of concd. sulfuric acid[4] was heated for 15 minutes at 100° and poured on 200 ml. of crushed ice. The sticky semi-solid was taken up in ether, washed with sodium bicarbonate solution and the ether solution dried with magnesium sulfate. After filtering, the ether was removed to leave 2.05 g. of crystalline VII. This amount of amide is equivalent to 1.83 g. of XIII in the mixture taken and suggested that the mixture contained at least 64% of XIII. Repeated recrystallization of the crude VII from hexane–benzene followed by sublimation *in vacuo* gave colorless VII of m.p. 107.5–108.5°.

Anal. Calcd. for $C_{10}H_{19}NO$: C, 70.95; H, 11.31; N, 8.28. Found: C, 70.91, 70.88; H, 11.22, 11.30; N, 8.25.

The infrared absorption spectra of this sample of VII and the sample of VII derived from II were identical. The melting point of a mixture of the two samples of VII was not depressed.

***t*-Amyl-(methyl)-malononitrile (XIV).**—A solution of 36.1 g. (58.2 ml., 0.5 mole) of isopentane (Phillips Commercial grade, dried with phosphorus pentoxide) and 41.5 g. (41.8 ml., 0.5 mole) of 94% I in 150 ml. of *sym*-tetrachloroethane was added dropwise over 47 minutes to a stirred suspension of 133.3 g. (1.00 mole) of anhydrous aluminum chloride in 250 ml. of *sym*-tetrachloroethane at 40°. Occasional cooling was required to keep the temperature below 40°. The reaction mixture was stirred without heating or cooling for a further 30 minutes and hydrolyzed as given for the preparation of II. The hydrolysis mixture was worked up as previously described to give 76.8 g. of crude XIV (freed of solvent at 60° and 4 mm.). A preliminary distillation gave 61.0 g. of colorless, impure XIV (to 80° at 1.8 mm.) and a brown residue weighing 12.5 g. Fractionation gave 30.17 g. of forerun to 70° (2.0 mm.) and a XIV fraction of 22.32 g. (29.7%) of b.p. 70–71° (2.0 mm.). The residue weighed 2.97 g. The XIV of b.p. 70–71° (2.0 mm.) was cooled in ice and filtered with suction to give 8.89 g. of waxy crystals of XIV having a final melting temperature of 41°. The solid was recrystallized from methanol at −78°, dried *in vacuo* and sublimed at 35° (0.02 mm.) to give pure XIV having a final melting temperature of 44.4°.

Anal. Calcd. for $C_9H_{14}N_2$: C, 71.96; H, 9.39; N, 18.66. Found: C, 71.58, 71.56; H, 9.34, 9.50; N, 18.73, 18.64.

***t*-Amyl-(methyl)-cyanoacetamide (XIX).**—Treatment of XIV with concd. sulfuric acid by a standard procedure[4] gave crude XIX. Four recrystallizations from benzene–hexane gave XIX of m.p. 123–124°.

Anal. Calcd. for $C_9H_{16}N_2O$: C, 64.25; H, 9.59; N, 16.66. Found: C, 64.07, 64.04; H, 9.58, 9.56; N, 16.76, 16.75.

Benzyl-(methyl)-malononitrile (XVI).—Reaction of the sodium derivative of benzylmalononitrile in ethanol (Commercial, anhydrous) with methyl iodide by the method of Hessler[10] gave a liquid distilling at 102–106° (0.4 mm.) which partly crystallized on standing. Hessler obtained pure monoimino ester of XVI as a liquid. The mixture of b.p. 102–106° (0.4 mm.) gave a precipitate of ammonium chloride when concd. hydrochloric acid was added to its ethanol solution. This test[10] indicated the presence of the imino ester of XVI. When 5.0 g. of the mixture was refluxed gently, 0.6 g. of ethanol distilled. This corresponded to 56.6% of imino ester in the mixture. The crystalline residue was recrystallized twice from ethanol and once from ethanol–water (Norit) to give XVI of m.p. 94.5–95.5°.[11]

Anal. Calcd. for $C_{11}H_{10}N_2$: N, 16.46. Found: N, 16.41.

2-Naphthylmethyl-(methyl)-malononitrile (XVII).—To a sodium ethoxide solution prepared from 1.8 g. (0.078 atom) of sodium and 40 ml. of ethanol (Commercial anhydrous) was added 16.1 g. (0.079 mole) of 2-naphthylmethylmalononitrile.[1] The mixture was heated to near the b.p. and a solution of 4.9 ml. (11.2 g., 0.079 mole) of methyl iodide in 10 ml. of ethanol was added dropwise over a 5-minute interval. When the spontaneous reaction was over the mixture was refluxed for 30 minutes at which time the mixture was neutral. The ethanol was distilled off, water was added, and the yellow liquid was taken up in ether and dried with magnesium sulfate. After filtering, the ether was removed to leave 20.0 g. of yellow viscous liquid. This liquid contained the monoimino ester of XVII as shown by the precipitation of ammonium chloride when concd. hydrochloric acid was added to an ethanol solution of the liquid.[10] The imino ester present was decomposed by boiling the liquid gently until ethanol no longer distilled. Volume of ethanol distillate was 2.9 ml. The brown residue of XVII weighed 16.6 g. (96.5%) and solidified when cool. One recrystallization from ethanol gave 12.7 g. (73.8%) of light tan XVII of m.p. 128–129.5°. Further recrystallization gave colorless XVII of m.p. 129.2–130°.

Anal. Calcd. for $C_{15}H_{12}N_2$: N, 12.72. Found: N, 12.70.

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(10) Reference 2, p. 195.

(11) J. C. Hessler, ref. 2, p. 194, reports m.p. 94–95° for XVI.

BRECKSVILLE, OHIO

[CONTRIBUTION NO. 1922 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Mercury-catalyzed Addition of Acetic Acid to 3-Hexyne[1]

BY HENRY LEMAIRE[2a] AND HOWARD J. LUCAS[2b]

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An equimolar solution of perchloric acid and mercuric acetate in anhydrous acetic acid exhibits a very rapid drop in acidity in the presence of 3-hexyne. This is due to the formation of a stable, reactive complex ion, 3-hexyneacetoxymercurinium ion, $C_6H_{10}{\cdot}HgOAc^+$. There is also a moderately rapid drop in unsaturation, which soon tapers off to a slow change. The tapering off is believed to be due to a reaction of mercuric ion with a product of the reaction, presumably 3-acetoxy-3-hexene. Since the initial drop in unsaturation is proportional to the concentration of the complex ion rather than to the concentration of 3-hexyne, the rate-determining step is the reaction of this ion, either by solvolysis or by rearrangement, to form 3-acetoxy-3-hexene. Excess perchloric acid causes a marked increase in the rate of change of unsaturation. Excess mercuric acetate has a much smaller effect. Structures are assigned to intermediate complex mercurinium ions.

Usually the addition of reagents to the carbon-carbon triple bond requires a combination of a mercuric salt and a strong acid as catalyst. One kinetic study of this type has been reported on acetylene.[3] The present investigation was undertaken to extend information to disubstituted acetylenes. The addition of acetic acid to 3-hexyne yields 3-acetoxy-3-hexene, as shown by eq. 1.

$$C_2H_5{-}C{\equiv}C{-}C_2H_5 + HOAc \longrightarrow C_2H_5{-}CH{=}C(OAc){-}C_2H_5 \quad (1)$$

Preparation of Materials.—The preparation of 3-hexyne from ethyl bromide and sodium acetylide

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(2) (a) Lever Brothers Research Center, Edgewater, N. J. (b) To whom requests for reprints should be sent.

(3) R. H. Frieman, E. R. Kennedy and H. J. Lucas, THIS JOURNAL, **59**, 722 (1937). A mechanism of addition to the triple bond has been proposed by G. F. Hennion, R. R. Vogt and J. A. Nieuwland, *J. Org. Chem.*, **1**, 159 (1936).

was carried out in liquid ammonia.[4] The crude product was purified by fractional distillation under nitrogen. Portions were redistilled from time to time to prevent accumulation of peroxides, or other substances resulting from contact with air; b.p., 81.3° (cor. to 760 mm.),[5] $n^{25}\text{D}$ 1.4082.

Anhydrous acetic acid, perchloric acid solutions in anhydrous acetic acid and solutions of the indicators, 4-chloro-2-nitro-N-methylaniline, 2,6-dichloro-N,N-dimethylaniline and 2,4-dinitro-N,N-diethylaniline in anhydrous acetic acid were prepared as previously described.[6] Solutions of mercuric acetate in acetic acid were prepared from General Chemical Co. C.P. grade without any purification. In standard solutions made by dissolving 0.100 mole of the acetate in 1 liter of anhydrous acetic acid, a trace of undissolved solid remained suspended. Intermediate solutions were made from this 0.1 M solution by dilution with anhydrous acetic acid.

Boron trifluoride etherate[7] was distilled in air to give a nearly colorless product. A solution 0.200 M in boron trifluoride was prepared by diluting 25.0 ml. of the distillate to one liter with anhydrous acetic acid.

Method of Analysis.—The sample for analysis was removed from the solution being investigated (in a 100 ml. flask) by means of a sampling device which permitted an aliquot sample to be forced up by nitrogen pressure into a pipet calibrated for total delivery.[8] The sample was washed out with solvent. The analysis, based on that developed earlier,[9] was modified in accordance with the suggestions of W. S. Dorsey.[10] A bromate–bromide solution, 0.01667 M in bromate ion and 0.0833 M in bromide ion (0.05 M in bromine), was measured into an erlenmeyer flask, which then was evacuated and covered with a black cloth. The amount of this standard solution, 5 to 20 ml., was designed to provide an excess (15 to 30%) over the theoretical needed to combine with the unsaturated compounds present. Then 5 ml. of 6 N sulfuric acid was added and after a 5-minute interval, to allow for the liberation of bromine, the sample in the pipet was added and the pipet was rinsed with enough acetic acid so that 45 to 60 ml. of it was present. Then 3 to 4 ml. of 0.6 M mercuric sulfate in 6 N sulfuric acid was added, and after a 5- to 10-minute interval, during which time the contents were shaken occasionally, 15 ml. of 3 M potassium iodide and 100 ml. of water were added. After about one minute for liberation of iodine, the vacuum was broken and the iodine was titrated with 0.05 N thiosulfate. The results by this method are accurate for acetoxyhexene and about 6% high for 3-hexyne.

Products of Reaction.—An acetic acid solution, 0.35 M in 3-hexyne, 0.020 M in boron trifluoride[11] and 0.005 M in mercuric acetate was allowed to stand 24 hours, by which time the solution had only one-half of the original unsaturation, as determined by standard bromate–bromide.[9] Considerable water was added and the product, 3-acetoxy-3-hexene, was collected by steam distillation, crude yields, about 50%. Purification by distillation gave a colorless liquid, b.p. 72.8° (40 mm.), $d^{25}25$ 0.888, $n^{25-26}\text{D}$ 1.4197.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93; M_r, 40.49; unsat., by bromine absorption,[12] calcd. per aliquot taken, 1.644 millieq. Found: C, 68.42; H, 10.26; M_r 40.33; unsat., 1.63, 1.648, 1.652 millieq.

With perchloric acid as the catalyst in place of boron trifluoride a lower concentration of hexyne was necessary in order to obtain a satisfactory conversion to acetoxyhexene. This lower concentration rendered recovery of the acetoxyhexene more difficult than in the previous case. A solution in acetic acid, 0.088 M in 3-hexyne, 0.030 M in perchloric acid and 0.005 M in mercuric acetate, lost one third of its original unsaturation in 4.5 hours. Steam distillation at this point gave a crude yield, 23%, of product that on distillation at 33 to 34 mm. had b.p. 67–74°, $n^{25}\text{D}$ 1.4229.

Anal. C, 65.9; H, 9.9; unsaturation, 0.278 millieq. (theory, 0.291 millieq.)

This last result indicates the presence of about 5.5% of a saturated compound. It is evident that the change of unsaturation in these solutions must be due, at least to a considerable extent, to the formation of acetoxyhexene. Any mechanism that explains the rate of change of unsaturation will necessarily have taken account of the formation of acetoxyhexene.

Solutions of hexyne with mercuric acetate and either perchloric acid or boron trifluoride usually became colored. An absorption curve of the yellow component was obtained in a Beckman ultraviolet spectrophotometer. The fine structure of this absorption curve lies entirely in the ultraviolet region. The yellow color results simply from a tapering off of the absorption curve from the last peak at 398 mμ. Nevertheless, the material responsible for the color will be called the "yellow by-product." It has not been isolated, consequently its structure and concentration in the solution are not known.

Solutions in which the concentration of mercuric acetate greatly exceeded that of perchloric acid (for example, run 138, Table IV) did not develop this yellow color. These solutions did, however, show the expected loss of unsaturation. Moreover, the color intensity reached a maximum in 20–30 minutes, long after the rate of change of unsaturation had tapered off sharply. It follows,

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[4] E. A. Bried and G. F. Hennion, THIS JOURNAL, **59**, 1310 (1937).

[5] Previous values: b.p., 81.2–81.3° (747 mm)., K. N. Campbell and L. T. Eby, *ibid.*, **63**, 2683 (1941); 81° (760 mm.), A. L. Henne and K. W. Greenlee, *ibid.*, **67**, 484 (1945); 81.43° (760 mm.), $n^{20}\text{D}$ 1.412, P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg and F. L. Howard, *J. of Research*, **52**, 51 (1954).

[6] H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).

[7] This was supplied by the General Chemical Co. The authors hereby express their appreciation of this courtesy.

[8] W. F. Ebers and H. J. Lucas, THIS JOURNAL, **56**, 1230 (1934).

[9] H. J. Lucas and D. Pressman, *Ind. Eng. Chem., Anal. Ed.*, **10**, 140 (1938). In the present work the solutions were homogeneous because no carbon tetrachloride and plenty of acetic acid was present.

[10] W. S. Dorsey, Thesis, California Institute of Technology, 1950.

[11] G. F. Hennion and J. A. Nieuwland, THIS JOURNAL, **56**, 1802 (1934).

[12] It was necessary to complete the titration within one minute after the potassium iodide had been added because of a returning starch-iodine color.

therefore, that either the by-product is present only in small concentration or its formation is not related to any change in the unsaturation of the solution.

Solutions of acetoxyhexene containing mercuric acetate and either perchloric acid or boron trifluoride continue to lose unsaturation. Those containing boron trifluoride were found to give 3-hexanone. Rate studies on the loss of unsaturation of isolated acetoxyhexene have shown that the rate is of the same order of magnitude as the reaction of 3-hexyne. This second reaction can be disregarded only if the initial rate of reaction of hexyne is considered.

The expected product of this second reaction would be 3,3-diacetoxyhexane. This, however, probably is unstable under the conditions of the experiment, decomposing to 3-hexanone and acetic anhydride (eq. 2).

$$C_2H_5CH_2C(OCOCH_3)_2C_2H_5 \longrightarrow C_2H_5CH_2COC_2H_5 + (CH_3CO)_2O \quad (2)$$

The effects of these subsequent reaction products, *viz.*, hexanone and acetic anhydride, on the course of the reaction are negligible, as shown by runs containing larger amounts of ketone (in these cases 3-pentanone) or acetic anhydride than could be present from hexyne. Another explanation of the formation of the ketone is decomposition of the diacetate during its isolation by steam distillation.

Nature of the Complex Involving 3-Hexyne and Mercuric Acetate.—During the course of kinetic studies it became evident that some sort of a complex was being formed rapidly in the anhydrous acetic acid solution containing hexyne, mercuric acetate and perchloric acid. It was necessary to determine the nature of this complex in order to interpret the kinetic data. This problem was investigated by the indicator method previously used for determining the basic strength of weak bases,[6] by measurements in acetic acid containing perchloric acid. In the present case it was noted that perchloric acid disappeared rapidly when mercuric acetate and 3-hexyne were also present in solution. This change might arise in one of three ways, as shown by eq. 3, 4 and 5.

$$C_6H_{10} + H^+ \rightleftarrows C_6H_{10}\cdot H^+ \quad (3)$$

$$(AcO)_2Hg + H^+ \rightleftarrows (AcO)_2Hg\cdot H^+ \rightleftarrows AcOHg^+ + AcOH \quad (4)$$

$$(AcO)_2Hg + C_6H_{10} + H^+ \rightleftarrows (AcO)_2Hg\cdot C_6H_{10}\cdot H^+ \rightleftarrows AcOHg\cdot C_6H_{10}{}^+ + AcOH \quad (5)$$

The three systems, namely, the hexyne–perchloric acid, the mercuric acetate–perchloric acid and the hexyne–mercuric acetate–perchloric acid systems were investigated by the indicator method,[6] the first with 4-chloro-2-nitro-N-methylaniline and 2,6-dichloro-4-nitro-N,N-dimethylaniline as the indicators, the second with 4-chloro-2-nitroaniline and the third system with 2,4-dinitro-N,N-diethylaniline. The values of the ionization constants in acetic acid, $K^{\mathrm{s}}_{\mathrm{aI}}$, are: 0.17 for 2,6-dichloro-4-nitro-N,N-diethylaniline,[6] 3.9 for 4-chloro-2-nitro-N-methylaniline and 0.06 for 2,4-dinitro-N,N-diethylaniline (Table I). In this method the drop in the acidity of the solution affects the indicator, which is colored in the uncombined form and colorless in its protonated form (conjugate acid). From the change in the concentration of the colored form of the indicator the concentration of free perchloric acid can be calculated.

TABLE I

INDICATOR CONSTANTS

Solution no., ref. 6	Indicator	Indicator concn. in anhyd. HOAc, $I \times 10^4$	$K^{\mathrm{S}}_{\mathrm{aI}}$ 10^3	pK_a
IIIB	4-Chloro-2-nitro-N-methylaniline	5.00	3.96	−1.48
IIID	4-Chloro-2-nitro-N-methylaniline	4.27	3.85	−1.47
VA	2,4-Dinitro-N,N-diethylaniline	3.18	0.0655	0.30
VC	2,4-Dinitro-N,N-diethylaniline	2.96	.0544	.38

No protonation of hexyne could be detected. Mercuric acetate, however, was found to be weakly basic. Its constant in acetic acid, $K^{\mathrm{s}}_{\mathrm{am}}$, calculated by the method described previously,[6] Table II, was found to be 0.014. Here K_a represents the ionization constant of the conjugate acid of the base, the superscript s indicates a solvent other than water, in this case acetic acid, and the subscript m stands for mercuric acetate. This corresponds to a pK_a of −2.02, which indicates that mercuric acetate is slightly more basic than water. The extent to which reaction takes place between mercuric acetate and perchloric acid at the concentrations prevailing is 2 to 10%. The extent of a second reaction yielding mercuric ion must be slight indeed, in view of the small change in the constant over a threefold range in the concentration of perchloric acid, Table II, and a sevenfold range in the concentration of mercuric acetate. According to these measurements, hexyne does not react at all with perchloric acid, and mercuric acetate reacts only to a limited extent.

Perchloric acid reacts extensively when 3-hexyne and mercuric acetate are both present, as shown by the marked drop in the acidity of the solution. In fact, it is necessary that the concentrations of all three substances be quite low, otherwise the reaction proceeds so far to completion that accurate measurements cannot be made. It is evident, therefore, that the change is due either to the reaction of eq. 5, or to one involving these three compounds in a different ratio.

On the assumption that the reaction is correctly represented by eq. 5, the equilibrium constant $K^{\mathrm{s}}_{\mathrm{bx^+}}$ is expressed by eq. 6. Here subscript x^+ represents the complex ion, K_b represents a basic constant, the reciprocal of the acid constant of the complex ion, $[X^+]$ is the molal (formal) concentration of this complex, $[H^+]$ is the molal concentration of the uncombined acid (solvated proton), [Hg] is the molal concentration of uncombined mercuric acetate, and $[Hx_t]$ is the molal concentration of total hexyne.

$$K^{\mathrm{s}}_{\mathrm{bx^+}} = \frac{[X^+]}{[H^+][Hg]([Hx_t] - [X^+])} \quad (6)$$

These values may be expressed in terms of quantities that can be determined, as shown by eq. 7, 8 and 9.

$$[\mathrm{H}^+] = K^{s}_{\mathrm{aI}}\,(S - T)/T \qquad (7)$$

$$[\mathrm{Hg}] = [\mathrm{Hg_t}] - [\mathrm{H_t}^+] + [\mathrm{H}^+] + [\mathrm{I_t}](S - T)/S \qquad (8)$$

$$[\mathrm{X}^+] = [\mathrm{Hg_t}] - [\mathrm{Hg}] - [\mathrm{Hg}][\mathrm{H}^+]/K^{s}_{\mathrm{am}} \qquad (9)$$

Here $[\mathrm{Hg_t}]$ is the molal concentration of the total mercuric acetate, $[\mathrm{H_t}^+]$ is the molal concentration of total perchloric acid, $[\mathrm{I_t}]$ (*C* in the previous paper[6]) is the molal concentration of total indicator, and the values of *S* and *T* are obtained from readings of the optical densities of the solutions,[13] which are made with a Beckman ultraviolet spectrophotometer.

TABLE II

BASIC STRENGTH OF MERCURIC ACETATE

Indicator soln.[a] No.	Optical density S	Indicator diln. factor, F	Test soln. HClO$_4$, total concn. $[\mathrm{H_t}^+] \times 10^2$	Test soln. Hg(OAc)$_2$, total concn. $[\mathrm{Hg_t}] \times 10^3$	Optical density $T \times F$	Basic strength[b] K^{s}_{bm}
IIIB	2.870	5/28	0.536	14.3	0.480, 0.480	70, 70[c]
IIID	2.455	5/28	1.783	2.14	.313$_5$	78

[a] Reference 6. [b] $K^{s}_{\mathrm{bm}} = \dfrac{[\mathrm{H_t}^+] - [\mathrm{I_t}](S-T)/S - K^{s}_{\mathrm{aI}}(S-T)/T}{\{[\mathrm{Hg_t}] - [\mathrm{H_t}^+] + [\mathrm{I_t}](S-T)/S + K^{s}_{\mathrm{aI}}(S-T)/T[K^{s}_{\mathrm{aI}}(S-T)/T]\}}$

[c] Duplicate determinations.

Two corrections have been made on the optical densities observed in the test solutions. First, the optical density of the yellow by-product was determined and subtracted from the observed optical density. The resulting difference is recorded in Table III as "Indicator Optical Density, *T* × *F*." Second, these values were extrapolated back to zero time because the equilibrium expressed by eq. 5 is affected by the conversion of 3-hexyne to acetoxyhexene. Fortunately the indicator optical densities did not change as rapidly as might have been anticipated from the data of Table IV. This probably is due, in part, to the fact that acetoxyhexene also reacts with mercuric acetate to lower the acidity by formation of a mercury complex.[14]

TABLE III

OBSERVATIONS ON THE HEXYNE–MERCURIC ACETATE–PERCHLORIC ACID COMPLEX

Run no.	Indicator No.	Indicator Optical density S	Indicator diln. factor, F	HClO$_4$ total $[\mathrm{H_t}^+] \times 10^3$	Hexyne total $[\mathrm{Hx_t}] \times 10^3$	(AcO)$_2$Hg total $[\mathrm{Hg_t}] \times 10^3$	Test solution: Indicator optical density, $T \times F$: Zero time[a]	1 min.	1.5 min.	2 min.	3 min.	4 min.
694a	VA	4.97	1/5	0.400	0.424	0.800	0.366	0.370	0.376		0.386	0.383
694b	VA	4.97	1/4	.500	.530	.500	.360	.373	385	0.394	.395	.400
696a	VA	4.97	10/33	.606	.643	.182	.227	.227	.227	.225	.228	.231
699c	VA	4.97	1/3	.467	.212	.667	.395	.398	.401	.388	387	.390
704a	VC	4.98	10/32	.750	.331	.312	.162	.165	.168	.166	.164	

[a] Extrapolated.

TABLE IV

COMPUTATION OF THE EQUILIBRIUM CONSTANT OF THE HEXYNE–MERCURIC ACETATE–PERCHLORIC ACID COMPLEX

Run no.	Perchloric acid combined with Indicator $[\mathrm{IH}^+] \times 10^3$	Perchloric acid combined with complex $[\mathrm{X}^+] \times 10^3$	Mer. acetate AcOHg$^+$ × 10^3	Free $[\mathrm{H}^+] \times 10^3$	Hexyne Total $[\mathrm{Hx_t}] \times 10^3$	Hexyne Free $([\mathrm{Hx_t}] - [\mathrm{X}^+])10^3$	Mercuric acetate Total $[\mathrm{Hg_t}] \times 10^3$	Mercuric acetate Free $[\mathrm{Hg}] \times 10^3$	$K^{S}_{\mathrm{bx^+}} \times 10^{-7}$
694a	0.360[a]	0.244	0.004	0.112	0.424	0.180	0.800	0.552	2.2
694b	.443	.280	.002	.161	.530	.250	.500	.218	3.2
696a	.524	.153	.001	.370	.643	.490	.182	.028	3.0
699c	.386	.169	.007	.210	.212	.043	.667	.491	3.8
704a	.668	.208	.003	.457	.331	.125	.312	.101	3.6

[a] $[\mathrm{IH}^+]$ is the concentration of the conjugate acid of the indicator.

The conditions and data of five tests to determine the value of $K^{s}_{\mathrm{bx^+}}$ are shown in Table III. The calculated values of free acid, free mercuric acetate and free hexyne are shown in Table IV. This also has values for the equilibrium constant calculated with eq. 6. The agreement is regarded as satisfactory in view of the wide range of concentrations covered by the free portion of each of the three components, and the sensitiveness of the calculation to small errors. The data, therefore, indicate a complex formed by the rapid reaction of one mole each of 3-hexyne, mercuric acetate and perchloric acid, according to eq. 5. The best value of the constant is about 3 × 10^7 liters^2 moles^{-2}.

Kinetic Studies.—Perchloric acid was selected as the acid catalyst in conjunction with mercuric acetate despite the evident superiority of boron trifluoride from the standpoint of ease of isolation of acetoxyhexene. This was done because considerable data are available on the properties of acetic acid solutions of perchloric acid,[6] and also because the ether–boron trifluoride complex would be a disturbing factor in kinetic investigations.

The initial rates of reaction were determined with solutions kept under nitrogen at all times, to avoid contact with oxygen. An aliquot of a dilute, intermediate solution of 3-hexyne in anhydrous acetic acid was added to a known volume of a freshly prepared solution containing the desired amounts of mercuric acetate and perchloric acid in anhydrous acetic acid. The amount of hexyne initially present was calculated from the analysis[9] of an aliquot of the intermediate solution. Analy-

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(13) *S* is the optical density of a stock indicator solution. *T* is the calculated optical density of a hypothetical solution and is obtained from the observed optical density of a test solution prepared from a second stock solution by addition of perchloric acid and solvent. This observed optical density divided by the dilution factor, *F*, gives the calculated optical density, *T*. In this way all optical densities are adjusted to a common basis. *S* is a measure of total indicator, and *T*, of just the unprotonated (colored) indicator concentration. *F* is so taken ($^1/_3$ to $^1/_{10}$) that observed readings (*T* × *F*) will lie in the range 0.2 to 0.5. Table II.

(14) This complex was investigated similarly to the hexyne complex. The data show that in solutions of acetoxyhexene, perchloric acid and mercuric acetate a considerable amount of the proton is combined.

sis for unsaturation was made as rapidly as possible on an aliquot of the final solution.

If the titer of an intermediate solution showed any change with time, the run was discarded because contamination by oxygen was suspected. For this reason run 134 was rejected. The runs were made at room temperature without additional control, mainly because of the necessity of preparing so many different solutions. Preliminary experiments had shown no decided temperature dependence.

Calculations.—An approximate balance between the initial concentration of hexyne, $[\mathrm{Hx}_0]$, hexyne at time, τ, $[\mathrm{Hx}_\tau]$, and the concentration of acetoxyhexene, [A], during the early stages of the reaction is given by eq. 10, in which the symbols represent moles per liter.

$$[\mathrm{Hx}_0] = [\mathrm{Hx}_\tau] + [\mathrm{A}] \qquad (10)$$

The unsaturation observed, that is, the apparent unsaturation, $[\mathrm{U_a}]$, in equivalents per liter, is given by eq. 11, provided there are no complications from the catalysts and taking account of the fact that the titer for hexyne is 6% high.

$$[\mathrm{U_a}] = 4(1.06)[\mathrm{Hx}_\tau] + 2\,[\mathrm{A}] \qquad (11)$$

Combining eq. 10 and 11, the concentration of hexyne is expressed in terms of measurable quantities by eq. 12, except for the fact that the apparent initial hexyne, $[\mathrm{Hx}_{a0}]$, is also 6% high, as shown by eq. 13. Thus the correction for this leads to eq. 14, the one used for calculations.

$$[\mathrm{Hx}_\tau] = \frac{[\mathrm{U_a}] - 2[\mathrm{Hx}_0]}{2.24} \qquad (12)$$

$$[\mathrm{Hx}_{a0}] = 1.06[\mathrm{Hx}_0] \qquad (13)$$

$$[\mathrm{Hx}_\tau] = \frac{[\mathrm{U_a}] - 1.89[\mathrm{Hx}_{a0}]}{2.24} \qquad (14)$$

The calculations are complicated by the rapid formation of the complex between hexyne, mercuric acetate and perchloric acid, as described earlier under Nature of the Complex. The minimum of time necessary for adding the hexyne solution to that of the catalysts, mixing thoroughly, taking a sample and adding this to the bromine solution is about 2.5 minutes. The drop in unsaturation at this point was always more than that corresponding to the formation of an addition product titrating as an alkene. This suggests that the complex, known to be formed rapidly between hexyne and mercuric acetate, may titrate as an alkene. If this is so, then the initial, precipitous drop in unsaturation is due to the effect of the formation of the complex superimposed on the effect caused by the change of 3-hexyne to 3-acetoxy-3-hexene. If the complex titrates as an alkene, then the equivalents of unsaturation present in the solution are given by eq. 15, in which $[\mathrm{Hx}_\tau]$ is still the total concentration of hexyne, including that in the form of the complex and $[\mathrm{X}^+]$ is the concentration of the complex that titrates as an alkene. Combining eq. 10 and 15 gives eq. 16.

$$[\mathrm{U_a}] = 4(1.06)([\mathrm{Hx}_\tau] - [\mathrm{H}^+]) + 2[\mathrm{H}^+] + 2[\mathrm{A}] \qquad (15)$$

$$[\mathrm{Hx}_\tau] = \frac{[\mathrm{U_a}] - 2[\mathrm{Hx}_0]}{2.24} + [\mathrm{X}^+] \qquad (16)$$

There is also the possibility that the complex titrates as an alkyne, consequently the initial rates of reaction are in doubt by a factor of more than two. However, the interpretation of the data can be made on either basis, with a similar conclusion.

The calculations are complicated also by a fairly rapid tapering off of the rate subsequent to the initial rapid drop in unsaturation. The tapering off is greater than would be expected in a first-order reaction and leads to the conclusion that the first reaction product, acetoxyhexene, markedly reduces the activity of the catalyst by combining with it, probably forming either a stable addition compound or a coördination complex, as noted in the case of cyclohexene.[15] There are indications that acetoxyhexene does indeed combine with mercuric acetate.[14] Thus the shape of the curve and its slope at zero time are not known with certainty because of these two complicating factors, namely, the rapid reaction of the catalyst (1) with hexyne to form an addition compound that may titrate as an alkene, and (2) with acetoxyhexene to cause a reduction in catalytic activity.

Because of the uncertainty as to whether the hexyne complex titrates as an alkyne or an alkene, two sets of values of $[\mathrm{Hx}_\tau]$ have been calculated for each run, one with eq. 14, and the other with eq. 16. From each set of values a curve of concentration *vs.* time is constructed and a chord is drawn between zero time and 2.5 minutes, the approximate time of the first analysis. The change in hexyne concentration in 2.5 minutes is divided by 2.5, to give an approximate slope of this chord. This treatment leads to the rate of change per minute on the assumption of a straight line drop in hexyne concentration to this point. This rate is then multiplied by 1.5, a factor believed to represent the best approximation of the ratio between the initial slope and that of the 2.5 minute chord. This estimated initial rate (slope at zero time) (last two columns, Table V) is then divided by the concentration of the complex in the solution calculated at zero time to give values of the reaction rate constant, *k* (Table VI).

Interpretation of the Kinetic Data.—In Table V are the data of a number of runs of 3-hexyne, mercuric acetate and perchloric acid in anhydrous acetic acid. The concentration of initial hexyne varies over a threefold range of concentration, those of mercuric acetate and perchloric acid also over a threefold range, excluding experiments with zero concentration. It will be observed that there is a rapid drop of hexyne, $[\mathrm{Hx}_\tau]$ by the time the first analysis is made, followed by a slower drop and a final tapering off. Also, in the absence of either mercuric acetate or perchloric acid the loss of unsaturation proceeds at a much slower rate.

The following conclusions in regard to the rate can be drawn from a casual perusal: (1) the initial rate is independent of the initial concentration of hexyne; (2) in those runs in which the concentra-

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[15] H. J. Lucas, F. R. Hepner and S. Winstein, THIS JOURNAL, **61**, 3102 (1939). See also J. Chatt, *Chem. Revs.*, **48**, 7 (1951). Objections have been raised to the idea of alkene mercurinium complexes, G. F Wright, *Chemistry in Can.*, **2**, 149 (1950); A. G. Brook, A. Rodgman and G. F Wright, *J. Org. Chem.*, **17**, 988 (1952); A. Rodgman and G. F Wright, *ibid.*, **18**, 1617 (1953).

TABLE V

DATA ON THE DISAPPEARANCE OF 3-HEXYNE WITH ANHYDROUS ACETIC ACID

Run no.	Temp., °C.	$(AcO)_2Hg$ $[Hg_t]$ $\times 10^3$	$HClO_4$ $[H_t^+]$ $\times 10^3$	Time, min.	$[U_a]$ equiv. $\times 10^3$	Hexyne concn. $[Hx_r] \times 10^3$ Eq. 14	Eq. 16	Estimated initial rate Eq. 14	Eq. 16
130	29	1.5	1.5	0		5.80	5.80	1.32	0.54
				3.5	19.1	3.34	4.74		
				31	16.9	2.37	3.77		
				60	16.2	2.04	3.44		
131	25	1	1	0		5.80	5.80	0.87	0.33
				2.7	21.2	4.30	5.22		
				10	20.0	3.75	4.67		
				44	18.7	3.16	4.08		
				131	18.6	3.12	4.04		
132	24	1	1	0		11.60	11.60	0.84	0.37
				2.7	46.0	10.15	11.09		
				10	44.7	9.60	10.54		
				36	43.5	9.05	9.99		
133	25	0.5	0.5	0		5.80	5.80	0.42	0.15
				2.3	23.0	5.10	5.55		
				10.2	22.6	4.91	5.36		
				39	22.3	4.78	5.23		
135	25	1	1	0		3.48	3.48	0.96	0.42
				2.5	11.17	1.88	2.77		
				9.7	9.97	1.35	2.24		
				45	9.58	1.17	2.06		
136	25	0.5	0.5	0		3.48	3.48	0.39	0.15
				3.5	13.18	2.78	3.21		
				13.7	12.70	2.56	2.99		
137	26	0.5	1.5	0		5.80	5.80	0.66	0.36
				3	22.0	4.66	5.16		
				11	21.0	4.22	4.72		
				39	19.1	3.34	3.84		
				143	15.6	1.80	2.30		
138	28	1.5	0.5	0		5.80	5.80	0.63	0.33
				2.3	22.2	4.75	5.25		
				9.5	21.3	4.32	4.82		
				48	21.4	4.36	4.86		
A1	27	0	0.5	0		5.80			
				58	24.7	5.85			
A2	27	0	1	0		5.80			
				26	24.5	5.75			
A3	25	0	2.5	0		5.80			
				2.5	24.0	5.55			
				32	24.0	5.55			
M1	23	0.5	0	0		5.80		0.09[a]	
				2.5	24.3	5.65			
				32	21.7	4.50(?)			
M2	24	1.0	0	0		5.80		0.18[a]	
				2.5	23.9	5.49			
				54	23.5	5.31			
M3	23	1.5	0	0		5.80		0.33[a]	
				2.5	23.4	5.26			
				26	23.7	5.38			

[a] Approximate only.

tions of mercuric acetate and perchloric acid are alike, the initial rate is roughly proportional to this concentration.

In Table VI are shown the ratios of the initial rates of reaction found in the ninth and tenth columns of Table V, to the concentration of the complex, calculated with the equilibrium constant, 3×10^7 liters^2 moles^{-2}. In those cases where the concentration of mercuric acetate equalled that of perchloric acid, runs 130 to 136, inclusive, the values of the two sets of ratios agree well with themselves. In the one in which mercuric acetate is in excess, run 138, the ratio is larger than in the other cases, but when correction is made for the catalytic effect of mercuric acetate alone, runs M1, M2 and M3, Table V, agreement is found with

TABLE VI

REACTION RATE CONSTANTS, INITIAL SLOPE/INITIAL CONCENTRATION OF COMPLEX ION

Run no.	Complex $[X^+] \times 10^3$	Rate constant, k, min.$^{-1}$	
		Eq. 14	Eq. 16
130	1.40	0.95	0.38
131	0.92	.95	.36
132	.945	.92	.39
133	.45	.93	.33
135	.89	1.1	.47
136	.43	0.91	.35
137	.50	1.3	.72
138	.50	0.92[a]	.33[a]

[a] Corrected for catalytic effect of excess mercuric acetate from exps. M1, M2 and M3, Table V.

the other values. With the exception of run 137, where perchloric acid is in excess of mercuric acetate, the rate of disappearance of 3-hexyne is proportional to the concentration of the complex.

Mechanism.—The mechanism of this reaction, therefore, involves the initial rapid formation of the complex, eq. 18, and a subsequent slower reaction of the complex, presumably with acetic acid, eq. 19.

$$\mathrm{Et{-}C{\equiv}C{-}Et + H^+ + Hg(OAc)_2 \longrightarrow [EtC{=}C(HgOAc)Et]^+ + AcOH} \quad (18)$$

$$\mathrm{[EtC{=}C(HgOAc)Et]^+ + AcOH \longrightarrow EtCH{=}C(OAc)Et + AcOHg^+} \quad (19)$$

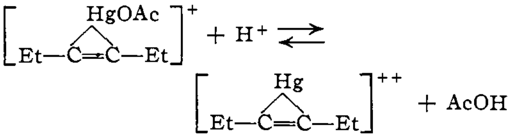
The reaction of the complex is the rate-determining step. This may be a reaction with acetic acid (eq. 19) or it may be a rearrangement in which acetate ion migrates from mercury to carbon, leading in the former case to the formation of 3-acetoxy-3-hexene and, in the latter case, to the formation of a second mercury complex. This would provide one explanation for the rapid loss of catalytic effect.

The actual value of the reaction rate constant is uncertain, because of the uncertainty as to how the complex titrates. If it titrates as an alkyne, the specific rate constant is 0.9 per minute (Table VI) and if it titrates as an alkene, 0.4 per minute. The former value is the more likely one, because the 3-hexyne–silver ion complex is known to titrate as an alkyne.[10]

The catalytic effect of mercuric acetate alone probably is due to the formation of the same complex, but to a less extent than in the presence of perchloric acid because of the formation of two oppositely charged ions, as shown by eq. 20. The

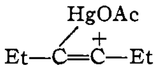
$$\mathrm{Et{-}C{\equiv}C{-}Et + (AcO)_2Hg \rightleftarrows EtC{=}C(HgOAc)Et^+ + AcO^-} \quad (20)$$

catalytic effect of excess perchloric acid probably is due to the formation of a small amount of a doubly charged complex possessing enhanced catalytic activity (eq. 21).

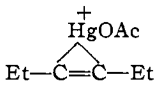


(21)

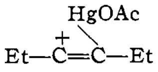
Structure of Complex Ions.—The complex ion that mercuric acetate forms with hexyne is stabilized by resonance, recalling the structure of the cyclohexene–mercury complexes,[15] the numerous olefin–silver ion complexes[16] and other three-membered ring complex ions. The possible resonance forms of the hexyne complex[17] are shown as I to III.



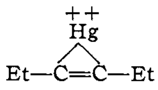
I



II



III



IV

The dipositive 3-hexynemercurinium ion, IV, which is formed by excess of perchloric acid, is also stabilized by resonance.[18] There are four non-cyclic forms and four other cyclic forms. Although none of these forms has anything other than a low stability, the contribution of so many resonance forms, nine in all, adds stability to the ion. Owing to its dipositive charge the ion would be expected to be strongly electrophilic and to react rapidly with acetic acid.

TABLE VII

RATIO OF OPTICAL DENSITY OF YELLOW BY-PRODUCT TO CONCENTRATION OF COMPLEX ION

Run no.	Optical density at 360 mμ in 1-cm. cell	Complex ion $[X^+] \times 10^3$	Ratio, density/concn.
C130	0.390	1.40	280
C131	.239	0.92	260
C132	.238	.945	250
C133	.105	.45	230
C135	.270	.89	300
C136	.112	.43	260
C137	.242	.50	480
C138	.000	.50	0

The Yellow By-product.—The intensity of the yellow color formed in these solutions seems to be related to the concentration of 3-hexyneacetoxymercurinium ion. Optical densities of solutions C130 to C138 (Table VII) similar to those of runs 130 to 138 (Table V) were measured in a 1-cm. cell of a Beckman ultraviolet spectrophotometer at 360 mμ 2.5 minutes after preparation. In the first six, in which the ratio of mercuric acetate to perchloric acid was unity, the ratio of intensity of color to concentration of the complex ion was fairly constant, Table VII. The spread in values could well be due to traces of water, for small amounts of water strongly inhibit the development of color. In run C137, which contained three moles of perchloric acid to one of mercuric acetate, the ratio was higher than in these six, while in run C138, which contained one mole of perchloric acid to three of mercuric acetate, there was no color. Attempts to isolate the colored product or to deduce its nature were unsuccessful.

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[16] F. R. Hepner, K. N. Trueblood and H. J. Lucas, THIS JOURNAL, **74**, 1333 (1952). These authors give a number of references.

[17] This might be called 3-hexyneacetoxymercurinium ion, or acetoxymercury(II)-3-hexynium ion according to a system recommended by N. H. Koenig, (Ph.D. Thesis, California Institute of Technology, 1950).

[18] This is 3-hexynemercurinium ion, or, according to Koenig, mercury(II)-3-hexynium ion.