solutions were found to be stable. Some solutions showed no change (0.0500 N to 0.0500 N for example) in two months while one, perhaps the least stable, changed from 0.0505 to 0.0501 in 40 days. Because the equivalents of thiosulfate used in a titration were usually about 25% of the equivalents of hexyne present and rarely more than 50%, the normality of the thiosulfate did not have to be known to an accuracy greater than about 4 parts in 1000.

Mercuric sulfate solutions were made up in 6 N sulfuric acid. The 0.2 M solutions presented no difficulties in their preparation. The 0.6 M solutions required heating and stirring. Potassium iodide solutions were made up in small quantity, to last only two or three weeks. The pure solutions slowly turned yellow, but since this color - even in 200-300 ml. of solution - could be discharged with a very few drops of 0.05 N thiosulfate solution, it was not considered detrimental. Potassium iodide solutions made up with a gram or two of potassium carbonate were quite stable.

III. Methods of Analysis

A. Analysis of 3-Hexyne

The carbon-carbon triple bond does not add bromine quantitatively in a simple bromate titration; but in the presence of mercuric sulfate a smooth, rapid addition can be secured[26]. It was found necessary to use a quantity of mercuric sulfate in excess of the total halide present during the bromination and then to add excess sodium chloride before the final iodide-thiosulfate titration. This procedure was further studied by Lucas and Pressman[27], whose directions are herewith summarized.

> A 10 to 15% excess of 0.1 N bromide-bromate solution is run from a burette into a conical flask having a ground-glass stopper bearing a sealed-in stopcock. Following the evacuation of the flask, 5 ml. of 6 N sulfuric acid are added and allowed to stand 2 to 3 minutes. Next, 10 to 20 ml. of 0.2 M (not 0.2 N - the correction is from a private communication from Dr. Pressman) mercuric sulfate and the solution to be analyzed, which should have about two milliequivalents of unsaturation, are run in. About 15 ml. of carbon tetrachloride were used for washing in the sample, which was a carbon tetrachloride solution of the unsaturated compound, and 20 ml. of acetic acid were added. The flask, wrapped in black cloth, was shaken for 7 minutes, and 15 ml. of 2 N sodium chloride and 15 ml. of 20% potassium iodide were then added. After 0.5 minutes final shaking, titration was made with 0.05 N sodium thiosulfate, using a starch solution as indicator.

The accuracy of this method varied with the different alkynes used, ranging from +2.2% for 1-pentyne to -3.5% for 2-heptyne.[27] (No acetic acid was used in the pentyne analyses.) Average deviations ranged up to 1.4%. In the course of the present work several changes were made in the above procedure, and they will be discussed in this section. Some of these changes, as noted, were suggested by Mr. W. Smith Dorsey, who has made an extensive investigation of the method. It is evident that an average deviation of 1.4%, representing, as it probably does, a dispersion of about 5%, is not satisfactory for kinetic studies.

When hexyne reacts with acetic acid to form hexenyl acetate, the amount of unsaturation changes. It is not possible to make the initial analysis recommended by Lucas and Pressman. In order to arrive at the suggested 10-15% excess of bromate over alkyne, it was necessary to guess at the amount of unsaturation present in successive aliquots. Much work was wasted and time lost before it was realized that about 15% excess bromate should be not a maximum but a minimum requirement. If less bromate than this excess is used, some of the hexyne will remain unreacted; and an apparent, but spurious, 10-15% excess bromine will be found. Therefore, by guessing that a reaction will take place and adjusting the bromate titers accordingly, it is possible to make the reaction seem to take place. By maintaining the concentration of bromate at least 15-20% in excess of the hexyne, this effect was eliminated. It was found that an excess of bromate up to 55% had little effect on the quantity of hexyne found. The data are shown in Table 5.

Table 5.

The Effect of excess Bromate Solution used in the Titration of Successive Aliquots of an Acetic Acid Solution of 3-Hexyne containing 1.50 Milliequivalents of Hexyne. (Analysis Method II) (Quantities are in milliequivalents.)

Titration No.	Time for Bromination (Min.)	Bromate Used	Hexyne Found
1	5	1.60	1.47
2	5	1.80	1.58
3	5	2.00	1.60
4	5	2.22	1.60
5	5	2.50	1.61
6	15	2.50	1.63

Titration No. 1 of Table 5 is an example of the fallacious results which are obtained when not enough bromate is present. The results of titrations 2-5 show an average deviation of 0.5%, as the excess bromate ranges from 14% to 55% of the hexyne found. In titration No. 6 the hexyne was left in contact with the large excess of bromine for 15 minutes before sodium chloride and potassium iodide were added and the solution was back-titrated with thiosulfate solution. It is of interest that even in these extreme conditions the hexyne found was only 1.4% above the mean of titrations 2-5.

As recommended by Lucas and Pressman, 5 ml. of 6 N sulfuric acid were added to the bromide-bromate solution. However, a minimum of five minutes were always provided for the liberation of the bromine.

Samples of the reaction solutions were taken in a pipette calibrated for total delivery[16]. Sampling was effected through an all-glass double stopcock assembly which allowed the sample to be forced up into the pipette by the pressure of nitrogen from a cylinder. Nothing but the nitrogen and pyrex glass came into contact with the solution. The sampling apparatus is shown in Figure 1. The nitrogen used for most of the work was water-pumped, 99.5% pure material dried by passage through a tower of calcium chloride. For the conclusive kinetic runs, nitrogen with a minimum purity of 99.99% was employed. During some preliminary work using a carbon tetrachloride solution of cyclohexene, an attempt was made to force the sample up with mercury. It was found that the metal reacted with the cyclohexene in solution!

The size of the aliquot of hexyne solution which it was convenient to take depended on the concentration of the hexyne. A list of the total delivery pipettes and their calibrations is shown in Table 6. In the present work the analytical solutions were homogeneous, since no carbon tetrachloride was present. In the preliminary work with acetic acid the bromine addition took place in a solution containing about 45 ml. of water and 15 ml. of acetic acid. Although these solutions appeared homogeneous, erratic results were often obtained. It seems probable that the hexyne was just barely soluble in the solutions and that much hexyne was vaporized in the 300 ml. flask. When 30 ml. of aqueous solutions were added (sodium

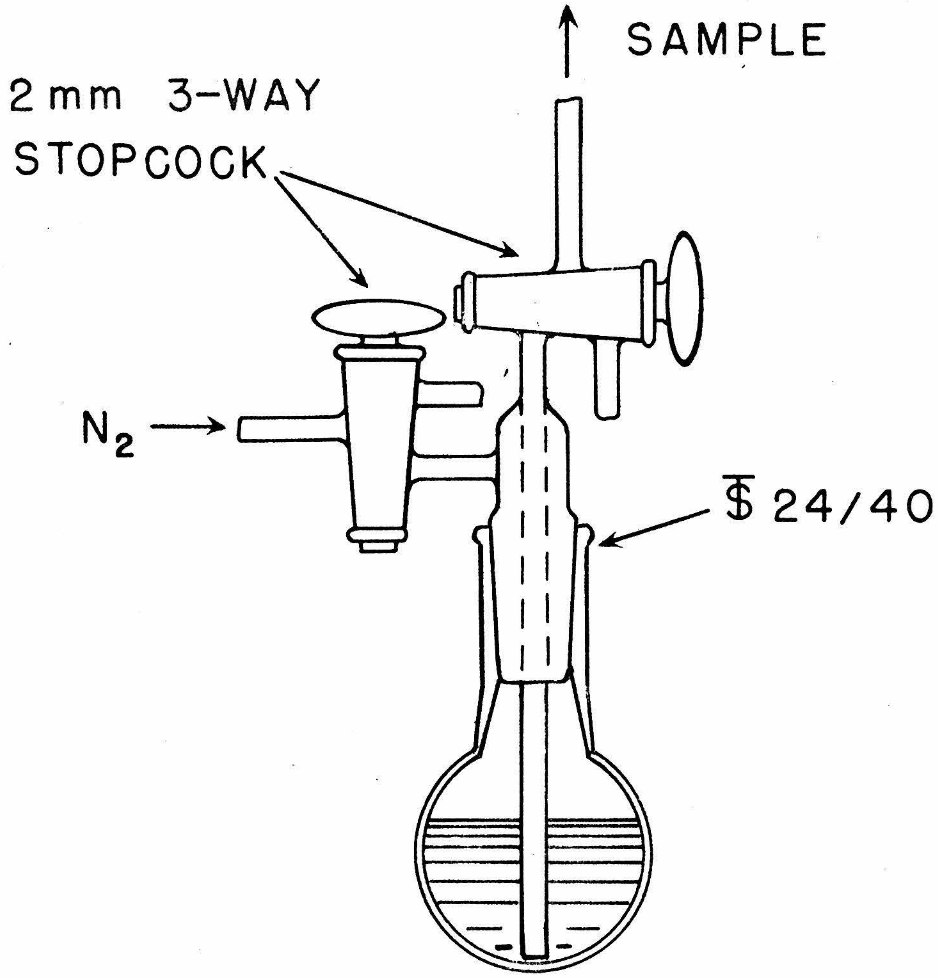


Figure 1

Apparatus for Sampling Under Nitrogen

Table 6.

The Calibration of Pipettes for Total Delivery

Weight of Mercury in grams	Temperature (Deg.)	Volume in milliliters
13.15, 13.19		0.973
20.027, 20.028	26	1.480
24.42, 24.37	20	1.801
63.12	24	4.663
63.11	27	
79.7, 79.4	21	5.88
78.87, 78.95	22	5.83
97.7, 95.6, 95.8	24	7.07
157.50	24	11.636
185.43, 185.46	28	13.71
253.8, 253.7	27	18.75
468.7, 468.4	29	34.66
484.4, 485.9	29	35.95

chloride and potassium iodide) a cloud appeared in the analytical solution. The amount of acetic acid used was increased to 30 ml. in the immediately succeeding runs, and gradually increased to 65 ml. during the rest of this work. There seemed to be no reason for limiting the amount of acid used for rinsing in the sample. This acid was not the high melting, purified acid but Baker's reagent grade, or, occasionally, the forecut from the acetic acid distillations.

In addition to the more liberal use of acetic acid rinse, it was made standard procedure to shake the analysis flask intermittently during the five to ten minutes allowed for the brominations.

Mr. Dorsey has found that there is no advantage to using sodium chloride but that the potassium iodide should be present in great excess over the mercuric sulfate. The use of sodium chloride was eventually abandoned. The various combinations of reagents used are shown in Table 7.

Method I, in which too little acetic acid rinse was used, has already been referred to. It was used in Runs 1-9. Method II was used for the hexyne determinations through Run 79. It seemed to be entirely satisfactory. Method III introduces the use of 5:1 bromide-bromate solution. The elimination of the free bromide made it possible to reduce the amount of mercuric sulfate and, therefore, the amount of potassium iodide. Method III was used for Runs 100 to 116 with no trouble, but was found to give poor results when more than two milliequivalents of hexyne were present. The conditions of Method IV were introduced at Mr. Dorsey's suggestion, and with slight modification in Methods VIII and IX were used for Runs 117 to 150. Water was added simultaneously with the potassium iodide because, in more dilute solutions, the starch-iodide endpoint is more readily determined. Moreover, dilution helps prevent the fading endpoint caused by hexenyl acetate. Method V was used for Runs 118 through 126 but was found to give erratic results with higher (>2 milliequivalents) quantities of hexyne.

Table 7.

Variations in Method of Analysis of 3-Hexyne with Standard Bromide-Bromate Solution. Volumes are in ml.

Method	Br^- - BrO_3^- 10:1[a]	5:1[b]	H_2SO_4 6 M	$HgSO_4$ 0.2 M	0.6 M	AcOH[c]	$HgSO_4$ 0.6 M	NaCl 2 M	KI 1 M	1.3 M	3 M	H_2O
I	20-30		5	15		15		15		15		
II	20-30		5	15		30-35		15		15		
III		10-10	5	5		40			10			
IV		20-30			5	45-65					15	100
V		10-20	5		3	45-65					5	100
VI		20	5		2	45-65					5	
VII		20	5		3	45-65					3	100
VIII		10-30	5		4	45-65					15	100
IX		5-10	5			45-65	3				15	100

a. 0.1667 M in Br^-; 0.01667 M in BrO_3^-.

b. 0.0833 M in Br^-; 0.01667 M in BrO_3^-, except that some analyses using method III were made with a solution half this strength.

c. Includes sample and rinse.

Table 8.

Reproducibility and Accuracy of Determinations of 3-Hexyne.

Method	Hexyne present in aliquot, m.e.	Hexyne found, m.e.	Accuracy (%)
II	1.50	1.58	105
		1.60	107
		1.60	107
II	1.87	1.97	105
		1.97	105
II	2.05	2.18	106
		2.20	107
		2.20	107
		2.19	107
III	2.06-	2.10	102+
III	0.994-	1.026	103+
V	1.970	2.062	105
		2.062	105
IV	?*	1.664	
V		1.668	
V		1.663	
V		1.661	
VI		1.650	
VI		1.665	
VI		1.657	
VII		1.653	
VIII	2.100	2.220	106
		2.215	105
		2.205	105
		2.213	105
VIII	2.100	2.172	103
		2.187	104

* The amount of hexyne present in these eight determinations was not accurately known. All had the same amount of hexyne, however, and the reproducibility of the "Hexyne found" is considered satisfactory.

Methods VI and VII were tried in a special experiment and seemed to be satisfactory. They were not, however, used at any other time. Typical results for most of these methods are shown in Table 8.

The calculation of the hexyne present in the aliquots (column 2, Table 8) was made by assuming additivity of volumes when hexyne was dissolved in acetic acid. On this basis it is seen that the hexyne found is about 6% high in these titrations. (The titrations using Method III were made on different dilutions of the same solution of hexyne in acetic acid which had been prepared two months before the determinations.) The reproducibility, however, is quite good. The spread in the values of hexyne found from any solution of hexyne is usually less than 1%.

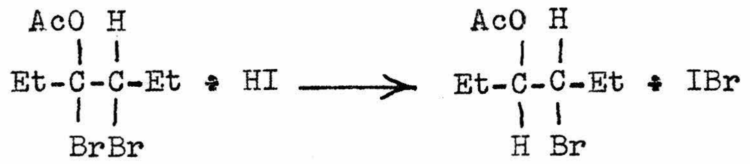
One titration of hexyne was made according to Method II with the mercuric sulfate and sodium chloride eliminated. Ten minutes were allowed for the bromination. Only 73% of the hexyne (1.60 instead of 2.20 millequivalents) were found

B. Determination of Hexenyl Acetate (3-Acetoxyhexene-3).

Method II for the determination of hexyne (3 millimoles of mercuric sulfate and 20 millimoles of potassium iodide) was the first method tried for the analysis of hexenyl acetate. An aliquot containing 1.644 milliequivalents of the ester was taken for the determination. When the final iodine solution was titrated with standard thiosulfate solution, it was found that, though the blue starch-iodine color was discharged as expected, it returned very rapidly. The thiosulfate burette reading the first time the solution became colorless corresponded to 1.63 milliequivalents of hexenyl acetate - a quite satisfactory check. The next day a similar titration was made on the same solution. By working rapidly the initial thiosulfate titer was secured about one minute after the addition of the potassium iodide. The indicated quantity of hexenyl acetate was 1.648 milliequivalents. On the third day a similar titration indicated 1.653 milliequivalents of ester. It was concluded that this method of titration gave satisfactory results, and it was used for Runs 48 through 50.

For the analyses of Runs 51 through 56, mercuric sulfate was omitted from the analytical solutions. The results seemed quite satisfactory. The method of choice for the analysis of hexenyl acetate is probably to add the solution of the ester to the acidified bromide-bromate solution with enough acetic acid rinse so that the solution is about 75% acetic acid. After five to ten minutes of intermittent shaking, 20 milliequivalents of potassium iodide and water to a total of about 100 ml. should be added and the solution titrated rapidly with sodium thiosulfate.

Drifting of the endpoint continued to be troublesome, however, and several further variations were tried. A reasonable hypothesis for the continued appearance of iodine in the solutions is shown in Equations 17 and 18.



$$\mathrm{Et{-}\overset{\overset{AcO}{|}}{\underset{\underset{Br}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}{-}Et} + \mathrm{HI} \longrightarrow \mathrm{Et{-}\overset{\overset{AcO}{|}}{\underset{\underset{H}{|}}{C}}{-}\overset{\overset{H}{|}}{\underset{\underset{Br}{|}}{C}}{-}Et} + \mathrm{IBr} \tag{17}$$

$$\mathrm{IBr} + \mathrm{HI} \longrightarrow \mathrm{I_2} + \mathrm{HBr} \tag{18}$$

On such a basis the drift should be diminished by diluting the solution and by using less potassium iodide, the source of the hydriodic acid. Some analyses were made without mercuric sulfate and with 0.9 milliequivalents of potassium iodide. In these solutions the drift was cut to negligible proportions by adding up to 100 ml. of water with the potassium iodide. However, the results were scattered and low. In one set of determinations, aliquots containing 0.684 milliequivalents of ester gave titers of 0.498, 0.482, 0.530, and 0.515 milliequivalents.

A return to the use of mercuric sulfate and somewhat larger concentrations of potassium iodide was then made. Two combinations of reagents were found to give satisfactory results. They are shown in Table 9. Five ml. of sulfuric acid and 60 ml. of acetic acid were present, as usual. Method I was used in two determinations of aliquots supposed to contain 1.50 milliequivalents of ester. The quantities found were 1.37 and 1.38 milliequivalents. Method II indicated 0.642 milliequivalents in an aliquot supposed to contain 0.685. These determinations were run on hexenyl acetate made with perchloric acid as catalyst (combined cuts

C and D, Table 4) and seem to indicate the presence of 6% of saturated impurity. Method II was used in Runs 200 through 208.

Table 9.

Methods of Analysis of Hexenyl Acetate. Volumes are in ml.

	$Br^- - BrO_3^-$	$HgSO_4$		KI		H_2O
	5:1	0.2 M	0.6 M	1.0 M	3.0 M	
I	18	5		10		
II	20*		2		5	100

---

* 0.0500 N

C. The Bromination of Diethyl Ketone

An analytical solution containing 1.2 milliequivalents of mercuric sulfate (Method II, Table 9) was found to brominate diethyl ketone. To a solution containing 10 ml. of 0.05 N bromide-bromate, 3 ml. (31 milliequivalents) of ketone were added. The bromine was completely reacted, no color being found on the addition of potassium iodide. When the vacuum was broken and the flask exposed to air, a small amount of color developed. An acetic acid solution 0.50 M in diethyl ketone was then prepared and 1 ml. aliquots taken for "determination" using an equivalent amount (one half a milliequivalent) of bromide-bromate solution. Only about 10% of the bromine was found to react under these conditions. It was concluded, therefore, that small quantities of ethyl propyl ketone, which bears a close resemblance to diethyl ketone and which is produced during kinetic studies, would not seriously affect the analytical data.

Some comparable studies were made in which the mercuric sulfate was omitted from the analytical solution. Two ml. (21 milliequivalents) of diethyl ketone reacted with most of 0.5 milliequivalents of bromide-bromate solution, a faint color appearing on the addition of potassium iodide. The returning end-point made the titration difficult, but it was found that at least half of the bromine must have reacted with the ketone. Using the 0.50 M solution of diethyl ketone, it was found that no reaction took place between 0.5 milliequivalent of ketone and 0.5 milliequivalent of bromine. Duplicate analyses with two ml. (1 milliequivalent) of ketone solution were also run. One showed no reaction. In the other about 3% of thebromine reacted. It was tentatively concluded that under these analytical conditions mercuric sulfate catalyzes the bromination of diethyl ketone.

D. The Action of Diethyl Carbitol in the Bromide-Bromate Titration.

A solution containing 0.4 milliequivalents of bromide-bromate solution, 3 milliequivalents of mercuric sulfate, and 20 milliequivalents of potassium iodide (Method I, Table 7) was titrated to the equivalence point with thiosulfate solution. To this solution some diethyl carbitol was added and a large amount of free iodine was immediately released. This test was run one month after the purification of diethyl carbitol described earlier. Even if the indicated oxidizing power resulted from the formation of peroxides within this period and was not an intrinsic property of the pure solvent, it suggested strongly that diethyl carbitol would not be an advantageous choice of solvent for this study.

IV. The Reaction of 3-Hexyne and 3-Hexenyl Acetate-3 with Acetic Acid. Preliminary Results.

A. The Reaction of 3-Hexyne

1. Calculations.

When acetic acid adds to hexyne to give hexenyl acetate (Equation 16), the unsaturation as measured by a bromine titration changes from four equivalents to two equivalents per mole of solute. The initial concentration of hexyne could be determined by titration according to Equation 19 if it were possible to make a titration at the moment of mixing the solutions. H_o is the initial concentration of hexyne

$$U = 4\ H_o. \qquad (19)$$

in moles per liter and U is the observed unsaturation in equivalents per liter. Only a small fraction of the change of unsaturation observed during the first few minutes of the reaction need to be ascribed to the subsequent reaction of the hexenyl acetate. This fact is indicated by the isolation of hexenyl acetate from the solution and will be discussed later in connection with studies on the rate of reaction of hexenyl acetate. An approximate material balance can, therefore, be written as in Equation 20. The moles per liter of hexyne and

$$H_o = H + V \qquad (20)$$

hexenyl acetate (diethylvinyl acetate) at any time after the start of the reaction are represented by H and V respectively. The amount of unsaturation in equivalents per liter at any time is dependent on the concentration of both the hexyne and hexenyl acetate as shown by Equation 21.

$$U = 4H + 2V \tag{21}$$

From Equations 20 and 21 V may be eliminated, giving Equation 22.

$$H = \frac{U - 2H_o}{2} \tag{22}$$

Because the titration of hexyne gives results about 6% high, these equations must be modified. Equation 21 becomes:

$$U_a = 4(1.06)H + 2V \tag{21a}$$

where U_a is now the observed unsaturation. Equation 22 must also be modified:

$$H = \frac{U_a - 2\ H_o}{2.24} \tag{22a}$$

In many runs the value of H_o was determined not by the weight of the hexyne used but from volumetric calculations. For example, in several runs a special pipette was used for adding about half a ml. of hexyne to 99.5 ml. of acetic acid solution. By making several titrations in the absence of catalysts, it was found that the apparent initial hexyne concentration, H_{ao}, was 0.0465 moles/liter. in such a solution. In other runs a special pipette was used for adding 0.27 ml. of hexyne to 20.0 ml. of acetic acid. Repeated titrations showed that such a solution had an apparent hexyne concentration of 0.123 moles/liter of hexyne and that if, for example, five ml. of this solution were added to 95 ml. of reaction solution, the apparent initial concentration would be 0.00615 moles/liter.

These apparent concentrations are related to the true concentration by Equation 23.

$$H_{ao} = 1.06\ H_o \tag{23}$$

Introducing Equation 23 into Equation 22a gives Equation 24.

$$H = \frac{U_a - 1.89\ H_{ao}}{2.24} \tag{24}$$

If the factor of 1.06 is ignored, the concentration of hexyne would be given by Equation 25.

$$H = \frac{U_a - 2\ H_{ao}}{2} \tag{25}$$

The difference between Equations 24 and 25 is often small.

2. Reactions catalyzed by perchloric acid and mercuric acetate. Preliminary results.

The data collected in ten runs catalyzed by perchloric acid and mercuric acetate are shown in Table 10. These data do not suffice to explain the mechanism of the catalysis, and the various attempts to correlate the runs will not be reproduced here. However, various points are worth commenting on.

A comparison of Tables 1, 3, and 10, shows that probably Run 24 or 25, Table 10, represent a more promising set of conditions for synthesizing hexenyl acetate than any that was actually used. Run 359, Table 1 is nearly the same as Run 24 except for the higher concentration of hexyne in Run 359. Evidently the high concentration of hexyne has a detrimental effect on the course of the reaction. In Table 3 lower concentrations of hexyne were used, and Run 19a, which was used for large scale production of hexenyl acetate, actually had less hexyne than Run 24 or 25. It can be seen from Table 10 that the concentrations of catalyst should have been kept somewhat higher than they were in Table 3.

Run 73 showed a marked "tapering off" effect. There was a sudden initial drop in the amount of unsaturation followed by a virtually static condition. The same effect was shown, somewhat less dramatically, by Runs 29, 32, 33, and 64. It is, of course, possible that Run 31 also tapered off after a very small initial drop. Run 26 seemed to continue better than the others, but even here the rate diminished faster than would be calculated for a mechanism depending on the zero or first power of the concentration of hexyne. This tapering off effect was noted throughout the work and no satisfactory explanation has yet been evolved for the phenomenon. The runs in which the hexyne continued to react were those in which the concentration of perchloric acid exceeded the concentration of mercuric acetate and in which the concentration of hexyne was not much greater than 0.1 M.

Runs 21, 27, and 28 are important for showing that neither perchloric acid nor mercuric acetate is, by itself, a very effective catalyst for the addition of acetic acid to hexyne.

Table 10.

The Rate of Reaction of Hexyne and Acetic Acid. Catalysis by Mercuric Acetate and Perchloric Acid.

Run No.	Temp. (Deg.)	HOAc M.P. (Deg.)	$Hg(OAc)_2$ M x 10^3	$HClO_4$ M x 10^3	Time Min.	Hexyne M x 10^3	Unsaturation Equivalents/ liter x 10^3	Color
24	30	16.0	10	40	0	(100)	400	Yellow
					1 day		182	
					2 days		163	
					3 days		152	
					7 days		120	Lt. Brown
25	30	15.8	10	60	0	(100)	400	Yellow
					2	21	237	
					145		178	
					11 days		81	Rd. Brown
26	30	15.8	5	22	0	(100)		Yellow
					4	64		
					28	45		
					4300	16		Colorless
29	30	15.8	2.5	11	0	(100)		Slight
					2	87		
					17	74		
					40	72		Gr. Yellow
30	30	16.2	5	20	0	(100)		Gr. Yellow
					13	53		
31	25	15.6	0.5	1	0	(100)		
					42	100		
					600	100		
32	25.1	16.2	1	5	0	(100)		Yellow
					3	96		
					15	92		
					29	91		
					78	89		

Table 10 (Continued)

Run No.	Temp. (Deg.)	HOAc M.P. (Deg.)	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Time Min.	Hexyne $\underline{M} \times 10^3$	Unsaturation Equivalents/ liter x 10^3	Color
33	25.1	16.6	1	4	0	(100)		
					4	94		
					16	92		
					31	91		
					59	90		
					134	89		
64	25	Excess AC_2O	1	6	0	(42.8)		Gr. Yellow
					9	39.4		
					47	37.6		
					106	36.7		Colorless
73	25	Excess AC_2O	3	6	0	(42.8)		
					6	31.6		
					30	29.6		
					62	30.0		
21	30	16.0	4	0	0	(100)		
					13	100		
					100	99.5		
					1300	98.7		
27	30	15.8	0	2	0	(100)		None
					5	100		
					160	101		
28	30	16.2	0	20	0	(120)		
					4	100		
					90	100		
					1300	98		

3. Reactions catalyzed by boron trifluoride and mercuric acetate.

Because boron trifluoride had proved to be such a successful catalyst for the synthesis of hexenyl acetate, a number of kinetic studies using boron trifluoride and mercuric acetate were made. They were notably unsuccessful. In several cases runs had to be abandoned or results discarded because precipitates were formed from the solutions. Of the "successful" runs the highly erratic nature can be seen from the brief summary in Table 11.

Boron trifluoride is an unusual acid and, in some ways, an exceptionally strong one. Ether and mineral acids are known to form loose complexes which do not withstand distillation. The ether-boron trifluoride complex, on the other hand, was purified by distillation. It is probable that slight amounts of water or acetic anhydride in the reaction solutions had a profound effect on the availability of the boron trifluoride. Moreover, the presence of the ether, added with the acid, was an additional complicating factor. The attempt to study the reaction of hexyne with acetic acid using boron trifluoride as the acid catalyst was abandoned.

4. Reactions catalyzed by sulfuric acid and mercuric acetate.

The data from nine runs catalyzed by sulfuric acid and mercuric acetate are shown in Table 11. Two ways in which these runs differ from the runs with perchloric acid

Table 11.

The Rate of Reaction of Hexyne and Acetic Acid - Catalysis by Mercuric Acetate and Boron Trifluoride

Run No.	Hg(OAc)$_2$ $\underline{M} \times 10^3$	BF$_3$ $\underline{M} \times 10^3$	Hexyne $\underline{M} \times 10^3$	Hexyne reacted in one hour (%)
41b	4.54	9.09	43.6	8
42a	5	20	50	9
42d	5	20	50	49
44a	3	20	50	75
45b,c,d	1	20	50	5

seemed to be significant. First, no colors were associated with the sulfuric acid runs. Second, and perhaps not coincidentally, the runs with sulfuric acid did not show the tapering-off phenomenon to anywhere near the extent that the runs with perchloric acid did. The rates did taper off, however, faster than could be accounted for on the basis of zero or first order dependence of the rate on the concentration of hexyne.

The absence of the by-product and the less marked divergence of the rates from zero or first order dependence on the hexyne, made it seem possible that the runs with sulfuric acid would be more amenable to interpretation than the runs with perchloric acid. It was known tht the catalyst would be complexed by the initial product, hexenyl acetate, and that a tapering off in the rate of reaction of hexyne was to be expected.

It was assumed that equilibrium reactions took place between the mercuric acetate and both hexyne and hexenyl acetate. No information was available at the time these runs

Table 12

The Rate of Reaction of Hexyne and Acetic Acid.
Catalysis by Mercuric Acetate and Sulfuric Acid.

Run No.	Temp.	HOAc M.P. (Deg.)	$Hg(OAc)_2$ M x 10^3	H_2SO_4 M x 10^3	Time Min.	Hexyne M x 10^3	Unsaturation Eq./1 . x 10^3
19	30°	16.0	5	1	0	(100)	(400)
					15	91	
					50	82	
					940	66	
					1060		230
					2340		150
					2750		130
20	30°	16.0	5	1	0	(100)	(400)
					17	92	
					56	88	
					120	81	
					182	74	
					1250		210
					2650		142
					5 days		16
65	25°	Excess Ac_2O	1	7.35	0	(44.5)	
					6	43.2	
					48	35.7	
					78	32.4	
					137	30.7	
66	25°	Excess Ac_2O	1	10.3	0	(45.0)	
					1	42.4	
					28	37.0	
					48	33.9	
					69	31.2	
					161	27.2	

- Table 12 (Continued)

Run No.	Temp.	HOAc M.P. (Deg.)	$Hg(OAc)_2$ $\underline{M}$ x 10^3	H_2SO_4 $\underline{M}$ x 10^3	Time Min.	Hexyne $\underline{M}$ x 10^3	Unsaturation Eq./ 1 . x 10^3
67	25°	Excess Ac_2O	1	4.4	(0)	(44.5)	
					12	42.6	
					37	39.4	
					67	37.1	
					103	35.6	
69	25°	Excess Ac_2O	1	8.82	0	(44.5)	
					7	41.9	
					26	38.0	
					53	34.9	
					77	32.9	
70	25°	Excess Ac_2O	1	11.76	0	(44.5)	
					7	42.0	
					27	36.5	
					47	32.7	
					66	30.0	
71	25°	Excess Ac_2O	1.39	4.41	0	(44.5)	
					6	43.0	
					30	38.8	
					53	36.7	
72	25°	Excess Ac_2O	1.39	5.88	0	(44.5)	
					6	42.7	
					24	39.0	
					45	36.5	
13	25°	16.4	0	0.78	(0)	(78)	
					5	77	
					160	77	
					200	76	

were made as to the exact composition of the complexes. Hugel and Hibou[5] (See Section I) had written $C_nH_{2n}\cdot(Hg(OAc)_2)$ for the complexes of simple alkenes in acetic acid. In analagous fashion, the complexes for hexyne and hexenyl acetate were now written $C_6H_{10}\cdot Hg(OAc)_2$ and $C_6H_{11}OAc\cdot Hg(OAc)_2$. The equilibrium constants are shown in Equations 26 and 27. Their ratio is to be denoted by n as shown in Equation 28.

$$K_H = \frac{(C_H)}{(C_f)(H)} \tag{26}$$

$$K_V = \frac{(C_V)}{(C_f)(V)} \tag{27}$$

$$n = \frac{K_V}{K_H} \tag{28}$$

C_H, C_V, and C_f are, respectively, the concentrations of the hexyne-mercuric acetate complex, of the hexenyl acetate-mercuric acetate complex, and of the free mercuric acetate. Because the hexyne is used in large excess over the mercuric acetate and because of the known stability of the mercuric complexes, C_f is believed to be small compared to C_H and to C_V. This approximation is expressed in Equation 29, in which C_o is the total mercuric acetate. The hypothesis was then made that the rate of disappearance of hexyne is proportional to the mercuric complex, as shown in Equation 30.

$$C_o = C_V + C_H \tag{29}$$

$$- \frac{dH}{dt} = k\ C_H \qquad (30)$$

Combining Equations 26 through 30 we get Equation 31.

$$- \frac{dH}{dt} = \frac{kC_o}{n\ \frac{V}{H} + 1} \qquad (31)$$

V and H may now be replaced by U and H_o by means of Equations 20 and 21.

$$\frac{dU}{dt} = \frac{2KC_o}{n\left(\frac{U - 4H_o}{U - 2H_o} \right) + 1} \qquad (32)$$

Integration and simplification give Equation 33 in which

$$F(U) = nH_o Cn \frac{2H_o}{U - 2H_o} - (n-1) \frac{4H_o - U}{2} = kC_o t \qquad (33)$$

U has been integrated between $4H_o$ and U and t from 0 to t.

Equation 33 was applied to runs 65-72 with various values of n being inserted. The left hand side of the equation was then plotted against t and the curves examined to see which value of n gave the best straight line. The curves for runs 69, which are typical, are shown in Figure 2. If only the origin and the first three points be considered, n = 9 gives a convex curve, n = 7 gives a straight line, and n = 5 gives a concave curve. In all cases the fourth experimental point deviates markedly. Increasing the value of n to bring this point into a straight line would make the first part of the curve increasingly convex. Actually the curve for n = 1 seems to be the smoothest curve and would indicate that some factor not being considered was responsible at least in part for the tapering off.

It was found that the value of the first point in the plot of F(U) against time was rather insensitive to the value of n selected. This fact suggests an alternative method of finding the value of k, Equation 30. If the value of n is, somewhat arbitrarily, set equal to one, then Equation 33 reduces to Equation 34. Accurate determinations should

$$H_o \ln \frac{H_o}{H} = kC_o t \qquad (34)$$

be made of H_o and of some value of H at a value of t low enough so that the branches of Figure 1 have not yet diverged. The rate constant could then be evaluated from Equation 34. The data of Table 12 are not suitable for this purpose because the values of H_o were not known with sufficient accuracy in these runs.

In addition to the unknown factor causing the tapering off, at least two other factors were not incorporated into the above equations. It seemed probable[7] that the acid catalyst, known to be necessary for the occurrence of the reaction at a significant rate, would play a role in the formation of the complexes. Equations 26 and 27 take no cognizance of this matter. Since neither K_H nor K_V but only their ratio appear in the subsequent equations, if acid happened to appear in the same way in the two equilibrium expressions it would cancel

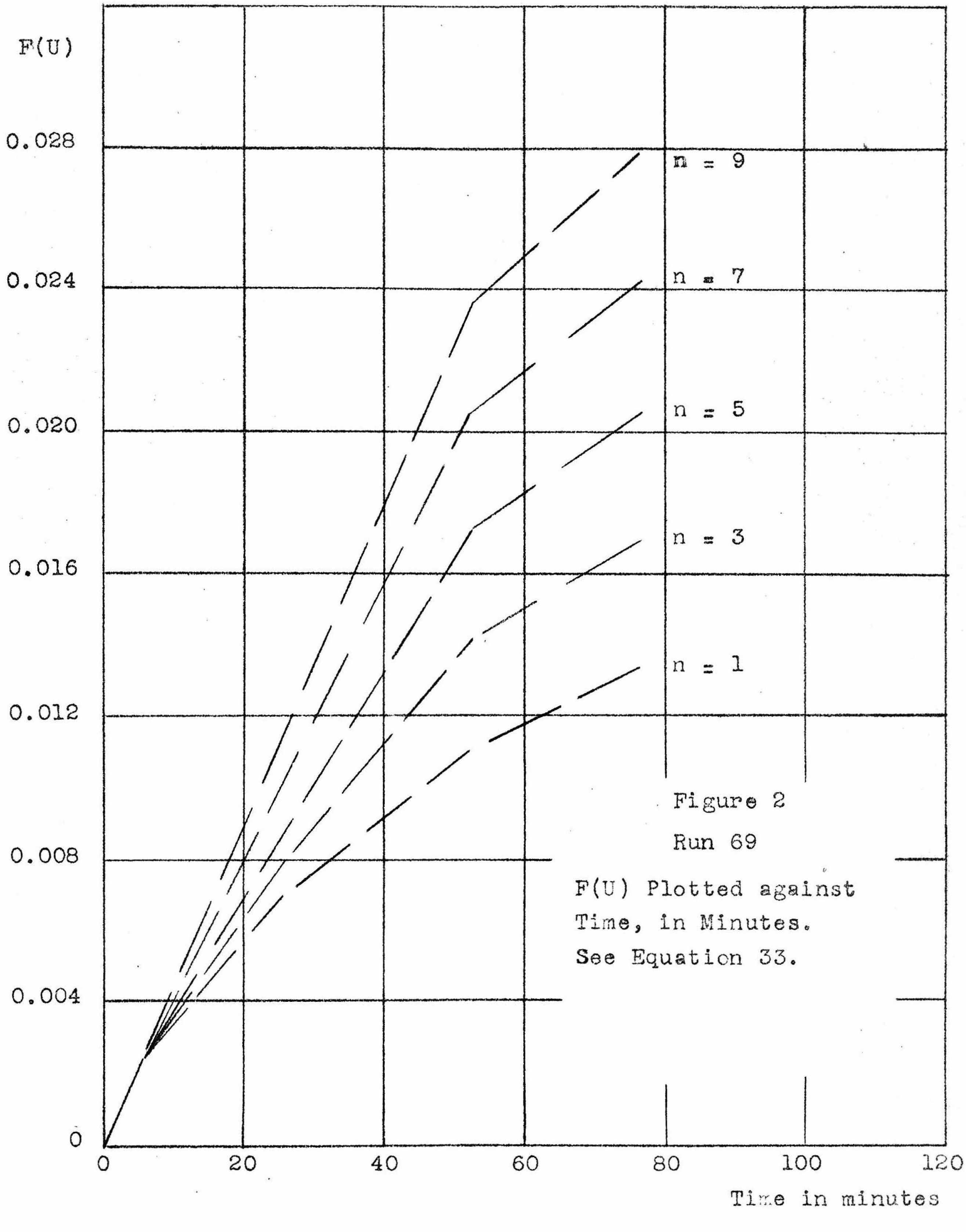


Figure 2

Run 69

F(U) Plotted against
Time, in Minutes.
See Equation 33.

out in Equation 28. In this case the later equations would still be correct but data on this point were not available. Allied to the question of the part played by the acid in forming the complexes was the question of how much free acid remained in solution. It seemed conceivable that this free acid played a role in the addition reaction. Since the hypothesis proposed in Equation 30 was not established by runs 65-72, an altogether different mechanism, depending on the free acid in solution, remained an active possibility. Some intimate method of determing the "location" of the available acid was therefore, needed and it was for this reason that the acidimetric work, discussed in Part V, was undertaken.

5. Studies relating to the yellow color appearing in solutions of hexyne, mercuric acetate, and perchloric acid.

Acetic acid solutions of hexyne, mercuric acetate, and perchloric acid were nearly always observed to be colored. Investigation of this color were made first because it was recognized that the color might be an intermediate - perhaps a mercuric carbonium complex - in the production of hexenyl acetate. This possibility seems to have been eliminated. Interest in the yellow material remains, however, both because it is an important by-product of the reaction being studied and because the material is of interest in its own right. Neither the isolation nor the concentration of the product have been accomplished and its structure is unknown. Information has been obtained, however, on the mechanism of its formation and its rate of appearance and disappearance.

Nine hours after the reaction had started, the solution of Run 30, Table 10, was put in a 1 cm. corex cell and the absorption curve of the yellow by-product determined by means of a Beckman spectrophotometer. Absorption peaks at 360 mμ (D = 1.52) and at 352 mμ (D = 1.512) were observed. The peak at 352 mμ was used for following runs C1 to C6.

In a set of preliminary runs it was found that the color density increased to a maximum in about 25 minutes and then decreased at a quite constant rate. Runs C1 to C6 were made to get preliminary data on this rate of disappearance and readings were not made on most of the solutions until about 25 minutes after mixing, when the peak of color density had just been passed. The data are presented principally as a guide to further work if this research is continued. In addition to the runs shown in Table 13, three determinations were made which are not shown in which the maximum density was very much less than expected from comparable runs. It is believed that water may have contaminated the solutions in these cases, and it was found that water acted rapidly to destroy the yellow color.

Table 13

Observations of Yellow By-product at 352 mμ in Anhydrous Acetic Acid.

Run No.	Hexyne $\underline{M} \times 10^3$	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Maximum Density	Density dimunution per min.	$\frac{E}{D}$	$\frac{D}{B \times C}$
	A	B	C	D	E	F	G
C1	100	0.75	3	1.35	0.0038	0.0028	0.60
C2	100	1	4	1.83	0.0067	0.0037	0.46
C3a	200	0.5	2	0.701	0.0027	0.0038	0.70
C4a	150	0.5	2	0.740	0.0025	0.0034	0.74
C3c	200	0.5	2	0.698	0.0030	0.0030	0.70
C5a	300	0.5	2	0.634	0.0021	0.0034	0.63
C6d	300	0.3	1.2	0.213	0.0006	0.0028	0.59

The runs in Table 13 were made in acetic acid of M.P. 16.6° prepared with acetic anhydride. Excess acetic anhydride was used in Runs C3c, C5a, and C6a. Since no temperature control was attempted, the runs which were made at the same time are shown grouped together.

Column F, Table 13, was an attempt to correlate the rates of disappearance of the color in different runs. Since it seemed reasonable that the rate of disappearance of the color would be proportional to the color, the rate (Column E) was divided by the maximum color density (Column D). The quotient, shown in Column F, is reasonably constant for the different runs, and the insertion of other figures from the table into this calculation does not improve the agreement. It may be, therefore, that the yellow compound breaks down spontaneously or reacts with the solvent without catalysis. In either case the difficulty of isolating the material would be predictable.

Column G is an attempt to use the data to explain the formation of the color. If the amount of color formed depended on the concentration of the mercuric acetate and the perchloric and but not of the hexyne, the ratio in Column G would be a constant for the different runs. The agreement is fairly good except for Run C2. That the maximum density for Run C2 is slightly low shows up in both Column F and Column G. The discrepancy may be due to a trace of water or it may be the result of the high rate of color disappearance in this run.

The high rate, operating during the 25 minutes the peak color was being built up, would, of course, lower the maximum value obtained.

The runs shown in Table 13 were all made with a considerable excess of perchloric acid over the mercuric acetate. A set of runs in which this condition did not obtain are shown in Table 14. These runs were made in acetic acid rectified by distillation, m.p. 16.6°. The observations were made at 410 mμ. It should be noted that Runs C9 and C10, also C11 and C14 are duplicates and that the reproducibility is fairly good. All runs were made with 0.0305 M hexyne.

At a constant concentration of mercuric acetate (Runs C7 to C12) the maximum optical density attained is proportional to the concentration of the perchloric acid, though the proportionality constant drifts when the mercuric acetate is in considerable excess over the acid (Column G). Surprisingly, however, the time needed to attain this maximum optical density is a constant independent of the acid concentration. Column H is a not too successful attempt to relate the rate of color dimunution to the maximum color. This rate seems to diminish with the acid concentration.

Four Runs (C13 to C16) were made in which the concentration of perchloric acid was constant and that of mercuric acetate varied. In all but the first of these runs the mercuric acetate was in excess. Strange results continued to be the rule, for it was found that with increasing concentration of mercuric

Table 14.

Observations of Yellow By-product at 410 mμ .

Run No.	Hexyne $\underline{M} \times 10^3$	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Maximum Density	Time at Max.D.,Min.	Density dimunution per Min.	$\frac{D}{C}$	$\frac{F}{D}$
	A	B	C	D	E	F	G	H
C7	30.5	2.07	2.58	0.562	23	.00100	0.22	0.0018
C8	30.5	2.07	2.24	0.485	22	.00080	0.22	0.0016
C9	30.5	2.07	1.72	0.370	21	.00055	0.22	0.0015
C10	30.5	2.07	1.72	0.362	26	.00060	0.21	0.0017
C11	30.5	2.07	1.21	0.239	25-35	.00029	0.20	0.0012
C12	30.5	2.07	0.86	0.150	27	.00015	0.17	0.0010
C13	30.5	0.69	1.21	0.283	45			
C14	30.5	2.07	1.21	0.241	25-35			
C15	30.5	4.14	1.21	0.146	23			
C16	30.5	6.90	1.21	0.076	20			

Table 15

Observations of Yellow By-product in Acetic Acid M.P. 16.6°

Run No.	Mμ.	Hexyne $\underline{M} \times 10^3$	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Color		Maximum Density	Color Time
					2 min.	2½ min.		
C17	375	0.42	0.80	0.40	0.056	0.059		
C18	375	0.53	0.50	0.50	0.074	0.081		
C19	375	0.64	0.18	0.60	0.056	0.061		
C20	375	0.21	0.67	0.47	0.032	0.035	0.072	
C21	375	0.33	0.31	0.75	0.066	0.072		
C130	360	5.8	1.50	1.50	0.356	0.390	0.681	40
C131	360	5.8	1.00	1.00	0.220	0.239	0.466	43
C132	360	11.6	1.00	1.00	0.221	0.238	0.470	35
C133	360	5.8	0.50	0.50	(0.100)	0.105	0.215	50
C135	360	3.5	1.00	1.00	0.247	0.270	0.461	35
C136	360	3.5	0.50	0.50	0.106	0.112	0.210	30
C137	360	5.8	0.50	1.50	0.226	0.242	0.519	44
C138	360	5.8	1.50	0.50	0.00	0.00		

acetate, the maximum absorption peak was reached more quickly, but that the maximum optical density obtained was lower.

Table 15 shows two sets of later data. Runs C17 to C21 were made in connection with indicator work to be described later. The conditions were deliberately random and no conclusions seem to be derivable from them. They are included here to make this section complete. Runs C130 to C138 were made in connection with kinetic work to be discussed later. These runs show a very neat pattern. In six runs (C130 to C136) the concentration of mercuric acetate equaled the concentration of perchloric acid. The amount of color developed at both 2 1/2 minutes and at maximum optical density is proportional to this single concentration. The relation is shown in Table 16. The dependence of the amount of color on the amount of catalyst and its independence of the excess of hexyne present suggests strongly that a complex of hexyne and the two catalysts is the intermediate in the formation of the by-product. Runs C137 and C138 diverge from this pattern. Run C137, with excess perchloric acid, gave more color than would be expected if the concentration of a 1 to 1 to 1 complex were the only concentration of significance. Run C138, with three times as much mercuric acetate as perchloric acid, had no color at all.

A complete investigation of the absorption spectrum of the yellow color was made with the solution from Run 130. Because the color density was not constant, a special technique was employed. Two and a half hours after the solution was mixed,

Table 16

Mechanism of Formation of Yellow By-product

Run No.	Concentration of Catalysts $Hg(OAc)_2$ = $HClO_4$	Maximum Color at 360 mμ.	Ratio of Color to Catalyst Concentration
C130	0.0015	0.681	450
C131	0.0010	0.466	470
C132	0.0010	0.470	470
C133	0.0005	0.215	430
C135	0.0010	0.461	460
C136	0.0005	0.210	420

a rapid set of readings were made at 10 mμ intervals from 400 mμ to 320 mμ . These readings were considered a base line. The optical density of separate portions of the spectrum were then determined at 1 mμ intervals. Such detailed readings always included one of the base line readings. The determinations could then be related back to the standard time, 2 1/2 hours, by simple proportion. This procedure assumes that the optical densities at different wave lengths maintain a constant ratio with each other as the color fades. To justify this assumption a new set of readings of the optical density of the solution was taken the next day. The readings and their ratios are shown in Table 17. It is evident that at wave lengths longer than 350 mμ the assumption is justified. The color behaves as though derived from a single molecular species.

The curve at 2 1/2 hours is shown in Figure 2. From the data the ratio of the optical density at 360 mμ to that at 352 mμ , 375 mμ , and 410 mμ is respectively 1.013, 1.200, and 2.663. Tables 13, 14, and 15 may thus be related.

Table 17.

The change of Optical Density of the Yellow By-product with Time at several Wave Lengths

Wave Length	Optical Density		
mμ.	2 1/2 hrs.	28 hrs.	Ratio
440	(0.044)	0.028	1.57
430	(0.077)	0.050	1.54
420	(0.137)	0.088	1.56
410	(0.210)	0.133	1.58
400	0.285	0.184	1.55
390	0.371	0.238	1.56
380	0.449	0.288	1.56
370	0.520	0.333	1.56
360	0.560	0.359	1.56
350	0.525	0.342	1.53
340	0.465	0.314	1.47
330	0.465	0.331	1.40
320	0.604		

To further demonstrate that only one molecular species was involved, three different peaks (at 345 mμ, 360 mμ, and 387 mμ) were followed during the appearance and disappearance of the color. Run C132 was repeated and the optical densities at these three points followed over a three hour period. The results are shown in Table 18. Because the ratio between different parts of the curve remained constant as the color developed and faded, it was concluded that only one species was contributing the color to the solutions.

The effect of water and acetic anhydride on the development of the color were studied in Runs 141 and 142. These runs resembled Run C131, Table 15, except that Run 141 was 0.277 M in water and Run 142 was 0.265 M in acetic anhydride. No color readings were made during the first hour or these runs, since this time was taken up with bromate titrations.

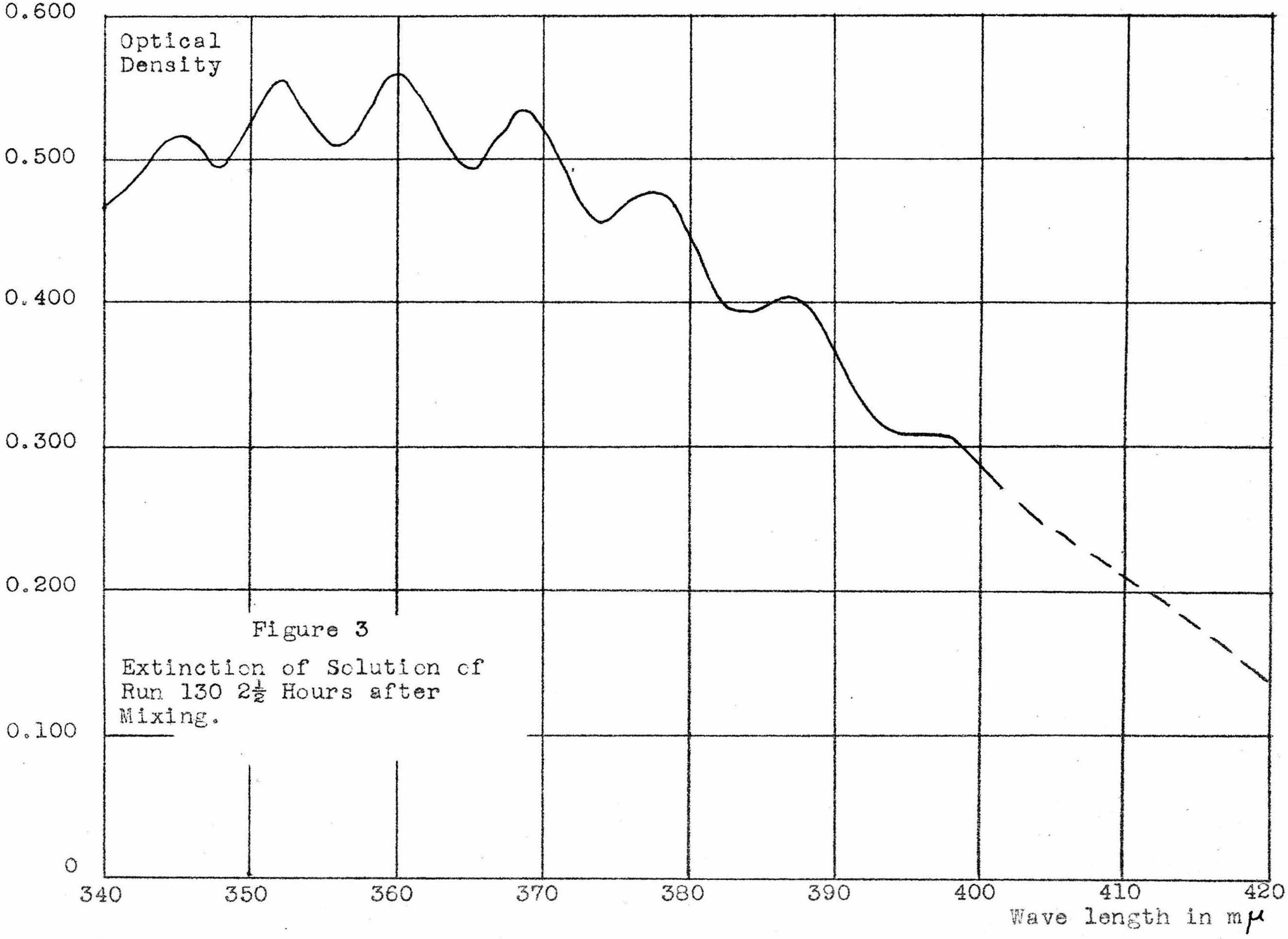


Figure 3

Extinction of Solution of Run 130 2½ Hours after Mixing.

Table 18.

The Ratio of Optical Densities of Three Absorption Peaks of the Yellow By-product during the Growth and Disappearance of the Color in Run C132.

Time Min.	Optical Densities 360 mμ	345 mμ	387 mμ	Ratio of Optical Densities
5	0.328	0.310	0.240	1.37:1.28:1
10	0.400	0.372	0.291	1.37:1.27:1
40	0.473	0.440	0.346	1.37:1.28:1
189	0.433	0.403	0.316	1.37:1.29:1

After 93 minutes, however, Run 141 had an optical density of only 0.165 at 360 mμ . The density rose slowly to 0.197 at the end of four hours. (Run C131 reached a maximum optical density of 0.466 in 43 minutes.) Run 142, on the other hand, showed virtually no deviation from C131. Readings of the optical density at 360 mμ after 115 and 130 minutes were 0.442 and 0.442. The absorption curves of solutions of each of these runs showed the characteristic 1.37:1.28:1 ratio shown in Table 18. The rate of change of unsaturation in these runs differed very little from that observed in Run 131.

In Table 14 there was noted a tendency for the rate of dimunution of color to be less when the acid concentration was low. As part of the general attempt to isolate the yellow product, some potassium acetate was added to the solution of Run C130 to see if, in the absence of acid, the color would be stable. Two and a half hours after the start of the reaction and an hour and a quarter after the color peak of 0.681 had been reached (see Table 15), enough potassium acetate, previously dried at 110°, was added to some of the solution to give a 0.1 M solution of the salt. The rate of color diminution was then determined. The data are shown in Table 19. It is evident that, despite the data of Table 14, potassium acetate increased

Table 19.

The Effect of Potassium Acetate on the Rate of Disappearance of the By-product. Run C130.

Time	Optical Density of Solution			Optical Density of KOAc Solution		
Min.	360 mμ	345 mμ	387m	360 mμ	345 mμ	387 mμ
40	0.681					
70	0.664					
145				KOAc added		
160	0.620	0.580	0.451	0.598	0.556	0.431
177	0.611			0.555		
182	0.609	0.570	0.442	0.541	0.509	0.394

the rate of disappearance of the yellow material. The curves of optical density against time have a round top, and it is possible that the rates of diminution shown in Table 14 represent merely the portion of the curve between the peak and the portion of linear decline. Alternatively, it is possible that the potassium acetate, which deliquesces rapidly, was wet. Water destroys the yellow color rapidly.

In an attempt to isolate the yellow factor 15 ml. of an acetic acid solution 0.44 M in hexyne, 0.0024 M in perchloric acid and 0.00065 M in mercuric acetate was prepared. After 20 minutes ligroin (B.P. 30°-60°) and aqueous sodium hydroxide were added. Most of the color was lost when the alkali was added, but the ligroin layer was separated and found to have a very faint yellow color. As shown in Table 20, enough of the absorption curve was taken to show that it was different from that shown in Figure 2. Even if the product were unchanged, of course, the change in solvent might have such an effect.

Table 20.

Absorption Spectrum of Yellow Color Extracted by Ligroin

Wave Length (mμ)	Optical Density
410	0.066
400	0.096
380	0.150
370	0.160
360	0.146

Twenty-two ml. of acetic acid solution were prepared 0.040 M in hexyne, 0.0091 M in mercuric acetate, and 0.023 M in perchloric acid. After 20 minutes carbon tetrachloride and water were added. Color was present in both phases. The phases were separated and the aqueous phase again extracted with carbon tetrachloride. Again the color was divided between the phases. After separation more carbon tetrachloride and sodium hydroxide were added to the aqueous phase. The color disappeared. The first two carbon tetrachloride layers were combined and split. Part was shaken with aqueous sodium bicarbonate and part with water. In each case the color disappeared.

A solution 0.096 M in hexyne, 0.025 M in mercuric acetate, and 0.050 M in perchloric acid was prepared. After 20 minutes

20 ml. of n-heptane and 30 g. of solid sodium bicarbonate were added. The bicarbonate dissolved quite slowly and the solution was warmed slightly. The mixture finally turned solid. Separation of the phases was attempted by centrifuging, which was not successful, and by filtration with suction, which yielded about 3 ml. of slightly yellow solution. The absorption curve of this solution was featureless, dropping from an optical density of 0.76 at 336 mμ to 0.057 at 386 mμ and tapering off to 0.037 at 430 mμ.

A similar solution (0.096 M in hexyne, etc.) was prepared and a few tenths of a gram of potassium acetate added after 20 minutes. The solution was then passed through a chromatographic column packed with activated alumina. No color appeared on the column, and the effluent solution was also colorless.

Only a limited number of formulae for the yellow material seem to be available even for conjecture. The yellow material is probably not an intermediate in the formation of hexenyl acetate, for the color reaches a maximum intensity in 20-30 minutes, after the rate of change of unsaturation in the solution has tapered off markedly. The color is probably not due to a polymer of hexyne. The rate of color formation and the amount of color formed are independent of the excess of hexyne present. Moreover the amount of color formed is nearly proportional to the first power, and certainly not proportional to a higher power, of a suggested 1:1:1 complex of hexyne, mercuric acetate, and perchloric acid. Moreover, the extreme lability of the color to alkali and even to water suggest that a hydrocarbon is not the colored species. None of the known products of the reaction is responsible in an simple way for the color. Hexenyl acetate, diethyl ketone, acetic anhydride, and even propylene diacetate do not give a color with the catalysts in acetic acid.

The amount of color formed is proportional to the hypothetical 1:1:1 complex as indicated in Table 16. This fact suggests strongly that a primary reaction product is either itself the colored species or is converted to the yellow product by a fast reaction. One species which seems to fit this specification is hexenyl perchlorate, $Et-CH=C(ClO_4)-Et$. This compound might be formed by the addition, to the 1:1:1 complex, of excess perchloric acid or of the acid in equilibrium with the complex. The formation of this compound would explain many of the observations, such as the tapering off phenomenon, the fact that excess acid reduces the tapering off, the dependence of the amount of color on the excess of perchloric acid, the fact that excess mercuric acetate inhibits the color (though why the color should drop to zero in C138 is not clear), and the difficulty in isolating the yellow product. However, Run 138, with no color, also showed the tapering off phenomenon, and it is not evident why hexenyl perchlorate should be colored. Organic perchlorates are not unknown[29] but no vinyl perchlorates seem to have been reported in the literature.

B. The Reaction of 3-Acetoxyhexene-3 with Acetic Acid Catalyzed by Mercuric Acetate and Boron Trifluoride.

The hexenyl acetate synthesized with mercuric acetate and boron trifluoride catalysts was used in a set of kinetic determinations with these same catalysts. The reaction (Equation 17) was followed by measuring the decrease in the amount of unsaturation. As with the hexyne runs with boron trifluoride, trouble was encountered with precipitates and erratic results. It is evident (Table 21) that Runs 52 and 54 proceeded many times more rapidly than the other runs, a fact that is difficult to interpret on the basis of the small increase in mercuric acetate. If the rate is indeed that sensitive to the concentration of mercuric acetate, then it becomes impossible to explain why Runs 52 and 54 give identical results. The data for these two runs fit very closely the first order Equation 35, where t is in minutes and V is hexenyl-acetate. For the same reasons that were discussed in connection

$$\frac{dV}{dt} = 0.0073V \qquad (35)$$

with hexyne, namely, the probable sensitivity of the activity of the boron trifluoride to the ether as well as to possible impurities, this phase of the investigation was abandoned.

Table 21.

The Rate of Reaction of Hexenyl Acetate with Acetic Acid at 25° in the Presence of Excess Acetic Anhydride. Catalysis by Mercuric Acetate and Boron Trifluoride.

Run No.	$Hg(OAc)_2$ M x 10^3	$BF_3 \cdot Et_2O$ M x 10^3	Time Min.	Hexenyl Acetate M x 10^3
48	1	20	7	75.8
			29	75.3
			58	75.5
			156	75.4
			4800	52.0
49	1	20	10	31.4
			200	30.7
50	1	20	7	17.7
			36	17.6
			83	17.5
			148	17.4
			181	17.3
51	2	20	8	18.3
			29	18.4
			94	18.1
			144	17.9
			202	17.8
			368	17.3
52	3	20	9	17.4
			32	14.3
			48	12.8
			70	11.0
			90	9.5
54	3.5	20	9	17.2
			24	15.4
			41	13.6
			58	12.0
			81 (cloudy)	10.5
55	none	20	6	17.5
			22	17.6
			40	17.5
			78	17.5
56	none	20	9	17.7
			31	17.6
			120	17.7
			1500	16.9
			2900	16.8

V. The Measurement of Basicity in Glacial Acetic Acid.

A. Preliminary Investigations with Sulfuric Acid.

The study of the rate of addition of acetic acid to hexyne, discussed in Section IV, led directly to the acidimetric measurements to be described below. Knowledge of the amount of free acid in the kinetic solutions was needed both because of the role this acid might itself play in the rate of addition, and because, by difference from the known amount of acid added, the amount of acid entering into the various complexes might be determined. Because perchloric acid gave a yellow by-product in the kinetic studies and because runs catalyzed with perchloric acid tapered off sharply for unknown reasons, it was planned that subsequent kinetic studies would be made with sulfuric acid. Acidimetric studies were, therefore, undertaken with sulfuric acid.

It was decided to use indicators for this investigation. Hammett[30] and various collaborators and Hall and Spengeman[31] had investigated the use of indicators for acidimetric work in formic and acetic acids. It had been found that substituted nitroanilines (a list is given in Physical Organic Chemistry[32] p. 266) were suitable indicators. They enter a rapid, reversible reaction with the solvated proton, forming anilinium ions, which are colorless.

Materials and apparatus. The indicator chosen for this initial work was 2-nitro-4-chloroaniline. The acetic acid and sulfuric acid solutions used had excess acetic anhydride in them.

After a few days spent in collecting erratic data, the conclusion was reached that the acetic anhydride was reacting with the amine. A fresh batch of acetic acid was prepared in which the acetic anhydride used was less than the amount calculated to react with the water present. From some of this solvent a sulfuric acid solution was prepared with 96% sulfuric acid. Eastman chloronitroaniline was dissolved in boiling water, filtered hot, and two crops of crystals collected as the solution cooled. The two crops melted indentically and very sharply at 116.0°. Some of the early readings of indicator density (Tables 22 and 23) were made in a Klett Colorimeter, which does not permit selection of wave lengths and the results of which do not seem to be highly reproducible. A change was soon made to a Beckman Spectrophotometer.

One tenth of a gram of the amine was dissolved in 25 ml. of acetic acid. This solution was labeled A. One tenth ml.of A was added to 50 ml. of acetic acid (solution A1) and the absorption spectrum investigated in the Beckman Spectrophotometer. A maximum was found at about 410 mμ at which point the optical density of this solution was 0.201. The top of the maximum was quite flat - readings between 406 and 412 mμ being indistinguishable - a fact which makes the readings highly reproducible and well suited for indicator work. The solutions were also quite stable, A1 showing no change at all in an hour.

Investigation of weak bases. Hexyne was the first material to be investigated for its effect on the acidity of the solutions.

A 0.10 M solution of hexyne was prepared and mixed with various amounts of 0.10 M sulfuric acid as shown in Table 22. Indicator Cl was prepared from 2 ml. of A and 50 ml. of anhydrous acetic acid. If the hexyne reacted with any appreciable portion of the acid, the optical density of the solution would depend on the concentration of the hexyne. It is evident that no such effect is operating in these solutions.

Hexenyl acetate (from the boron trifluoride synthesis) and diethyl ketone were also tested for their effect on the acid-indicator system. The results of a test with hexenyl acetate are shown in Table 23. Because the optical density of the solution changed so rapidly that a satisfactory initial reading could not be obtained, the solutions were kept overnight and the readings obtained after this period of standing are also shown. It seemed necessary to assume that a reaction was taking place, and a reasonable assumption was that, in the presence of sulfuric acid, acetic acid was adding to hexenyl acetate to give hexanone and acetic anhydride as shown in Equation 17. One or both of these products could then react with the indicator, the acetic anhydride to form an anilide, the ketone to form a Schiff's base. By eliminating some of the indicator from the aniline-anilinium ion equilibrium, either of these reactions would raise the optical density of the solution. If this interpretation of the change of optical density is correct, it demonstrates that the hexanone diacetate is indeed unstable in this system. The test with diethyl ketone is shown in Table 24 and it is evident that here too a reaction took place.

Table 22.

The Effect of Hexyne on the Acidity of Solutions Containing 4-Chloro-2-nitroaniline.

Hexyne 0.10 M	H_2SO_4 0.10 M	HOAc ml.	Indicator ml. A	Cl	Optical Density (Klett)
15	5	--	0.2		0.253
10	5	5	0.2		0.265
5	5	10	0.2		0.264
--	5	15	0.2		0.260
--	5	10		5	0.248
10	5	--		5	0.251

Table 23.

The Effect of Hexenyl Acetate on the Acid-Indicator System. Volumes are in ml.

$C_6H_{11}OAc$ 0.10 M	H_2SO_4 0.10 M	HOAc	Cl	Optical Density (Klett) 5 min.	24 hrs.
--	5	10	5	0.242,4	0.252
10	5	--	5	0.254,9, 0.261	0.325

Table 24.

The Effect of Diethyl Ketone on the Acid-Indicator System. Volumes are in ml.

Et_2CO 0.50 M	HOAc	H_2SO_4 0.10	Cl	Optical Density, 410 mμ 5 min.	5 hrs.	24 hrs.
5	0	5	3	0.504	0.540	0.588
70	5	5	3	0.407	--	--

It is possible that a Schiff's base was formed by a reaction between diethyl ketone and chloronitroaniline.

B. Extended Investigations with Perchloric Acid.

1. Introduction and theory of calculation.

It was decided to make an extended investigation of the indicator method of determining the strength of weak, colorless bases in glacial acetic acid. The method had been introduced by Hammett and Deyrup[33] who made a single measurement on propionitrile and a single measurement on water. They used benzene sulfonic acid as their strong acid and formic acid as the solvent. No further use had been made of the method, which seemed to be suitable for measuring the basic strength of bases too weak or too insoluble to be measured readily in water.

Hammett and Deyrup found that sulfuric acid was a completely ionized monobasic acid in formic acid and that benzene sulfonic acid was nearly as strong. In acetic acid, however, Hall and Spengeman found that the mean activity coefficient of sulfuric acid is strongly dependent on the concentration. Perchloric acid is known to be stronger than sulfuric acid, and it was used in the present work to minimize the effect of concentration on acidity.

A solution consisting of solvent and an acid solute has a certain tendency to give a proton to a neutral base in solution. This tendency may be called the acidity. The ability of a neutral base to take a proton from the solution is measured by the ratio $(BH^+)/(B)$, and this ability is proportional both to the acidity of the solution and the strength of the base, K_b. The symbols B and BH^+ refer to the neutral base and its conjugate acid. Parentheses, (), signify concentrations, and brackets, [ ], will be used for activities. Basic strength, K_b, is defined by Equation 36.

$$K_b = \frac{1}{K_a} = \frac{[BH^+]}{[B]\ [H^+]} \qquad (36)$$

If the proportionality between the ratio $(BH^+)/(B)$ on the one hand and the basic strength of the base and the acidity of the solution on the other is set equal to unity, we may write Equation 37.

$$\frac{(BH^+)}{(B)} = h\ K_b \qquad (37)$$

The symbol h is a measure of the acidity of the solution. Taking the logarithms of Equation 37, and defining $Ho = -\log h$, we get Equation 38.

$$Ho = \log \frac{(B)}{(BH^+)} + pK_a \qquad (38)$$

Here Ho is Hammett's acidity function[32]. There are both theoretical and experimental reasons for believing that the acidic tendency of the solution may be represented fairly accurately by Equations 37 and 38. When a base is also an indicator, we will write I and IH^+ for B and BH^+. If an indicator and another base are present in the same solution, the acidity will, of course, be the same for each base. Eliminating Ho from Equation 38 we may write Equation 39 for such a solution.

$$\log \frac{(I)}{(IH^+)} + pK_{aI} = \log \frac{(B)}{(BH^+)} + pK_{aB} \tag{39}$$

It is necessary to distinguish between K_b and K_a, the thermodynamic, or activity, constants of Equation 36, and the ionization, or dissociation, constants defined in Equations 40a, b. (The symbol s is used for "solvent".)

$$K^s_{aB} = \frac{1}{K^s_{bB}} = \frac{(H^+)(B)}{(BH^+)} \tag{40a}$$

$$K^s_{aI} = \frac{1}{K^s_{bI}} = \frac{(H^+)(I)}{(IH^+)} \tag{40b}$$

If Equation 38 is written for the indicator, and if log (H^+) is added to each side of the equation, we may combine the resulting equation with Equation 40b to get Equation 41.

$$pK_{aI} = pK^s_{aI} + Ho + \log (H^+) \tag{41}$$

Since pK_{aI} is constant and pK^s_{aI} is also constant, subject, perhaps, to small concentration effects, Ho + log (H^+) will be a constant. If (H^+) is calculated from the total perchloric acid present, corrections being made for any IH^+ or BH^+ formed but no correction taken for molecular $HClO_4$, then if Ho + log (H^+) remains constant over a range of concentrations, the inference may be drawn that the perchloric acid is fully ionized. Table 25 shows for four determinations the constancy found for Ho + log (H^+) calculated in this way. These runs were deliberately chosen to represent extreme conditions, for -3.77 and -3.95 are the smallest and largest values determined for Ho + log (H^+) and -3.30 and -1.03 are the lowest and highest values of log (H^+) found in any runs during this study in which no base other than the indicator was present. In the determinations with urea very low concentrations of acid were employed. The lowest value of log (H^+) was -4.12 and in this solution Ho + log (H^+) was -3.87. Similarly, in some runs with acetonitrile some very high acid concentrations were employed. The highest value of log (H^+) was -0.85 and the corresponding value of Ho + log (H^+) was -3.82. Thus the sum Ho + log (H^+) was found to be constant, with a maximum and random variation of 6%, over a four thousand-fold range of concentration of perchloric acid. The calculations were made on the assumption that there is no interaction between the solvated proton and perchlorate ion, and this assumption was thus found to be justified.

Even the slight variation found in the value of the sum (Equation 42) may be readily explained and corrected.

$$Ho + \log (H^+) = -3.88 \qquad (42)$$

It was shown in Table 25 that the ionization constants of the indicators, pK^s_{aI}, show some variation. For any one base, of course, pK^s_{aI} should be constant; and the explanation offered for the variation is that other bases are present. In the case of the 4-chloro-2-nitroaniline, the other base is probably an oxidation product, since the amine used in 541a had been exposed to air for some time and was noticeably darker than the product used for 561a. In the case of the 4,6-dichloro-2-nitroaniline the other base was water. The more concentrated perchloric acid used in 561b had been made up with undistilled acetic anhydride and the test solution had an unknown but rather large amount of water present. If the ratios of the bases present are not varied too greatly, the systems are still acceptable for acidimetric determinations, since each base responds separately and in a quantitative manner to the acid present. Because the contaminants do not have the same basic strength as the indicators, however, the apparent basicity of the indicator solution, measured as pK^s_{aI}, will be different from the value found in an uncontaminated solution. Corresponding to the change in pK^s_{aI} a change should be made in the value of pK_{aI}, or else Equation 41 and, therefore, Equation 38 will no longer be valid. Although no such correction could be made in the original calculations, it was noted that $Ho + \log (H^+)$ was reasonably constant as was seen in Table 25.

Table 25.

The Constancy of Ho + log (H^+) in Indicator Measurements.

Run	Indicator	pK_{aI}	pK^s_{aI}	Ho	log (H^+)	Ho + log (H^+)
541a	Chloronitroaniline	-0.91	2.88	-0.48	-3.29	-3.77
568a	Chloronitroaniline	-0.91	3.00	-0.61	-3.30	-3.91
561b	Dichloronitroaniline	-3.67	0.15	-2.80	-1.03	-3.83
561d	Dichloronitroaniline	-3.67	0.28	-2.92	-1.03	-3.95

A correction can be applied to the value of pK_{aI} for the different indicators, however, by combining Equation 42 and 41 to give Equation 43.

$$pK_{aI} = pK^{s}_{aI} - 3.88 \tag{43}$$

New values of pK_{aI} for each indicator solution can now be calculated from the observed values of pK^{s}_{aI} as will be done in Table 26.

Rather than determining the values of pK_{aI} from Equation 43 and substituting the result in Equation 39, these equations may be combined to give Equation 44. It is from Equation 44 that the strengths of weak bases in acetic acid may most readily be calculated.

$$pK_{aB} = pK^{s}_{aB} - 3.88 \tag{44}$$

2. Detailed method of calculation. The limitations of the method.

Stock solutions of the indicators were prepared in acetic acid in concentrations of about 0.0005 M. (The acetic acid used here and in all subsequent work was purified by distillation and had a melting point of 16.6°). The absorption curve of one solution of each indicator was taken in order to find an absorption peak for the compound in this solvent. Readings of the test solutions were usually made at the appropriate peak in order to permit using minimal amounts of the indicator.

For each batch of indicator solution the optical density was specifically determined by reading known dilutions of the solution at the absorbtion peak (or, occassionally, at some other specified wave length). Multiplication by the appropriate dilution factor gave the calculated optical density of the stock solution.

Dilutions were so chosen both for these neutral solutions and for test solutions containing perchloric acid so that the observed optical densities were usually between 0.200 and 0.400. Different dilutions of the same stock indicator solution gave the same calculated optical density. (When the indicator was a strong enough base to react appreciably with the solvent, a dependence of the calculated optical density on the concentration was observed. For these indicators, the optical densities of the stock solutions were calculated from dilutions containing aniline or potassium acetate. In such solutions, different dilutions of the same stock indicator solution gave the same calculated optical density.) In this way Beer's law was found to apply in the 0.200 to 0.400 range in which observations were made.

The indicator constant, K^{s}_{aI}, was determined by mixing known amounts of indicator solution, perchloric acid solution, and (usually) extra acetic acid. The optical density of this test solution was then determined and multiplied by the dilution factor of the indicator solution in this particular test solution. That is, if 5 ml. of indicator solution were made up to a total of 28 ml. of acid-indicator mixture, the optical density observed would be multiplied by 28/5. The resulting value could then be compared with the calculated optical density of the stock indicator solution. The difference between the figures would be ascribed to the production of the colorless species, IH^+. The optical density of one stock solution was 2.742 and that of a test solution containing perchloric acid was 2.344. The ratio $(IH^+)/(I)$ was, therefore, equal to (2.742-2.344)/(2.344). The concentration of IH^+ in the solution was calculated from the known concentration of the stock indicator solution, the dilution factor, and the ratio of the loss of optical density to the optical density of the indicator solution. In the above case, the concentration of the stock indicator solution was 0.000493 M. The concentration of IH^+ in the test solution was, accordingly, (0.000493)(5/28)(2.742-2.344)/(2.742). The concentration of free acid in the solution was determined by calculating the stoichiometric quantity of perchloric acid present and subtracting from this figure the concentration of IH^+. The concentration of free acid was then divided into the ratio $(IH^+)/(I)$ to give the value of the indicator constant, K^s_{aI}.

No corrections were made for the effect of the ionic strengths of the solutions on the observed values of the ionization constants of either the indicators or the weak, colorless bases. Some justification is found for this simplification in the fact that the basic constant found for acetonitrile seemed to be independent of the concentration of perchloric acid over a 200-fold range of concentration of the acid (Table 29).

The basic constants of colorless bases, K_{aB}^{s}, were determined from data on the optical densitiesof solutions containing known amounts of indicator, perchloric acid, and colorless base. In such a solution the valuesof (IH^+) and of the ratio $(IH^+)/(I)$ were determined as in the solutions without colorless base. The value of the indicator constant now being known, the concentration of free acid could be calculated by multiplying the ratio $(IH^+)/(I)$ by K_{aI}^{s}. In these solutions the material balance for the perchloric acid is shown in Equation 45.

$$(H_t) = (H^+) + (IH^+) + (BH^+) \qquad (45)$$

The value of (H_t), the concentration of the total perchloric acid added, was known, and (IH^+) and (H^+) could be calculated as shown above. Equation 45 could therefore be solved for (BH^+). The material balance for the colorless base in this solution is shown in Equation 46. The value of (B_t), the

$$(B_t) = (BH^+) + (B) \qquad (46)$$

total concentration of the weak base in the solution was known, and (BH^+) was calculated from Equation 45. The value of (B) could accordingly be derived from Equation 46. With (B), (BH^+), and (H^+) all known, K_{aB}^{s} was readily calculated. Equation 44 could then be used to find pK_{aB}.

The successive subtractions needed for these calculations limit the accuracy of the method. If (H^+) and (H_t) are too nearly equal, the subtraction to give the value of (BH^+) will not give accurate results. Of course, more colorless base may be added to make (H^+) smaller; but if (B) is made too large, the nature of the solution will change, and it is not certain that the indicator will continue to react as in more dilute solutions. If the maximum value of (B) is taken as 0.5 M, and if it is decided that at least 10% of the acid (ignoring that present as IH^+) react to form BH^+, then the strength of the weakest base which can be measured is shown in Equation 47. The corresponding value of pK_a is -4.5. If the value of (BH^+) is too close to that of (B_t), the subtraction to give (B) will not be accurate. Of course, the amount of perchloric acid may be diminished to make (BH^+) lower, but if the value of (H^+) becomes too low the ionization of the solvent will no longer be suppressed and interaction of the bases with the solvent will become important. If the lowest value of (H^+) considered acceptable is 0.0001 M and if it is decided that at least 10% of the total base should remain unreacted, the strength of the strongest base which may be measured is shown in Equation 48. The corresponding value of pK_a is 1.1.

$$K^s_{bB} = \frac{(BH^+)}{(B)(H^+)} = \frac{(0.1H_t^+)}{(0.5)(0.9H_t^+)} = 0.22 \qquad (47)$$

$$K^{s}_{bB} = \frac{(BH^{+})}{(B)(H^{+})} = \frac{(0.9B_t)}{(01.B_t)(0.0001)} = 90,000 \qquad (48)$$

3. The Preparation of indicators and the properties of their solutions in acetic acid.

Eastman 4-chloro-2-nitroaniline was recrystallized from boiling water and stored in a desiccator over sodium hydroxide. It melted sharply at 116.0°. (All melting points were taken in an oil bath. The temperatures are uncorrected.) Indicator solution IA (see Table 26) was made up two months after the recrystallization and IB about five weeks later. A new recrystallization was made before preparing solution ICa. Solution ICa was found to be unstable, and new data, found after three weeks, are shown in Table 26 for solution ICb. A final recrystallization was made before preparing solution ID. In this case special precautions were taken to avoid exposing the crystals to air and this material was probably the purest obtained. It is evident that high purity is associated with a high value of pK_a (enhanced basicity).

To test the reversibility of the reaction of 4-chloro-2-nitroaniline with perchloric acid, two solutions of the indicator and acid were prepared. To one solution 5 ml. of 0.46 $\underline{M}$ aniline was added (the solution contained only 5 ml. of 0.005 $\underline{M}$ perchloric acid) and to the other 5 ml. of 0.04 $\underline{M}$ potassium acetate (this solution had 15 ml. of 0.005 $\underline{M}$ perchloric acid). The optical densities of these solutions were then determined. It was found that not only was the reaction reversible but the optical density of each test solution was 1% greater (after adjustment with the dilution factors) than the optical density of the stock solution. Evidently, at the concentrations employed, 1% of the indicator reacted with the solvent in the readings made to determine the optical density of the stock indicator solution. This effect was suppressed by the stronger bases in the two runs just discussed. The effect would also be suppressed in all the runs made with perchloric acid. Therefore, to make comparable the readings made in tests with perchloric acid and readings of neutral solutions, all readings made in neutral solutions were increased 1%. With indicators which were weaker bases than 4-chloro-2-nitroaniline, this correction was not considered necessary. With indicators which were stronger bases, all neutral readings were made in solutions containing aniline or potassium acetate.

To provide a base which could be used as an indicator in solutions of high acidity, the dichlorination of o-nitroaniline was carried out in concentrated aqueous hydrochloric acid.[34] Chlorine from a cylinder was passed through a one-liter solution containing 17 gm. of nitroaniline for about two hours. The yellow product was obtained by adding water. The 4,6-dichloro-2-nitroaniline was recrystallized from hot ligroin (b.p. 90-127°) to give a product with m.p. 100.7-101.0° (literature value: 101-102°). Solution IIA was used with two different batches of 0.467 M perchloric acid. The first (the data for which are shown as IIA-1) probably had a rather large amount of water in it since it was prepared from undistilled acetic anhydride.

The second batch of perchloric acid was made with distilled acetic anhydride, and the proportions of aqueous perchloric acid and acetic anhydride were calculated to give an anhydrous solution. The new data are shown for indicator IIA-2. After four and a half months, the amine was recrystallized from ligroin and solution IIB prepared. Although this solution was used with the anhydrous perchloric acid, the data resemble those for IIA-1. A new, anhydrous perchloric acid solution was prepared to check these results on indicator IIB, but the indicator data remained unchanged. The appropriate indicator constant was always used with the different solutions.

The methylation of 4-chloro-2-nitroaniline was accomplished with methyl sulfate. The chloronitroaniline was recrystallized from hot water. The dimethyl sulfate was freed from sulfuric acid by shaking with water in a small separatory funnel. Four and one half grams of the amine (0.026 moles) and 2.5 ml. of dimethyl sulfate (0.026 moles) were heated together in a test tube over a small flame until a single liquid phase was obtained. The test tube was then placed in a beaker of boiling water for forty-five minutes. An additional 0.4 ml. dimethyl sulfate was added and the heating continued for 15 minutes. Six ml. of 5 N sodium hydroxide were added and the product dissolved in hot ligroin (b.p. 90-107°). The material obtained on cooling the ligroin was recrystallized from hot water to give crystals which softened at 90° and melted at 106°. A further recrystallization from ligroin gave 4-chloro-2-nitro-N-methylaniline with

Table 26.

Properties of Solutions of Indicators in Acetic Acid.

Indicator No.	Indicator Name	Conc. M x 10^4	Absorp. Max. m	Molar Extinct. Coefficient at Absorp. Max.	pK_{aI} Lit.	K^s_{aI} x 10^3	pK_{aI} Eq. 43
1A	4-chloro-2-nitroaniline	5.81	410	4470	-0.91	1.22	-0.97
IB	" "	5.53		4700	"	1.33	-1.00
ICa	" "	5.52		4840	"	1.08	-0.91
ICb	" "	5.52		4620	"	1.08	-0.91
ID	" "	5.75		4930	"	0.97	-0.87
IIA-1	4,6-dichloro-2-nitroaniline	5.40	408	4540	-3.67	701	-3.73
IIA-2	" "				"	537	-3.61
IIB	" "	6.10		4460	"	725	-3.74
IIIA	4-chloro-2-nitro-N-methylaniline	4.93	437	5560		3.08	-1.37
IIIB	" "	5.00		5620		3.96	-1.48
IIIC	" "	4.27		5830		3.78	-1.46
IIID	" "	4.27		5780		3.85	-1.47
IV	2-chloro-4-nitro-N,N-dimethylaniline	4.88	370	4640	very small		
VA	2,6-dichloro-4-nitro-N,N-dimethylaniline	5.91				0.193	-0.17
VB	" "	6.78				0.172	-0.11
VC	" "	5.51				0.145	-0.04
VIA	2,4-dinitro-N,N-diethylaniline	3.18	375	15,700		0.0655	0.30
VIA-2	" "	1.27		15,700		0.0667	0.30
VIB	" "	2.96		16,700		0.0544	0.38
VIC	" "	2.78		15,400		0.0725	0.26

m.p. 106.0-106.5°. A melting point of 108° has been reported.[35] Analysis showed, calc'd. for $C_7H_7O_2NCl$: C, 45.05%; H, 3.78%; found: C, 45.04%; H, 4.08%. Several attempts to make the dimethylaniline by subsequent methylation of the monomethylaniline were unsuccessful.

The first indicator solution to be prepared from the chloronitromethylaniline was indicator IIIA. A redetermination of its optical density and K^{s}_{aI} after three weeks showed that no change had occurred in solution. Solution IIIB was prepared six weeks later and showed that the crystals had undergone a considerable loss of basic strength. Successive recrystallizations from ligroin and ethyl alcohol (solutions IIIC and IIID) gave solutions similar to solution IIIB rather than IIIA. The crystals from ethyl alcohol melted at 106.0-106.5°.

Because none of the indicators studied by Hammett or Hall were monomethylanilines, a test was made to show that the anilinium ion of this indicator was colorless and that its formation was reversible. Three solutions were prepared as shown in Table 27, and their optical densities read at 437 mμ. In addition the optical densities of two of the solutions were read at several wave lengths as shown in Table 28.

Table 27.

The Indicator Properties of 4-Chloro-2-nitro-N-methylaniline. Volumes are in ml.

Run No.	III D 0.000427 M	HOAc	$HClO_4$ 0.005 M	$HClO_4$ 0.525 M	Optical Density 437 mμ
616a	3	20	--	--	0.322,3
616b	3	15	5	--	0.253,4,2
616c	3	15	--	5	0.013

Table 28.

The Optical Densities of Solutions of Indicator IIID at Several Wave Lengths.

mμ	Run. No. 616a	Run No. 616b	Ratio
437	0.322	0.253	1.27
420	0.289	0.225	1.28
400	0.188	0.148	1.27
380	0.093	0.070	1.3
360	0.036	0.029	1.2
340	0.014	0.013	1.1

From Runs 616a and 616b, the value of K^{s}_{aI} was found to equal 0.00390. (This result was one of two averaged to give the 0.00385 in Table 26). Using the value $K^{s}_{aI} = 0.00390$, the optical density for Run 616c was calculated to be 0.011, a good check with the observed 0.013. A larger concentration of anilinium ion is present in 616c than in any normal observation with this indicator. If the color calculated for the free base corresponds this well to the color observed, the interference due to any color from the conjugate acid, IH^{+}, must be very small. Confirmatory evidence is offered by the data shown in Table 28. The ratio of optical densities of Runs 616a and 616b at different wave lengths should be a constant in the absence of interference from the conjugate acid. The ratio is indeed found to be constant down to 400 mμ and perhaps past 380 mμ.

One pellet (0.14 g.) of sodium hydroxide was added to the solution of Run 616c. The next day the optical density of the solution was found to be 0.326 at 437 mμ, demonstrating perfect reversibility of the acid-indicator equilibrium. In fact, as with chloronitroaniline, the color returned to an optical density 1% greater than anticipated. (It was expected to equal the density found for Run 616a). In the present case, it was decided that no correction need be applied to the readings of optical density of chloronitromethylaniline in pure acetic acid. The neutralized solution had stood overnight before the reading was made. Only one solution was available to supply data for such a correction, and a spread of 1% between duplicate solutions was common. Finally the chloronitromethylaniline was a weaker base than the primary amine and would not be expected to require such a correction.

The chloronitromethylaniline was used as an indicator without trouble in solutions containing aldehydes and ketones. (Chloronitroaniline was found unsuitable for use with carbonyl compounds.) Even the secondary amine, however, gave strange results in solutions containing hexyne and mercuric acetate, the optical densities dropping below values which could be explained by any known reaction. The synthesis of 4-chloro-2-nitro-N,N-dimethylaniline was, therefore, undertaken. The successful nitration of dimethylaniline was accomplished by Tingle and Blank[36], who secured crystals with m.p. 162-165° by the action of nitric acid on the tertiary amine. Acetic acid was used as the solvent and oxalic acid was also present during the synthesis. The authors, however, claim no special advantage nor do they give any reason for the presence of oxalic acid. They make reference to an older paper in which the nitration was accomplished in acetic acid with no oxalic acid present.[37]

In the attempted syntheses without oxalic acid, four different, colored products seemed to be formed - a yellow one (desired), a green one (nitroso?), a red one, and, sometimes, a brown one. Dimethylaniline was dissolved in acetic acid at various concentrations. Nitric acid was added slowly and with swirling. No advantage was found in using fuming nitric acid, which often led to decomposition. At least the stoichiometric quantity of nitric acid had to be used or no product was obtained. After standing overnight, water was added and the crystals obtained by filtration. Even in the most successful runs (15 ml. of aniline and 8 ml. of concentrated nitric acid in 400 ml. of acetic acid, for example) the product was quite green. The material was recrystallized from strong hydrochloric acid by dilution (always followed by washing with aqueous ammonia) and then from water or ethyl alcohol. The green color persisted through all recrystallizations, though a melting point as high as 163-165° was obtained for one product. It was found that if the crystals were taken up in warm pyridine, the addition of 30% hydrogen peroxide discharged much of the green color. Attempted syntheses in the presence of sulfamic acid gave no product even after standin a week.

Tingle and Blanck's method was found to be much more successful. To 100 ml. of acetic acid were added 36 gm.

anhydrous oxalic acid (which did not all dissolve), 13 ml. dimethylaniline, and 7 ml. of nitric acid. Frothing and red color were noted in the solution when only half the nitric acid had been added, but best results were obtained if the rest was added anyway. The best run was made in the presence of 1/2 gm. of urea and 5 ml. of acetic anhydride. The reaction was quenched by adding water after about one minute and the product worked up in the usual way. The purest material was obtained from an unsuccessful attempt at chlorination in a solution of acetic acid and concentrated hydrochloric acid. Dropping concentrated potassium permaganate on concentrated hydrochloric acid did not generate enough chlorine to effect a chlorination, but beautiful yellow needles of p-nitrodimethylaniline were recovered, m.p. 163-165°.

The chlorination of p-nitrodimethylaniline[38] was accomplished by passing chlorine from a cylinder through a solution of 4 g. of the amine in 8 ml. of acetic acid and 16 ml. of concentrated hydrochloric acid. After 2 gm. (85%) of chlorine had dissolved, the chlorine was turned off and stirring continued for 15 minutes. The product was obtained by adding ice, sodium bicarbonate, and sodium hydroxide. Successive recrystallizations from ethanol and ligroin gave yellow plates of 2-chloro-4-nitro-N,N-dimethylaniline, m.p. 73-75°. (Drake reported 76-77°.) Analytical results were: calc'd. for $C_8H_9O_2N_2Cl$; Cl, 17.67%; found: Cl, 17.85%.

Indicator IV was prepared from this material. The maximum optical density was at about 370 mμ; but a test, analagous to that demonstrated in Table 28, indicated that interference from the color of the IH^+ ion was noticeable at wave lengths shorter than 390 mμ. Readings were therefore made at 410 mμ. It was found that in a solution only 0.000536 M in perchloric acid, 98% of the color of this indicator was discharged. Since the use of perchloric acid in concentrations much lower than five thousandths molar were not contemplated, no further work was done with this indicator.

The preparation of dichloronitrodimethylaniline was next undertaken. The p-nitrodimethyl aniline was dissolved in acetic acid and hydrochloric acid as before, the intention being to pass in a considerable excess of chlorine. However, dark colored material appeared soon in the solution so the reaction was stopped and the monochlor product isolated and recrystallized from alcohol, m.p. 65-72°. These crystals were then chlorinated further, the solution remaining a pale yellow. It was noted that the solution became warm during the chlorination, and so the flow of chlorine was continued until the heat effect was no longer noticeable. The crystals of 2,6-dichloro-4-nitro-N, N-dimethylaniline were obtained by pouring the solution onto ice and were recrystallized from ethyl alcohol. They melted 105-107° (literature value; 104-105° [38].)

From this material indicator solutions VA,B, and C were prepared. The absorption maximum was found to lie at about

380 mμ, but by the techniques already described, it was found that the conjugate acid was not colorless in this region. Readings of test solutions were, therefore, made at 420 mμ. The solutions were unstable. The optical density of VC changed from 1.41 to 1.56 in nine days. Moreover, these solutions, too, gave strange results in solutions containing hexyne and mercuric acetate. These new data made it seem possible that the chlorine atom or atoms, rather than the amine hydrogen atom (of which there are none in indicator V) were responsible for the anomalous results obtained with indicators III and V in solutions containing hexyne and mercuric acetate.

The synthesis of 2,4-dinitro-N,N-diethylaniline was, therefore, undertaken. Some of the indicators investigated by Hammett were polynitro bases, and they were reported as suitable for this work. Ten grams of Eastmann 2,4-dinitrochlorobenzene (0.05 moles) were dissolved in 20 ml. of butyl alcohol. Ten ml. (0.10 moles) of Eastman diethyl amine were added. The solution slowly became warm and then quite hot. The flask was fitted with a reflux condenser. After the spontaneous heat of reaction had subsided, in about five minutes, the solution was refluxed for 15 minutes. Water was then added and the crystals recrystallized twice from ethyl alcohol. They softened at 70° and melted 78.8-79.2°. Some of the material was then recrystallized from strong hydrochloric acid by the addition of sodium bicarbonate. Recrystallization from ethyl alcohol gave crystals of 2,4-dinitro-N,N-diethylaniline, m.p. 78.5-79.0°. The previously reported value was 80° [39].

Solution VIA was prepared from this material after ten days and solution VIA-a was made by making 20 ml. of VIA up to 50 ml. with glacial acetic acid. Four days later solution VIB was prepared, and showed a marked increase in basic strength. For solution VIC an entirely new preparation of the amine was used and dissolved in acetic acid only three days after being prepared. Unlike the other indicators this material seems to gain in basic strength on standing in air.

4. The purification of the colorless bases and the determination of their basic strengths.

Purified dioxane was generously furnished by M. Pierre Leroux. It had been refluxed for five hours over sodium hydroxide and for five hours over sodium before distillation. Its refractive index, $\underline{n}_D^{25}$, was 1.4195. (Literature value is 1.4220 at 20°[40].) Two solutions in acetic acid were prepared; one, 0.926 $\underline{M}$ in dioxane, was used for the first determination (Table 29); and the other, 1.40 $\underline{M}$, was used for the other three determinations. A definite concentration effect is to be noted in the calculated basic constants for dioxane. The best value for pK_a is about -4.

Eastman acetonitrile was dried with phosphorus pentoxide and distilled. The observed index of refraction, $\underline{n}_D^{25}$, was 1.3409. The literature[41] values are 1.34604 at 15°; 1.33934 at 30°. Linear interpolation gives 1.3413 at 25°. The first four readings in the table were made with a 1.90 $\underline{M}$ solution prepared from this material. The next five readings were made from a similar solution prepared from newly purified acetonitrile. The best value for pK_a is -4.2. Hammett and Deyrup found -4.19 for propionitrile.[33b,42]

Dr. Judd Nevenzel was kind enough to furnish some p-toluenesulfonamide which had been recrystallized from ethyl alcohol and found to melt from 137-138°. The material was not very soluble in acetic acid. An attempt to dissolve 1.50 gm. in 25 ml. of acetic acid failed, but 1.026 gm. did dissolve to give the 0.248 M solution used in the three determinations shown in Table 29. The best value for pK_a is -3.2.

Laboratory distilled water was employed for determining the basicity of water. Since only 1% of the water reacted in the first determination and 3% in the third, the satisfactory agreement between these runs serves to demonstrate that no strong base (such as ammonia) played an appreciable part in these determinations. The best value for the pK_a of water was about -2.3_5. Hammett and Deyrup found -3.72. No explanation for the discrepancy is known.[33b,42]

Recrystallized acetanilide was generously furnished by Dr. Fern Mitchell. It was dried in a vacuum over phosphorus pentoxide at the temperature of boiling ethyl alcohol for two days and was then found to melt 113.0-113.3°. One solution of the amide was used for the first and third determinations; another, for the second; and still another, 4 months later, for the last three. At the time the last three runs were made,

Table 29.

The Determination of the Strength of Weak Bases.

	Indicator Solution (Table 26)			Test Solution			Basic Strength	
Base	No.	Opt.Dens.	Indicator dilution factor	$HClO_4$ total conc. $\underline{M} \times 10^3$	Base total conc. $\underline{M} \times 10^3$	Optical Density Observed	K^s_{aB}	pK_{aB}
Dioxane	ID	2.836	1/5	1.000	556	0.313	2.74	-4.32
			1/5	1.000	840	0.325	2.66	-4.31
			1/5	1.000	280	0.3035	2.30	-4.24
			5/23	1.087	183	0.315	1.73	-4.12
Acetonitrile	IB	2.60	1/4	1.250	951	0.400	2.15	-4.21
			1/5	1.000	381	0.318	2.96	-4.35
			5/28	0.536	680	0.355	2.66	-4.30
			1/8	0.625	476	0.235	2.50	-4.28
	ICb	2.55	5/28	0.536	680	0.3325	2.42	-4.26
			1/4	1.250	951	0.361	2.14	-4.21
	IIA-1	2.452	1/5	186.8	761	0.4085	2.17	-4.22
			1/6	78.2	633	0.379	1.47	-4.05
			1/5	93.4	381	0.442	1.69	-4.11
p-Toluene-solfonamide	ID	2.836	1/5	1.000	149	0.362	0.200	-3.18
			1/5	1.000	44.2	0.309	0.263	-3.30
			5/23	1.087	28.8	0.320	0.202	-3.19
Water	IA	2.60	1/6	1.67	100	0.326	0.0319	-2.38
			1/7	2.14	85.7	0.250	0.0328	-2.40
			1/4	2.50	50.0	0.369	0.0300	-2.36
	IIIA	2.742	5/28	0.893	119	0.465	0.0266	-2.31

Table 29 (Continued)

Base	Indicator Solution (Table 26) No.	Indicator Solution (Table 26) Opt.Dens.	Indicator dilution factor	Test Solution HClO$_4$ total conc. $\underline{M}$ x 10^3	Test Solution Base total conc. $\underline{M}$ x 10^3	Optical Density Observed	Basic Strength K^s_{aB}	Basic Strength pK_{aB}
Acetanilide	IB	2.60	1/5	1.00	1.86	0.3865	0.00121	-0.96
			1/4	1.25	0.820	0.400	0.00103	-0.89
			1/5	1.00	0.620	0.3315	0.00153	-1.06
			1/8	0.625	0.410	0.2375	0.00123	-0.97
	IIIA	2.742	1/6	0.833	0.940	0.395	0.000885	-0.83
			1/6	0.833	0.470	0.377	0.00126	-0.98
			5/28	0.893	0.302	0.394	0.00111	-0.93
Acetamide	ICa	2.67	1/8	0.625	1.802	0.3125	0.000166	-0.10
			1/6	0.833	1.202	0.384	0.000146	-0.04
			5/23	1.087	0.941	0.435	0.000125	+0.06
			1/8	0.625	1.470	0.307	0.000169	-0.10
			1/6	0.833	0.982	0.363	0.000174	-0.11
			5/23	1.087	0.769	0.4135	0.000113	0.07
Urea	ICa	2.67	1/9	0.556	0.791	0.279	0.0_4478	0.48
			1/9	0.556	0.791	0.2775	0.0_4436	0.44
			1/9	0.556	0.648	0.4445	0.0_4408	0.51
			5/28	0.536	0.635	0.3665	0.0_4316	0.62
			5/33	0.455	0.443	0.2725	0.0_4355	0.57

the acetanilide was found to melt from 113.0-114.5°. The test solution for the fourth determination was prepared by diluting an aliquot from the second test solution 1:1 with acetic acid. The satisfactory agreement between these runs serves to demonstrate the reversibility of the reaction between acetanilide and the acid as well as confirming the reversibility of the indicator-acid equilibrium. The values of pK_a average about -0.9. Hammett and Deyrup reported values of -1.89 and -1.74.[33b,42]

Acetamide (Merck, reagent) was recrystallized from freshly distilled isopropyl ether and dried in a vacuum desiccator over phosphorus pentoxide. The needle-like crystals, very dry and crisp, melted 80.0-80.8°. Two acetic acid solutions were prepared, one used for the first three determinations and the other for the last three. Except for the fifth determination it will be noted that with higher ratios of perchloric acid to amide the apparent basicity of the amide increases. This observation may be associated with the ability of two moles of the amide to react with one mole of strong acid.[43] The best value for pK_a with the acid in excess is probably about 0.1. Previous results in the literature average about -0.5.[44]

Urea (Eastman) was recrystallized from absolute ethyl alcohol and dried in a vacuum desiccator, m.p. 132.2-133.5°. Three different solutions were prepared. One was used for the first determination; one, for the second and fourth; and one, for the third and fifth. The ratio between acid and base was not varied enough to make any trend recognizable. The values of pK_a averaged about 0.5. Previous values in the literature average about 0.1[44]. The greater basicity observed for urea and acetamide in these measurements as compared with older constants measured in water may be due in part to the high concentrations which had to be used in aqueous solutions to measure the basic strength.

In addition to these colorless bases whose strengths were determined, a number of colorless compounds were investigated for which values of pK_a could not be found because they lay outside the range from -4.5 to 1.1. As a test of the method heptane (a highly purified sample generously furnished by the Philips Petroleum Co.) was dissolved in acetic acid and used as a base in a several determinations with indicators IB and IIIA. In concentrations ranging up to 0.9 $\underline{M}$, K_b^s was found to equal 0.00 well within the experimental error. Benzophenone, ethylene diacetate, and cyclohexene all failed to show measurable basic strength. Dibutyl ether, acetone, and acetophenone were on the borderline. The readings made on solutions of these materials indicated a small degree of basic strength, but the differences from blank readings were too small to be safely distinguished from normal dispersion. Diphenylamine and o-chloroaniline were found to be too strongly basic for their basic strengths to be measured by this method.

C. The Formation of Complexes with Mercuric Acetate by Hexyne and Hexenyl Acetate.

The experience gained from the indicator studies on colorless bases was now applied to the study of the mercury complexes. That Equations 26 and 27 were written without acid was simply due to lack of knowledge. If acid did form part of the complexes, the measurement of the acidity of the medium might permit calculation of the equilibrium constants of the complexes.

First, the effect of hexyne and mercuric acetate separately on the acidity of perchloric acid solutions was studied. Using indicator IIID, it was found that 0.30 M hexyne had no effect on the acidity of a 0.0017 M solution of perchloric acid in acetic acid. Two later tests with indicator VC confirmed the knowledge that hexyne, by itself, would not effect the acidity of acetic and solutions of perchloric acid. Mercuric acetate, however, was found to be somewhat basic. The probable reaction of mercuric acetate with the solvated proton in acetic acid is shown in Equation 47 and the equilibrium constant, K_b^s, is defined in Equation 48.

$$Hg(OAc)_2 + H^+ = HgOAc^+ + HOAc \qquad (47)$$

$$K_b^s = \frac{(HgOAc^+)}{(Hg(OAc)_2)(H^+)} \qquad (48)$$

Two similar tests of the value of K_b^s were made with indicator IIIB and perfect agreement was obtained as shown in Table 30.

A third test with indicator IIID gave good agreement, and the value of K_b^s is probably quite close to 70. (In this case K_b^s instead of K_a^s is listed, since it seems far-fetched to call mercuric monoacetate ion a conjugate acid. However, despite the slight difference between Equations 44 and 47, the calculations for Table 30 are virtually identical with those for Table 29.)

Table 30.

The Basic Strength of Mercuric Acetate in Acetic Acid

		Test Solution				
Indicator Solution No.	Opt.Dens.	Indicator Dilution Factor	$HClO_4$ total conc. $\underline{M} \times 10^3$	$HgOAc_2$ total conc. $\underline{M} \times 10^3$	Optical Density Observed	Base Strength K_b^s
IIIB	2.804	5/28	0.535	14.3	0.480	74,74
IIID	2.455	5/28	1.783	2.14	0.3135	66

The acidity of solutions containing both hexyne and mercuric acetate in addition to perchloric acid were then investigated. Because of the yellow by-product formed in such solutions, blank runs, without indicator, had to be run to correspond to each test solution containing indicator. The optical densities of the blanks - taken at the same wave length and after the same time interval as for the test solutions - were subtracted from the optical densities of the test solutions. The difference, called the "indicator optical density", was then inserted in the usual calculations.

Indicator IIID was the first indicator to be tried in solutions containing mercuric acetate and perchloric acid.

The indicator optical density was found to drop precipitously to a value so low that it could not be explained even on the assumption that no perchloric acid was being bound by the hexyne or mercuric acetate or any complex of the two. This observation would be expected if the basic nature of the indicator were being diminished without any corresponding diminution of the light-absorbing quality of the nitro groups. The same type of results were obtained with indicator VC.

It was with indicators VI A and VI B (2,4-dinitro-N,N-diethylaniline) that the nature of the hexyne-mercuric acetate complex was finally elucidated. The conditions of the experiments are shown in Table 31. (Some data on the equivalent blank determinations were given in Table 15, runs C17-C21.) An attempt to extrapolate the indicator optical densities back to zero time gave 0.366, 0.360, 0.227, 0.400, and 0.165 as the best values for the five runs. From these figures the concentrations of IH^+, of free H^+, and of combined acid (exclusive of IH^+) were calculated in the usual manner. (See Table 32.) The hypothesis was then made that the mercuric acetate and the perchloric acid combined in a 1 to 1 ratio. On this basis the amount of free mercuric acetate could be determined. It was then possible to calculate the concentration of mercuric monoacetate from the data of Table 30 and to allocate the combined acid - part to the mercuric monoacetate and part to the hexyne-mercuric acetate complex. The additional hypothesis was then made that there was one molecule of hexyne in each molecule of complex. The amount of free hexyne could then be calculated.

Table 31.

Observations on the Hexyne-Mercuric Acetate-Perchloric Acid Complex.

Run No.	Indicator No.	Indicator Optical Density	Test Solution Indicator Dilution Factor	$HClO_4$ total M x 10^3	Hexyne total M x 10^3	$Hg(OAc)_2$ total M x 10^3	Indicator Optical Density 1 min.	$1\frac{1}{2}$ min.	2 min.	3 min.	4 min.
694a	VIA	4.97	1/5	0.400	0.424	0.800	(0.370)	0.376		0.386	0.383
694b	VIA	4.97	1/4	0.500	0.530	0.500	0.373	0.385	0.394	0.395	0.400
696a	VIA	4.97	10/33	0.606	0.643	0.182	0.227	0.227	0.225	0.228	0.231
699c	VIA	4.97	1/3	0.467	0.212	0.667	0.398	0.401	0.388	0.387	0.390
704a	VIB	4.98	10/32	0.750	0.331	0.312	0.165	0.168	0.166	0.164	

Table 32.

Computation of the Equilibrium Constant of the Hexyne-Mercuric Acetate-Perchloric Acid Complex. All concentrations are M x 10^3.

Run No.	Perchloric Acid Total-IH^+	Free	Combined Complex	$HgOAc^+$	Hexyne Total	Free	$Hg(OAc)_2$ Total	Free	K Equation 49
694a	0.366	0.115	0.247	0.004	0.424	0.177	0.800	0.549	2.2×10^7
694b	0.451	0.163	0.286	0.002	0.530	0.244	0.500	0.212	3.4×10^7
696a	0.533	0.375	0.157	0.001	0.643	0.486	0.182	0.024	3.6×10^7
699c	0.387	0.209	0.171	0.007	0.212	0.041	0.667	0.489	4.1×10^7
704a	0.667	0.456	0.208	0.003	0.331	0.125	0.312	0.101	3.6×10^7

From the amount of complex and the amounts of free acid, mercuric acetate, and hexyne, the equilibrium constant for a 1 to 1 to 1 complex was calculated according to Equation 49.

$$K = \frac{\text{Complex}}{(C_6H_{10})(HClO_4)(Hg(OAc)_2)} \qquad (49)$$

The good agreement obtained in the widely diversified runs lends credence to the hypotheses used in the calculations. Of course, the data show only the ratio in which the constituents enter the complex and give no information concerning its structure. The most reasonable theory seems to be that the role of the acid is to combine with one of the acetate radicals, leaving the complex as a hexyne-mercuric monoacetate cation. This suggestion is embodied in Equation 50. Regardless of the structure of the complex, it is concluded that a 1 to 1 to 1 complex is

$$C_6H_{10} + Hg(OAc)_2 + H^+ \longrightarrow (C_6H_{10} \cdot Hg)Ac)^+ + HOAc \quad (50)$$

formed from hexyne, mercuric acetate, and perchloric acid. The best value for the equilibrium constant is about 3.5×10^7 $\text{moles}^{-2}\ \text{liters}^2$.

One surprising feature of the data in Table 31 should be pointed out. The value of the equilibrium constant depends directly on the amount of excess hexyne in solution. The amount of this excess is believed to be rapidly changing as the hexyne reacts with the solvent to form hexenyl acetate. However, only in the first two runs does there appear an initial trend of any important size in the indicator optical density.

Similar determinations were then made with solutions containing hexenyl acetate, mercuric acid, and perchloric acid. The data and the results of the calculations are shown in Table 33. The figure shown for the concentration of the complex in each run is simply the concentration of the acid not otherwise identified as free or present as IH^+. At the concentrations used, no correction had to be made for mercuric monoacetate. The values of K were calculated, as in Table 32, on the assumption that a 1 to 1 to 1 complex was being formed. Many of the results lie between 3.2 and 6.0 x 10^7, but the discrepancies seem to be significant. When the perchloric acid is in considerable excess over the hexenyl acetate and mercuric acetate (Runs 737b and 737c), the value of K is smaller than usual. When the hexenyl acetate and mercuric acetate are present in markedly unequal amounts (Runs 745c and 745d), the concentration of complex formed seems to nearly equal the concentration of the reagent present in smaller quantity. If the equilibrium constant were calculated in the usual way for these tests, the values would be very large or infinite. The hexenyl acetate has three sites available for possible complexing with the mercury. It seems reasonable that the equilibrium involved should be more complicated than with mercuric acetate and hexyne.

Table 33.

Observations on the Hexenyl Acetate-Mercuric Acetate-Perchloric Acid Complex

Run No.	Indicator Dilution Factor	$HClO_4$ total M x 10^3	Hexenyl Acetate total M x 10^3	$Hg(OAc)_2$ total M x 10^3	Indicator Optical Density				Calculated Quantities	
					Initial Est.	1 min.	2 min.	3 min.	Complex M x 10^3	K x 10^7
737b	3/16	0.312	0.148	0.156	0.186	0.188	0.190	0.192	0.031	0.88
737c	3/14	0.214	0.163	0.179	0.316	0.319	0.322	0.324	0.037	1.5
740a	2/13	0.116	0.182	0.192	0.377	0.377	0.378	0.379	0.044	3.9
740b	2/15	0.100	0.263	0.167	0.356	0.356	0.357	0.358	0.052	4.9
740c	2/11	0.136	0.216	0.136	0.408		0.409	0.409	0.046	4.6
739a	3/16	0.156	0.148	0.156	0.378	0.378	0.379	0.379	0.047	5.2
739b	1/6	0.139	0.219	0.139	0.353	0.355	0.356	0.357	0.041	3.2
742e	1/6	0.139	0.219	0.139			0.353	0.355		
741a	3/19	0.132	0.125	0.079	0.318	0.321	0.320	0.320	0.027	6.0
742b	3/19	0.132	0.125	0.079		0.319	0.320	0.320		
741b	1/8	0.104	0.099	0.063	0.268	0.272	0.274	0.275	0.014	5.0
742c	1/8	0.104	0.099	0.063		0.268	0.271	0.272		
742f	3/23	0.109	0.172	0.109	0.304	0.304	0.305	0.307	0.031	3.8
745c	1/7	0.119	0.378	0.071	0.408	0.408	0.410	0.412	0.067	?
745d	1/7	0.119	0.113	0.238	0.572	0.572	0.572	0.572	0.109	?

D. The Acidity of Solutions of Sulfuric Acid in Acetic Acid.

An important paradox must be pointed out in connection with the acidity of acetic acid solutions of sulfuric acid. Hall found that his and Hammett's data suggested that sulfuric acid was a strong acid in acetic acid solutions less than 0.2 M in sulfuric acid. A plot of Ho against log(H_2SO_4) gave a straight line with a slope of -1. This observation is equivalent to Equation 51, which resembles Equation 42. It might, therefore,

$$Ho + \log (H^+) = Q \qquad (51)$$

be concluded (and Hall and Spengeman did conclude) that sulfuric acid is a strong monobasic acid in acetic acid. Table 34 shows the calculation of Q. The first two runs were made as part of the present research, using indicator IIID. The other runs were reported by Hall and Spengeman.[31]

Table 34.

The Acidity of Solutions of Sulfuric Acid in Acetic Acid

H_2SO_4, M	Ho	Ho + log (H_2SO_4)
0.00332	-0.15	-2.63
0.00909	-0.58	-2.62
0.00315	0.05	-2.45
0.00590	-0.30	-2.53
0.00954	-0.60	-2.62
0.0103	-0.49	-2.48
0.0411	-1.10	-2.49
0.241	-1.93	-2.55
0.651	-2.65	-2.84
1.794	-3.21	-2.96

It will be observed the Q is, indeed, fairly constant for solutions in which the acid concentration is 0.2 M or less. Instead of agreeing with Equation 42, however, it turns out that Q has a value of about -2.55. Sulfuric acid solutions, then, are much less acidic than solutions of perchloric acid. In fact, a solution of sulfuric acid must be twenty ($10^{1.3}$) times as concentrated as a solution of perchloric acid to give a solution of equivalent acidity.

There is no evidence that makes it necessary to revise the theory that perchloric acid is fully ionized. It is necessary to postulate, however, either that sulfuric is rather slightly ionized or that some process other than ionization into proton and bisulfate ion uses up molecular sulfuric acid. Because the surprisingly low acidity of the sulfuric acid solutions had no known explanation, it was decided to use perchloric acid in the kinetic studies which were now to be resumed.

VI. Reaction of 3-Hexyne and 3-Hexenyl Acetate-3 with Acetic Acid. Final Results.

A. The Mechanism of the Reaction of 3-Hexyne.

Runs 101 to 116. These determinations were made after the decision had been reached to use perchloric acid for the final kinetic tests but before the hexyne-mercuric acetate-perchloric acid complex had been successfully measured. The hexyne which was present in these runs was pipetted from a stock solution of hexyne in acetic acid which had been prepared two months earlier. Bromate-bromide titrations of known dilutions of this solution were only about 3% high instead of the usual 6% (see Table 8). It is probable that about six percent of the hexyne had reacted to form hexenyl acetate during the interval. The formation of peroxides may also have occurred. Therefore, the data for these runs must be evaluated with some caution. They are shown in Table 33.

No general interpretation was found which would fit all these runs. However, certain qualitative conclusions can be drawn from the data. The tapering off phenomenon was most noticeable when the concentration of hexyne was in considerable excess over the concentration of the catalysts. When the initial concentration of the hexyne was low, a large fraction of the hexyne reacted very quickly as in Runs 110a and 113. However, in all the runs in which successive readings could be obtained, the rate was found to taper off from a zero or first order dependence on the concentration of the hexyne. Runs 105 and 109 were duplicates and agreed quite well, but Runs 110a and 110b

Table 33.

Run No.	Hg(OAc)$_2$ $\underline{M}$ x 10^3	HClO$_4$ $\underline{M}$ x 10^3	Time Min.	Hexyne $\underline{M}$ x 10^3
101	5	5	0	(44.2)
			4	38.3
			21	32.4
			41	28.7
			58	27.8
102	5	5	0	(88.5)
			2.5	76.7
			24	73.3
105	2	2.5	0	(13.2)
			3.75	12.5
			24.5	7.1
			44	5.5
106	2	2.5	0	(6.62)
			4.25	5.10
			27	2.35
			49	1.20
109 (105b)	2	2.5	0	(13.2)
			2.75	12.3
			25	7.1
110a	2	2.5	0	(3.98)
			3.5	1.61
			25	0
110b	2	2.5	0	(3.98)
			3	2.41
			25	1.29
111	3	2.5	0	(13.2)
			3	12.3
			24	6.8
112	3	2.5	0	(6.62
			2.75	5.50
			22	3.10
113	3	2.5	0	(3.98)
			3	0.62
			22	0
114a	6.0	0.5	0	(2.65)
			3.75	1.47
			24	1.47
114b	6.0	0.5	0	(2.65)
			3.5	1.35
			26	1.55
116	0.6	0.5	0	(2.65)
			2.75	1.98
			22.5	1.62

are noticeably different. Some of the runs catalyzed by 0.002 M mercuric acetate and 0.0025 M perchloric acid seem to have a faster initial rate than runs catalyzed by 0.003 M mercuric acetate and 0.0025 M perchloric acid.

From these runs it was concluded that catalyst concentrations of about 0.0005 M to 0.0010 M would provide rates which it would be convenient to determine.

Runs 117-128. Following the determination of the equilibrium constant of the hexyne-mercuric acetate-perchloric acid complex, a set of kinetic determinations was made in which the perchloric acid and mercuric acetate concentrations were the same in any one run. This single concentration was varied between 0.0003 M and 0.0017 M to include the range suggested in the last paragraph. The data are shown in Table 34. Six runs are omitted from the table. Runs 122 and 123 were made after the stock supply of hexyne had been exposed to air and before it was redistilled. Runs 124, 125, and 126 unaccountably gave precipitates. Run 124 was 0.038 M in hexyne, 0.001 M in mercuric acetate, and 0.0005 M in perchloric acid. Runs 125 and 126 had the same concentrations as Run 127. The case of Run 119 is discussed in the next paragraph.

The kinetic determinations were usually made with solutions having a volume of 50 or 100 ml. A solution of 100 ml. 0.01 M in hexyne would have less than 0.1 ml. of hexyne, an amount too small to pipette accurately. In Runs 101 to 116 a stock solution of hexyne in acetic acid was used as an intermediate between the hexyne and the kinetic solution. However, evidence was presented that a slow reaction took place in this solution. In Run 117 and in most succeeding runs, a fresh intermediate solution was prepared for each kinetic determination. Occassionally, one such solution would be used for two runs if it was possible to start the second run within three hours after preparing the intermediate solution. The concentrations of the intermediate solutions were determined by the titration of aliquots until sufficient data were available to allow the prediction of the concentration of a certain dilution of hexyne. From the known dilution of the intermediate solution used in the kinetic solution, the initial concentration of hexyne in the kinetic solution could be calculated. In Run 119 the concentration of the intermediate solution was found to change with time; and this run is, therefore, omitted from Table 34. This instability is believed to be related to oxygen dissolved in the hexyne. Mr. Dorsey has found that the rate of disappearance of unsaturation in an aqueous solution of hexyne is increased by the presence of oxygen.

Run 117 was made with hexyne which had not been distilled for six months. The initial rate in this run was the largest in Table 34. The hexyne was then distilled for use in Runs 118-121. In these determinations the rates were slower than in Run 117. Finally the hexyne was redistilled for Runs 127, 128, and 128s. Run 127, which had the same amount of catalyst as Runs 118, 120, and 121, was found to react much more slowly

Table 34

The Rate of Reaction of Hexyne and Acetic Acid. Catalysis by Mercuric Acetate and Perchloric Acid at 25°.

Run No.	$Hg(OAc)_2$ M x 10^3	$HClO_4$ M x 10^3	Time Min.	Hexyne M x 10^3
117	0.5	0.5	0	(52)
			3.25	46
			30	33
			91	31
			125	32
			153	32
118a	0.5	0.5	0	(24.2)
			3.5	23.8
			9.5	23.3
118b	0.5	0.5	0	(24.2)
			3.7	23.8
			17	23.4
120a	0.5	0.5	0	(55.3)
			3.2	53.7
			14.5	53.5
120b	0.5	0.5	0	(55.3)
			2.5	54.2
			20	52.5
121	0.5	0.5	0	(10.1)
			2.75	9.7
			14.5	9.1
127a	0.5	0.5	0	(34.0)
			2.1	34.0
			5.2	34.0
127b	0.5	0.5	0	(34.0)
			117	34.0
128	0.33	0.33	0	(34.0)
			2.1	34.0
			4.2	34.0
128s	1.67	1.67	0	(34.0)
			2.5	32.2
			5.5	32.2

than the earlier three runs. In fact no change in unsaturation seemed to take place in either Run 127 or 128.

It was concluded that the kinetic determinations should be made under nitrogen, using hexyne which had never been exposed to air. It was further decided that if catalyst concentrations of about 0.001 M were to be employed, lower initial concentrations of hexyne would have to be used to prevent masking a small amount of change with a large amount of unchanged materials.

Runs 129 through 138. The experience gained in the previous work was applied to Runs 129 through 138, from which the mechanism of the reaction was finally deduced. The runs were made under nitrogen, and nitrogen was also used to protect the intermediate hexyne solution. Because of the number of different solutions (4) which had to be mixed to make the kinetic solutions, because no convenient method was available for thermostating the aliquots during the time needed for sampling, and because previous experience had demonstrated no strong temperature effect on the rate, these runs were made at room temperature. The results are shown in Table 35.

If just Runs 129 through 136 be considered first (runs in which the concentration of mercuric acetate equaled the concentration of perchloric acid), it will be seen that the tests can be divided into three groups on the basis of the change in hexyne concentration in the first 2 1/2 minutes of each run. (The concentration at the end of 2 1/2 minutes was determined for each run by reading from a graph of concentration vs. time. The first aliquot was usually taken at about 2 1/2 minutes.) In Runs 133 and 136 this change is about 0.00070M; in Runs 129, 131, 132, and 135 it is about 0.00150 M; and in Run 130 it is 0.00225 M. It is immediately evident that this diversion has grouped the runs according to the amount of catalyst present and that the grouping is independent of the total concentration of hexyne. Moreover, the three concentration changes, 0.00070, 0.00150, and 0.00225 M, are approximately in the ratio 1:2:3, which is exactly the ratio of the concentration of catalysts in the respective runs.

The only mechanismthat is believed toaccount for these findings is that the reacting species is a complex, formed by the hexyne with the catalysts. Only in this way can the independence of the initial rate of reaction of the hexyne from the initial concentration of the hexyne be explained. In order to determine the ratio of perchloric acid to mercuric acetate in this complex, Runs 137 and 138 were made with unequal amounts of the two catalysts. In Run 137, which was 0.0005 M in mercuric acetate and 0.0015 M in perchloric acid, the concentration of hexyne dropped 0.00105 M in the first 2 1/2 minutes. In Run 138, which was 0.0015 M in mercuric acetate and 0.0005 M in perchloric acid, the concentration dropped 0.00110M in the first 2 1/2 minutes. These data do not fit perfectly the initial rates of Runs 129 through 136. If the complex contained one mole each of mercuric acetate and perchloric acid, the concentration of

Table 35.

The Rate of Reaction of 3-Hexyne with Acetic Acid, under Nitrogen. Catalysis by Mercuric Acetate and Perchloric Acid.

Run No.	Temp. (Deg.)	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Time Min.	Hexyne $\underline{M} \times 10^3$
129	29	1	1	0	(5.80)
				3.5	4.02
				6.5	3.92
				45	3.48
130	23	1.5	1.5	0	(5.80)
				3.5	3.34
				31	2.37
				60	2.04
				1640	1.79
131	25	1	1	0	(5.80)
				2.67	4.30
				10	3.75
				44	3.16
				131	3.12
132	24	1	1	0	(11.60)
				2.75	10.15
				10	9.60
				36	9.05
				800	8.85
133a	25	0.5	0.5	0	(5.80)
				3.1	5.26
				11	4.95
				46	4.91
133b	27	0.5	0.5	0	(5.80)
				2.25	5.15
				9.5	4.85
133c	25	0.5	0.5	0	(5.80)
				2.25	5.10
				10.2	4.91
				39	4.78
135	25	1	1	0	(3.48)
				2.5	1.88
				9.7	1.35
				45	1.17

Table 35 (continued)

Run No.	Temp. (Deg.)	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Time Min.	Hexyne $\underline{M} \times 10^3$
136	25	0.5	0.5	0	(3.48)
				3.5	2.78
				13.7	2.56
137	26	0.5	1.5	0	(5.80)
				3	4.66
				11	4.22
				39	3.34
				143	1.80
138	28	1.5	0.5	0	(5.80)
				2.25	4.75
				9.5	4.32
				48	4.36

hexyne should have dropped 0.00070 M in the first 2 1/2 minutes in Runs 137 and 138. If the complex contained two moles of one catalyst and one mole of the other, then either Run 137 or 138 should have lost 0.00150 M in the first 2 1/2 minutes, the other losing 0.00070 M. The values actually found, 0.00105 M and 0.00110 M, suggested that the complex actually contained only one mole of each catalyst. The extra hexyne reacting might be the result of the catalytic action of excess perchloric acid (in Run 137) or of excess mercuric acetate (in Run 138) on the excess hexyne present in these runs. ("Excess" is used to mean the material not involved in the complex.)

In order to determine the probable rate at which the excess hexyne would react in the presence of an excess of one catalyst, a series of determinations was made in which only one catalyst was present. The data are shown in Table 36. It is evident that the small size of the effect being investigated placed a great strain on the techniques of mixing, sampling, and titrating these solutions. The results in the three acid-catalyzed tests (A1, A2, and A3) were scattered, and only in Test A3, with a relatively high concentration of perchloric acid, was a clear-cut effect demonstrated. On the basis of the three tests, the best value for the amount of hexyne reacting in 2 1/2 minutes in the presence of 0.0010 M perchloric acid is 0.00010 M. If this figure is subtracted from the 0.00105 M found in Run 137, the difference, 0.00095 M, should be the initial loss of hexyne due solely to the reaction of the complex. This value is still intermediate between 0.00070 M and 0.00150 M, the values which would indicate, respectively, the inclusion of one or two moles of perchloric acid in the complex. However, another effect was operating to make Run 137 different from Runs 129-136. Run 137, with the excess perchloric acid, showed the tapering-off phenomenon much less than the earlier runs. This resistance to tapering off must have been effective during the first 2 1/2 minutes of Run 137 as well as during the later portions of the run. Therefore, Run 137 would be expected to show a greater loss of unsaturation than a run which had the same initial concentration of complex, but no excess perchloric acid. The magnitude of this effect could not be ascertained, but qualitatively it would be in the direction of making the 0.00095 M or 0.00105 M value for Run 137 comparable to a value of 0.00070 M for the initial drop in Runs 129-136. It could, therefore, be concluded that the formation of one mole of the complex required one mole of perchloric acid.

The discrepancy in the case of Run 138 could be much more easily resolved. The data for tests M1-M3 (Table 36) showed clearly that, in the presence of mercuric acetate, hexyne was converted to an alkene even in the absence of perchloric acid. In these runs, too, the results are somewhat random. The best value for the amount of hexyne reacted in 2 1/2 minutes in the presence of 0.0010 M mercuric acetate was 0.00035 M. Subtracting 0.00035 M from 0.00110 M gave 0.00075 M as the amount of hexyne reacted in 2 1/2 minutes in Run 138 by way

Table 36.

The Rate of Reaction of 3-Hexyne with Acetic Acid. Catalysis by either Mercuric Acetate or Perchloric Acid.

Test No.	Temp. (Deg.)	$Hg(OAc)_2$ $\underline{M} \times 10^3$	$HClO_4$ $\underline{M} \times 10^3$	Time Min.	Hexyne $\underline{M} \times 10^3$
A1	27		1.5	0	(5.80)
				2.5	5.63
				58	5.85
A2	27		1	0	(5.80)
				2.5	5.55
				26	5.75
A3	25		2.5	0	(5.80)
				2.5	5.55
				32	5.55
M1	23	0.5		0	(5.80)
				2.5	5.65
				32	4.50
M2	23	1.0		0	(5.80)
				2.5	5.26
				20	5.35
M2b	24	1.0		0	(5.80)
				2.5	5.49
				54	5.31
M3	23	1.5		0	(5.80)
				2.5	5.26
				26	5.38

of the complex. This value was in close agreement with the value of 0.00070 M which was to be expected if one mole of the complex included one mole of mercuric acetate.

The kinetic data, then, can be interpreted only on the basis that the reactive species is a complex including mercuric acetate and perchloric acid as well as hexyne. The fact that the rate of reaction is much greater in the presence of both catalysts than of either one alone shows that the complex must be formed relatively rapidly. Kinetic studies, moreover, furnish the information that this complex includes one mole of mercuric acetate and one mole of perchloric acid. Independent corroboration is thus furnished for the indicator studies which also demonstrated the existence of this complex and showed that its formation was complete in less than one minute (Tables 31 and 32). From the indicator measurements the additional information is available that the complex includes one mole of hexyne. The mechanism of the catalytic addition of acetic acid to 3-hexyne, therefore, has been established. It is represented in Equations 49 and 50. The rate-determining step is shown in Equation 50.

$$\text{Et-C}\equiv\text{C-Et} + \text{Hg(OAc)}_2 + \text{H}^+ \longrightarrow \text{Et-C}\equiv\text{C-Et}\cdot\text{HgOAc}^+ + \text{HOAc} \qquad (49)$$

$$\text{Et-C}\equiv\text{C-Et}\cdot\text{HgOAc}^+ + 2\text{HOAc} \longrightarrow \text{Et-CH}=\underset{\substack{|\\ \text{OAc}}}{\text{C}}\text{-Et} + \text{Hg(OAc)}_2 + \text{H}^+ \qquad (50)$$

As has already been pointed out, the exact nature of the 1:1:1 complex of hexyne, mercuric acetate, and perchloric acid has not been demonstrated. The hypothesis that the complex is a cation, however, is especially well suited to this mechanism. The driving force of Equation 50 would then be the electrostatic attraction of this cation for electron-rich oxygen atoms of the acetic acid.

B. Special Tests

Four special runs were made to test, respectively, the effect of a high catalyst concentration and the effect of adding acetic anhydride, water, and diethyl ketone on the rate of addition of acetic acid to hexyne. The data are shown in Table 37.

The run with high concentration of catalysts was Run 139. It is seen that the unsaturation dropped quickly to half its original value and then remained constant. (The erratic nature of the results may have been due, in part, to the fact that suction, as well as nitrogen pressure, was used in taking the aliquots.) This result, barring a coincidence, must represent the immediate reaction of the alkyne to give an alkene or alkenes. The static nature of the solution after the initial drop confirms the assumption, previously made, that the rate of the reaction of hexenyl acetate to form hexanone is slow compared to the rate of reaction of hexyne.

Runs 140 through 142 resemble Run 131 with respect to initial concentrations of catalysts and hexyne. Run 131 showed a loss of 0.00150 moles per liter of hexyne in the first 2 1/2 minutes. The corresponding figures for Runs 140-142 are:

Table 37.

The Effect of Special Conditions on the Rate of Addition of Acetic Acid to 3-Hexyne.

Run No.	Temp. (Deg.)	$Hg(OAc)_2$ M x 10^3	$HClO_4$ M x 10^3	Additive M	Time Min.	Hexyne M x 10^3	Unsaturation N x 10^3
139	29	10	10	--	0	(3.48)	(13.9)
					1.5		6.9
					9		6.5
					28		6.6
					120		7.5
					155		6.9
140	25	1	1	1.9a	0	(5.80)	
					2	4.15	
					11	3.57	
					114	3.04	
141	25	1	1	0.277b	0	(5.80)	
					2.5	4.51	
					12.25	4.11	
					57	4.02	
142	26	1	1	0.265c	0	(5.80)	
					2.5	4.11	
					10	3.66	
					45	3.17	

a. Et_2CO

b. H_2O

c. Ac_2O

140 (with added diethyl ketone), 0.00170 moles per liter; 141 (with added water), 0.00129 moles per liter; 142 (with added acetic anhydride), 0.00169 moles per liter. All three figures probably differ just enough from 0.00150 moles per liter to represent a significant difference from Run 131. It was, therefore, tentatively concluded that diethyl ketone (in a relatively high concentration) and acetic anhydride exert an accelerating effect and water a retarding effect on the rate of addition of acetic acid to hexyne. In Run 141, with added water, the amount of yellow color formed is much less than usual, and it may be that the reason for the slower rate observed is interference with the formation of the by-product.

It should be noted that the effects caused by the water and the acetic anhydride are rather small. The amount of water in Run 141 is about the same as in commercial, C.P. acetic acid (m.p. 15.6°), and the effect on the rate is only about 15%. It is concluded that the early kinetic experiments, in which excess water or acetic anhydride were often present, were not seriously effected by these contaminants.

C. The Correspondence of the Amount of Yellow By-product to the Loss of Unsaturation.

Runs C130 through C138, which appeared in Table 15 and were discussed in Section IV A5, were exact duplicates of Runs 130-138 just discussed. From the data of Table 15, it was learned that, in most runs, the amount of color produced was proportional to the concentration of the hexyne-mercuric acetate-perchloric acid complex. Since the amount of unsaturation lost is also proportional to this concentration, it follows that, in most runs, the amount of yellow color is proportional to the loss of unsaturation. The possibility must be considered, therefore, that in measuring the rate of change of unsaturation, it was the rate of production of the yellow species rather than of hexenyl acetate that was being determined.

In Section II the preparation of 6 1/2 ml. of hexenyl acetate from 40 ml. of hexyne was reported. If correction is made for the fact that only 1/3 instead of 1/2 of the unsaturation was lost in the synthetic media, the indicated yield on the basis of the hexyne reacted is about 25%. Correction for material left in the water-acetic acid solution during the steam distillation and for product lost into the Dry Ice trap during the vacuum distillation would further increase the indicated yield. On the other hand, the product obtained was not pure. The possibility must be considered that the yellow material, and not hexenyl acetate, is the major product formed during the reaction.

The formation of hexenyl acetate, however, even in a yield of only 25%, must have had an effect on the rate of loss of unsaturation. The data of Runs 129-138, from which it was concluded that the rate of loss of unsaturation was proportional to the concentration of the complex, covered a 3-fold change in the initial rate. The total concentration of hexyne was also changed more than 3-fold in these runs. Had the hexenyl acetate been formed by some other mechanism, it probably would not have been found that the rate of loss of unsaturation was proportional to the concentration of the complex in each of these runs.

There were, moreover, two runs in which the amount of color formed was not proportional to the rate of change of unsaturation but in which the rate of change of unsaturation was nearly proportional to the concentration of complex. In Run 141, with 0.277 M of water, the yellow-color reached less than 1/3 of the optical density of Run 131. The initial rate of change of unsaturation, however, agreed within 15% for the two runs. Of greater significance is a comparison of Run C138 and 138. These runs were 0.0015 M in mercuric acetate and 0.0005 M in perchloric acid. It will be recalled that no color at all was formed in Run C138, but that the initial rate of loss of unsaturation in Run 138 was greater than in Run 133b. After correction was made for the catalytic effect of the excess mercuric acetate in Run 138, the initial change of unsaturation of Runs 133 and 138 agreed closely despite the absence of yellow color in Run 138. It is, therefore, concluded that the yellow color, if its formation coincides with a change in unsaturation, is formed only in very small quantity. It is further concluded that the mechanism elucidated for the rate of change of unsaturation may be safely ascribed to the formation of hexenyl acetate.

D. The Rate of the Reaction of the Hexyne-Mercuric Acetate-Perchloric Acid Complex with Acetic Acid.

It was shown to be possible to arrange Runs 129-138 into three groups on the basis of the initial rates of reaction and the concentration of the 1:1:1 complex in these solutions. The first group (0.0015 moles per liter of complex) included Run 130; the second group (0.0010 moles per liter of complex) included Runs 129, 131, 132, and 135; the third group (0.0005 moles per liter of complex) included Runs 133 and 136 as well as Run 138 (after correction for the catalytic effect of the excess mercuric acetate). Run 137, with 0.0015 M perchloric acid and 0.0005 M mercuric acetate did not fit into these groups, having an initial rate somewhat greater than group three.

It will be noted that the values given for the concentrations of the complex equal the concentrations of the limiting constituent of the complex. This approximation follows from the equilibrium constant for the complex (3.5×10^7 liters^2 moles^{-2}) and the relatively high concentrations of solutes in Runs 129-138. Run 136 had the lowest concentrations of solutes, being 0.0058 M in hexyne and 0.0005 M in both mercuric acetate and perchloric acid. The complex in this solution had a concentration of about 0.00044 M and thus included about 90% of each of the two catalysts. The equivalent fraction in the other runs was even higher.

Runs 130, 131, 133c, and 137 can be chosen as representative of the set of determinations. A plot of the concentration of hexyne against time for each of these four runs is shown in

Figure 4. The difficulty of determining the tangent to these curves at zero time is immediately apparent. The "tapering-off" phenomenon is so marked that the shape of the curves at any time before the first reading is almost unknown. It is for this reason that comparison among the runs has been made on the basis of the loss of hexyne after 2 1/2 minutes.

A further disconcerting fact in connection with determining the true initial rates is the lack of certainty that the complex titrates as an alkyne. It is conceivable that only two equivalents of bromine add to each mole of complex. Even if this were true, the grouping of Runs 129-138 and the proof of the mechanism of the reaction would not be changed. The initial, 2 1/2 minute loss of unsaturation would be 0.0075 moles per liter, 0.0050 moles per liter, and 0.0020 moles per liter respectively for the three groups - values which are still proportional to the concentrations of complex in each case. The apparent initial rates, however, would be considerably decreased.

On the grounds that rough approximations may be better than no values whatever, two estimates will be made as to the value of k in Equation 30. For the first value it will be

$$-\frac{dH}{dt} = k\,C_H \qquad (30)$$

assumed, as seems most likely on chemical grounds, that the complex titrates as a triple bond. The approximation will then be made that the initial slope is twice as great as the slope that would be obtained by drawing a straight line between the initial concentration and the 2 1/2 minute point. The three

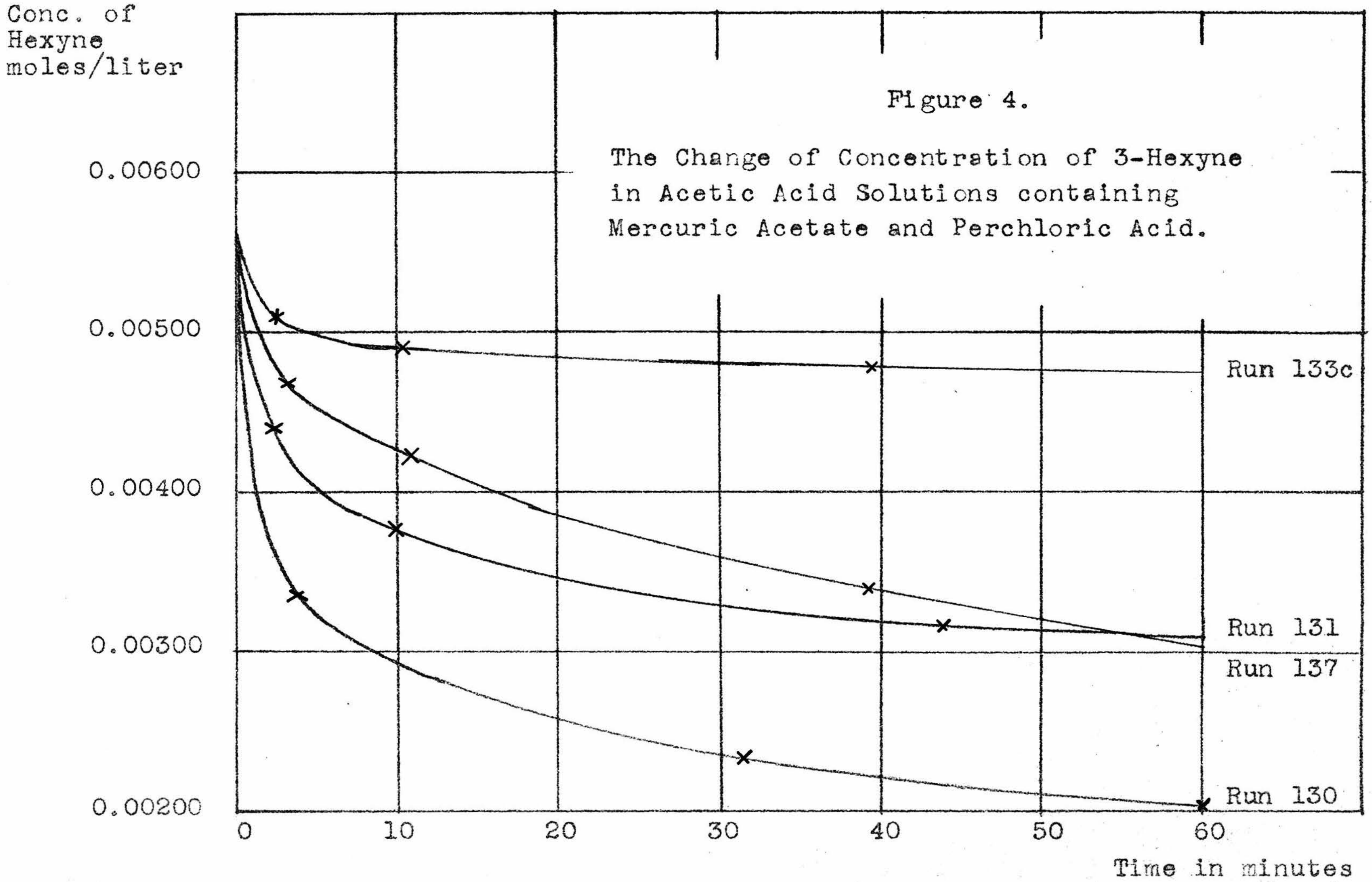


Figure 4.

The Change of Concentration of 3-Hexyne in Acetic Acid Solutions containing Mercuric Acetate and Perchloric Acid.

values of k for the three groups of runs will then be: (0.00225)(2)/(2.5)(.0015); (0.00155)(2)/(2.5)(.001); (0.00075)(2)(.0005). The value calculated for the rate constant in each case is $k = 1$ min.$^{-1}$ On the other hand, the hypothesis may be made that the complex titrates as an alkene. In this case the abrupt tapering-off phenomenon would be explained away. There would be simply an immediate drop in unsaturation caused by the formation of the complex followed by a nearly linear succession of points on the unsaturation vs. time graph. The initial rate would be about 1/6th of the value calculated above, or, approximately, $k = 0.2$ min.$^{-1}$

E. The Rate of Reaction of 3-Acetoxyhexene-3 with Acetic Acid. Catalysis by Mercuric Acetate and Perchloric Acid.

As a final step in the study of the rate and mechanism of the addition of acetic acid to 3-hexyne, a few runs were made to study the rate of addition of acetic acid to hexenyl acetate. The runs were made under approximately the same conditions as Runs 129-138, their purpose being to confirm the hypothesis, drawn from Run 139, that the reaction rate of hexenyl acetate is slow compared to the reaction rate of hexyne. Precautions to exclude oxygen were taken as in Runs 129-142.

The data are shown in Table 38 and Figure 5. It is evident that, Run 139 notwithstanding, the reaction of hexenyl acetate with acetic acid proceeds at a rate which is approximately equal to the rate of reaction of hexyne. Runs 132 and 205 have the same concentrations of catalysts and about equal concentrations of hexyne and hexenyl acetate respectively. In Run 132 0.0014 moles per liter of hexyne (or else 0.0005 moles per liter - depending on the hypothesis taken for the effective unsaturation of the complex) reacted in the first two and a half minutes. In Run 205, the loss of hexenyl acetate in the first 2 1/2 minutes was 0.0008 moles per liter. Nevertheless, it is probable that the initial rates observed in Runs 129-138 were not significantly affected by the reaction of hexenyl acetate. In Runs 203-207, the absence of hexyne left the catalysts free to catalyze the reaction of the vinyl ester, whereas in Runs 129-138 the relatively large excess of hexyne would have effectively complexed the catalysts and inhibited the reaction of hexenyl acetate.

This set of data may be examined for the information it gives on the mechanism of the catalytic addition of acetic acid to 3-acetoxyhexene-3. It is evident, to begin with, that these runs are nearly free of the tapering-off phenomenon present in similar determinations with hexyne. The runs do taper-off slightly - both from zero-order dependence on the concentration of the ester, as shown in Figure 5, and from first-order dependence, as can be seen if the data is plotted on semilogarithm paper. It is probable that the products (in this case ethylpropyl ketone and acetic anhydride) exert an inhibiting effect. Comparison of Runs 203 and 205 suggests that the initial rate of reaction depends on the concentration of the

Table 38.

The Rate of Reaction of Hexenyl Acetate and Acetic Acid. Catalysis by Mercuric Acetate and Perchloric Acid.

Run No.	Temp. (Deg.)	$Hg(OAc)_2$ M x 10^3	$HClO_4$ M x 10^3	Time Min.	Hexenyl Acetate M x 10^3	Initial Slope x 10^3
202	25	00	0.56	0	(25.0)	--
				2.5	24.8	
				10	24.9	
				39	24.4	
				110	24.8	
203	25	1	1	0	(27.0)	0.28
				2.5	26.0	
				11	23.8	
				42	17.3	
				76	12.1	
				180	6.1	
204	25	1	0.4	0	(27.0)	0.10
				2.75	26.4	
				11.8	25.8	
				49	23.3	
				105	20.8	
				191	18.4	
205	26	1	1	0	(13.5)	0.22
				2.3	12.8	
				10.5	11.1	
				33	7.0	
				49.5	5.2	
206	25	0.4	1	0	(27.0)	0.18
				3	26.7	
				10.5	25.0	
				37.5	20.4	
				63	17.1	
207	26	0.4	0.4	0	(27.0)	0.045
				2.25	26.4	
				42.2	25.0	
				76	22.9	
				116	21.8	
208	27	--	1	0	(27.0)	--
				2.5	26.3	
				9.5	25.9	
				41	25.9	

hexenyl acetate only very slightly - somewhere between zero and first-order dependence but closer to zero-order. This result would be expected if the reaction took place by way of a complex the equilibrium constant of which was moderately large. Increasing the concentration of ester would then cause some increase in the concentration of the complex.

The data of Runs 203, 204, 206, and 207 indicate that the rate of reaction was dependent on the concentration of both the perchloric acid and the mercuric acetate. The dependence on the concentration of perchloric acid was somewhat greater than first power and on the mercuric acetate somewhat less than first power. In this case the absence of a complex or else a complex with a very low equilibrium constant seemed to be indicated. Increasing the concentration of either the mercuric acetate or the perchloric acid caused an increase in the observed rate, whether or not the two catalysts were present in equal concentrations. Because of these divergent indications, these runs are not considered sufficient to establish the mechanism. The indicator studies of the hexenyl acetate-mercuric acetate complex also led to results which were not found to be interpretable. It seems evident that there must be a relationship between the two sets of data, but it has not been found.

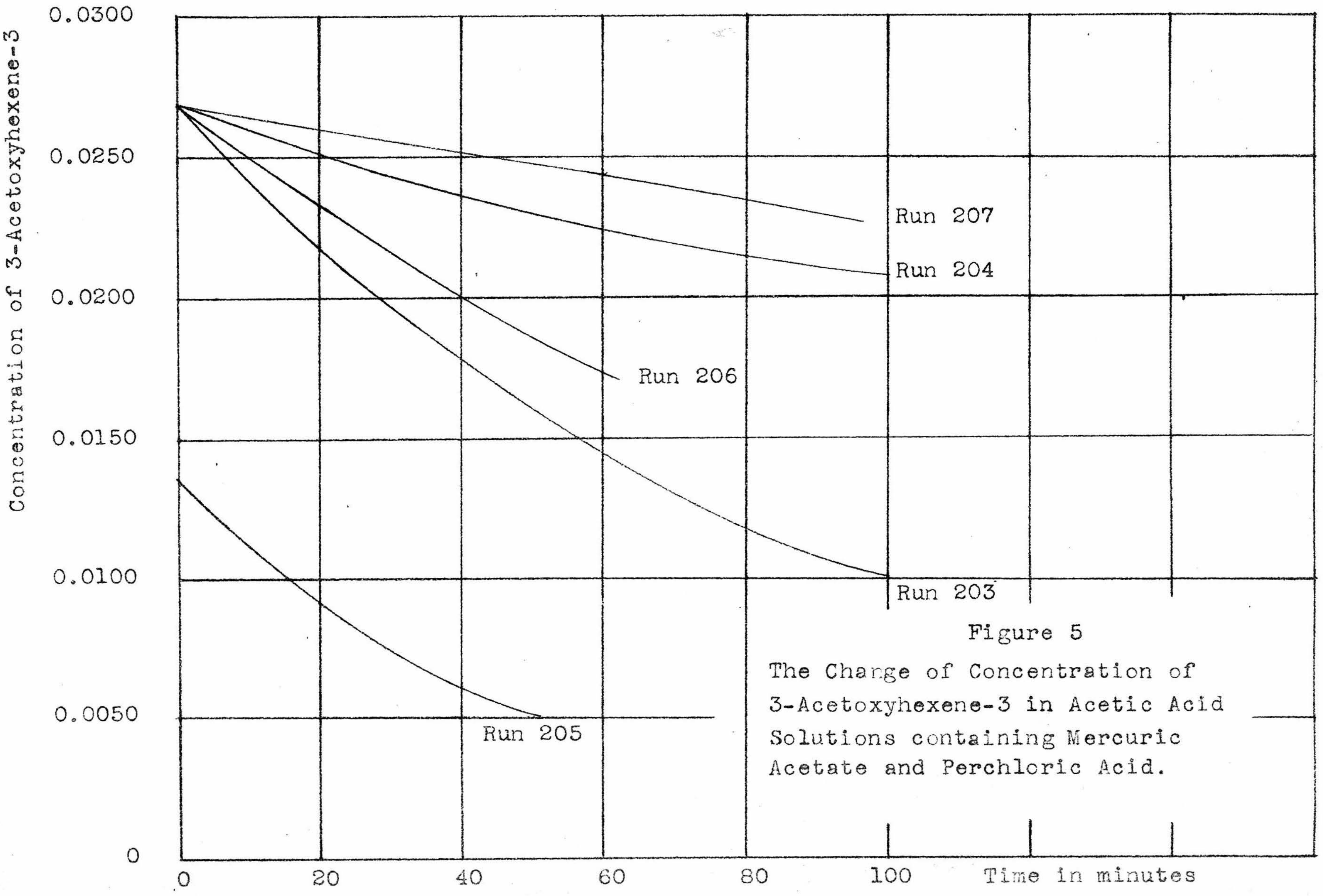


Figure 5

The Change of Concentration of 3-Acetoxyhexene-3 in Acetic Acid Solutions containing Mercuric Acetate and Perchloric Acid.

VII. Summary

The reaction of 3-hexyne with glacial acetic acid has been studied in acetic acid. In the presence of a mercuric salt and a strong acid, two moles of acetic acid were found to add to the triple bond of the hydrocarbon, forming, successively, 3-acetoxyhexene-3 (hexenyl acetate) and 3,3-diacetoxyhexane (3-hexanone diacetate). The isolation of 3-acetoxyhexene-3 and 3-hexanone was accomplished by steam distillation of particular solutions.

Because the hexanone might have been produced by hydrolysis of the hexenyl acetate during isolation, two subsidiary proofs were offered that the second mole of acetic acid does add. The acetic acid solution from which the ketone was isolated lost 95% of its initial unsaturation before the steam distillation was begun. Moreover, appropriately catalyzed solutions of hexenyl acetate in acetic acid were themselves found to lose unsaturation. The isolation of the hexanone rather than its diester is due to the instability of the diester, not only during the steam distillation but also, probably, in the acetic acid solution.

The reaction solutions were usually catalyzed both by mercuric acetate and by one of three acids - perchloric acid, sulfuric acid, or boron trifluoride. The course of each reaction was followed by bromine titration. Inconclusive results were secured using boron trifluoride, perhaps because this acid is an unusually strong electron acceptor and, therefore, more affected by impurities than the other acids. Many data were collected from runs in which sulfuric acid was the acid catalyst. No mechanism was ever found to interpret these data. By means of indicator studies it was learned that the acidity of acetic acid solutions of sulfuric acid is proportional to the concentration of the sulfuric acid at dilutions greater than 0.2 M, but that the acidity of these solutions is much less than the acidity of solutions containing equal concentrations of perchloric acid. Since no explanation for this anomaly was known, the studies using sulfuric acid were abandoned.

The mechanism of the reaction was finally elucidated from a set of runs using perchloric acid as the acid catalyst. It was found that a complex of hexyne with one mole of mercuric acetate and one mole of perchloric acid was rapidly formed in the solutions and that this complex (probably a hexyne-mercuric monoacetate cation) was the reactive species. Catalysis by either mercuric acetate or perchloric acid in excess of the complex did occur but at a slower rate.

The rate of the addition of acetic acid to this complex is in doubt because of the uncertainty as to whether the complex titrates as an alkyne or an alkene. The first order rate constant is probably between 0.2 and 1 min^{-1}.

Some data were collected on the rate of the reaction of hexenyl acetate with acetic acid in the presence of mercuric acetate and perchloric acid. Smooth, almost linear, curves of concentration against time were obtained, but no satisfactory interpretation as to mechanism was deduced.

Indicator studies were undertaken in an attempt to secure information concerning the hexyne-mercuric acetate complex. It was found that the complex included one mole of hexyne in addition to one mole each of mercuric acetate and perchloric acid. The equilibrium constant was found to be 3.5×10^7 moles^{-2} liters^2. A similar set of investigations with hexenyl acetate proved that complexes were formed with this ester but no equilibrium constant could be found which would fit all the data. The indicator studies were extended to the investigation of weak bases. The following activity constants (pK_a) were calculated for seven weak bases from observations made in acetic acid: acetonitrile, -4.2; dioxane, -4; p-toluenesulfonamide, -3.2; water, -2.3_5; acetanilide, -0.9; acetamide, 0.1; urea, 0.5.

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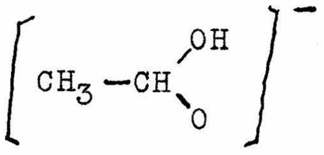
Propositions

I. Bartlett and Dauben found that trichlorophenol was a stronger acid but a weaker hydrogen donor than other phenols which they investigated. Their explanation for this apparent anomaly is probably wrong. A simpler explanation is proposed, based on the tendency of the ortho-chloro atoms to prevent either the approach of the hydrogen ion to the phenolate oxygen atom or the approach of a base to the phenol group.

Bartlett, P. D. and Dauben, H. J., J. Am. Chem. Soc., 62, 1339 (1940).

II. The effect of the presence of mercuric salts on the ozonolysis of alkenes and alkynes should be investigated with a view to increasing the yields and the rates of the reactions.

III. It is proposed that the reactive intermediate for aldol condensations occurring in water is an anion of the form shown here.



$$\left[CH_3-CH\begin{matrix} OH \\ O \end{matrix} \right]^-$$

Remick, A. E. Electronic Interpretations of Organic Chemistry, New York, 1949., p. 466.

IV. a. The steric inhibition of resonance is an accepted explanation for the enhanced basicity of N-alkylated, Propositions (continued)

ortho-substituted anilines over the free, ortho-substituted anilines. It is proposed that the same effect also plays a part in the greater basicity of N-alkylated anilines as compared to aniline itself.

b. The compound produced by the alkylation of an aromatic amine is usually a stronger base than the parent amine. An exception is 4-chloro-2-nitro-N-methylaniline. An explanation, based on the B-strain hypothesis, is proposed for this phenomenon.

H. C. Brown, 67, 1452 (1945).

V. a. Acidimetric measurements in acetic acid provide a promising tool for studying the complexes formed by metallic ions and organic compounds in solution. The investigation by this method is proposed for saturated carbocyclic and unsaturated aliphatic hydrocarbons, for aromatic hydrocarbons, including carcinogenic materials (proposed in conference with Prof. Lucas), for carbonyl compounds, and for esters.

b. The electronic configurations of the atoms which most readily form metal-olefin coordination complexes suggest that a full d subshell underlying the valence electrons may be a characteristic feature of the metallic atom in these complexes. It is proposed that barium, one of the rare earch metals, and gold be investigated for their ability to form such complexes.

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Propositions (continued)

VI. The effect of the presence of mercuric salts on the rate of bromination of ketones should be investigated.

Thesis, pp. 37-38.

VII. The indicator method of measuring the basic strength of weak bases in acetic acid should be a useful tool for the investigation of the following problems: 1) the structure of certain aliphatic amides[1]; 2) the dibasic nature of acetamide[2]; 3) the rate of the acid-catalyzed esterification of alcohols; 4) the effect of ring-strain on the basic strength of ethylene- and polymethylene- oxides; 5) the effect of a positive pole on the basic nature of an amine group in the same molecule (idea for this problem suggested by Prof. Niemann); 6) the basicity of pyrrole, isocyanates, and mesitylene[3].

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VIII. a. An investigation of the ability of butadiene to catalyze the conversion of parahydrogen to orthohydrogen would permit evaluation of the postulate[1] that one of the resonance forms of butadiene has two unpaired electrons.[2]

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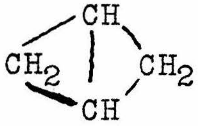
2. Selwood, P. W., _Magnetochemistry_, Evanston, 1943.

Propositions (continued)

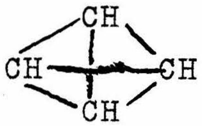
VIII. b. A surprising α, δ-migration in a pinacalone rearrangement has been reported.[1] It is proposed that a π-complex[2] is formed between the carbon-carbon triple bond and the migrating phenyl group.

1. Kleinfeller, and Eckert, Ber., 62, 1598 (1929).
2. Dewar, M. J. S., The Electronic Theory of Organic Chemistry, Oxford, 1949.

IX. The syntheses of the hydrocarbons



and



would be accomplished by the decarboxylation of the corresponding tricarboxylic acids[1]. It is proposed that this decarboxylation be attemped by treatment with silver oxide and bromine[2].

1. Thorpe, J. F. and Beesly, R. M., J. Chem. Soc., 117, 591 (1920).
2. Hunsdiecker, H., and Hunsdiecker, Cl., Ber. 75, 291 (1942).

X. On the basis of currently available information, the production of a hydrogen bomb seems highly improbable.

Time, Dec. 12, 1949., p. 48.