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The Homogeneously Catalyzed Hydration of Acetylenes by Mercuric Perchlorate-Perchloric Acid: Evidence for a Bis-(acetylene)-Mercuric Ion Complex as an Intermediate

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RECEIVED MARCH 28, 1963

The effects of the relative concentrations of phenylacetylene, mercuric perchlorate, perchloric acid, and water in dioxane solution on the yields of acetophenone produced by the hydration of the acetylene were studied. With relatively small amounts of water brilliantly yellow-colored solutions formed on mixing the reactants. As the color dissipated acetophenone was formed in highly reproducible yields. With phenylacetylene to mercuric ion ratios of one, nearly 50% yields were obtained. Increasing the ratio of substrate to mercuric ion increased the production of acetophenone, while decreasing this ratio led to reductions in yield. These results are interpreted in terms of a bis-(acetylene)-mercuric ion complex as a critical intermediate in the hydration process. This intermediate is responsible for the yellow coloration and is the only species in which phenylacetylene is rapidly hydrated. This hypothesis is supported by the identification of a bis-(diphenylacetylene)-mercuric ion complex in the same medium. The spectral and other properties of these catalyst systems are discussed, and the synthetic potential of this catalyst system is considered.

The addition of water to acetylenes (hydration), which is catalyzed by acids and/or mercury compounds, is a well-known process. The carbon-carbon triple bond also adds, in similarly catalyzed reactions, a variety of alcohols, acids, amines, and in certain instances, the mercury compounds themselves.

The purely acid-catalyzed reaction is rare, apparently occurring readily in only a very few cases, namely functionally substituted acetylenes such as acetylenic ethers and thioethers. Mechanistic studies on the hydration of the latter have been conducted by Drenth and co-workers.³

The mercury-catalyzed reactions have been the objects of considerable study; in particular, the hydration of acetylene, because of the obvious commercial application, has been the object of intense interest. Yet despite these efforts and considerable mechanistic speculation, virtually no contemporarily acceptable evidence is available concerning the precise role of mercury in these reactions. Many workers have suggested that acetylene-mercury π -complexes are intermediates, but very little information is available to support these suggestions. Kinetic studies of the hydration of acetylene in aqueous sulfuric acid solutions of mercuric sulfate have been cumbersome, inconclusive, lacking in detail, and contradictory.⁴⁻⁶ Lemaire and Lucas⁷ have presented some evidence for a 3-hexyne-acetoxymercuric ion complex as an intermediate in the mercuric acetate-perchloric acid-catalyzed addition of acetic acid to 3-hexyne in glacial acetic acid. This information, although useful, is lacking in detail and clearly does not necessarily apply to hydration reactions in aqueous or mixed aqueous-organic solutions.

The present research has been concerned with a detailed study of the role of mercury in the catalysis of the hydration of simple, nonfunctionally substituted terminal acetylenes.

A detailed study of the kinetics and mechanism of the reaction of organomercuric halides with these same acetylenes in basic aqueous dioxane mixtures has been conducted.⁸ The latter is pertinent to the former in the sense that many workers have suggested the intermediacy of materials containing carbon-mercury bonds in the mercury-catalyzed hydration of acetylenes.

The precise conditions favoring their formation in basic solution have been established in the latter study.

In preliminary studies involving the system *phenylacetylene, mercuric chloride, hydrochloric acid, ethanol, and water*, a highly complex and insoluble "intermediate" was observed. The recognition that chloride ion, as shown by its presence in the composition of the "intermediate" and by its inhibiting effect when present in too high a concentration, plays an important role in the reaction led to the conclusion that more fundamental information with respect to the interaction of mercury compounds and acetylenes could be gained by utilization of a mercury salt whose anion had a considerably smaller tendency to complex than chloride ion. To this end mercuric perchlorate was selected for study.

Experimental

Diphenylacetylene, mercuric chloride, mercuric oxide (yellow), lithium perchlorate, and deoxybenzoin were all commercially available reagent grade chemicals and were used without further purification. Lithium chloride, similarly reagent grade, was dried to constant weight and protected from moisture during storage. Concentrated perchloric acid was Baker Analyzed Reagent, lot 29031, which had a manufacturer's perchloric acid assay of 71.1%. This reagent was stored in a tightly capped bottle at 22° in an area of low atmospheric moisture content. All calculations of acid and water concentrations were made with the assumptions that the perchloric acid assay was correct and that the water content was 28.9%. Dioxane was Matheson Coleman and Bell Spectral grade. Phenylacetylene (b.p. 46-47°, (21 mm.)), 1-hexyne (b.p. 70-71° (740 mm.)), acetophenone (b.p. 201-202° (760 mm.)), and 2-octanone (b.p. 172-174° (760 mm.)) were commercially available materials which were fractionally distilled and stored in sealed ampoules in a refrigerator until used.

Infrared spectra were obtained with a Baird-Atomic spectrophotometer, ultraviolet spectra with a Cary Model 11 spectrophotometer, and nuclear magnetic resonance spectra with a Varian Associates Model A-60 spectrophotometer. Infrared spectra of aqueous solutions were obtained with the use of Eastman Kodak Irtran-2 cell windows.

Aqueous Perchloric Acid-Dioxane Solutions of Mercuric Perchlorate.—The appropriate amount of mercuric oxide, carefully weighed on an analytical balance into a volumetric flask, was treated with a similarly weighed portion of concentrated perchloric acid. After solution was complete, any additional amounts of water which were desired were added by pipet or syringe. The clear colorless solution was cooled in an ice bath and dioxane was added carefully with continuous cooling. Occasionally a white precipitate appeared after addition of the initial portion of the dioxane, but this dissolved readily in excess solvent with carefully controlled warming to room temperature. The final dilution to the mark of the flask was made after 2-24 hr. equilibration at 22°.

The mercuric perchlorate solutions were stored at 22° and in general remained homogeneous for up to several weeks. With those solutions of relatively low water content, a highly crystalline material formed after 2 to 4 days. Although perfectly stable for long periods of time when in equilibration with the solution, the crystalline material was highly unstable when exposed to the atmosphere and disintegrated rapidly into a fine dark gray hygroscopic mass. Rapid infrared analysis showed bands at 1138, 937, and 630 cm^{-1} which are associated with

(1) Diamond Alkali Co. Predoctoral Fellow.

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(3) W. Drenth and H. Hogeveen, *Rec. trav. chim.*, **79**, 1002 (1960).(4) R. H. Frieman, E. R. Kennedy, and H. J. Lucas, *J. Am. Chem. Soc.*, **59**, 722 (1937).(5) K. Schwabe and H. Berg, *Chem. Abstr.*, **49**, 5091f (1955); *Z. physik. Chem.*, **203**, 383 (1954).(6) M. K. Kal'fus and D. V. Sokol'skii, *Chem. Abstr.*, **52**, 2510c (1958); *Vestnik Akad. Nauk Kazakh. S.S.R.*, **13**, 74 (1957).(7) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.*, **77**, 939 (1955).(8) R. E. Dessy, W. L. Budde, and C. Woodruff, *ibid.*, **84**, 1172 (1962).

the perchlorate anion. A band near 3300 cm^{-1} indicated water and since all other absorptions were identical, although in some cases broadened, with those appearing in the spectrum of pure dioxane, it was concluded that this material was mercuric perchlorate containing some loosely bound dioxane.

Analysis of Hydration Reaction Yields.—All reactions were allowed to proceed for 45.0 min. at 22°, quenched with ~200 ml. of water which contained sufficient sodium hydroxide to neutralize the perchloric acid, and gravity filtered from the precipitated mercuric hydroxide which was extensively washed with water. The filtrate was saturated with sodium chloride; 1.00 ml. of dioxane solution 0.50 *M* in 2-octanone (0.5 mmole) was added and it was extracted three times with portions of carbon tetrachloride such that the combined organic layer totaled 10 ml. A 0.03-ml. sample was analyzed gas chromatographically on a Beckman GC-2 instrument utilizing a 6-ft. firebrick supported silicone column at 130° and 25 p.s.i. of helium carrier gas. Under these conditions the 2-octanone internal standard was eluted after 10.5 min. and acetophenone after 24 min. as symmetrical peaks. The yield was determined from a previously prepared calibration of the ratio of the peak height of acetophenone to the peak height of 2-octanone vs. the concentration of acetophenone.

Deoxybenzoin.—To 4.5 mmoles of diphenylacetylene, dissolved in dioxane, was added 2.25 mmoles of mercuric perchlorate, 5 mmoles of perchloric acid, and 24 mmoles of water also in dioxane. The intensely yellow-colored solution darkened to a deep amber color after several days at 22°. After 2 weeks the solution contained a quantity of off-white precipitate. The reaction solution was added to 5 mmoles of sodium hydroxide which was dissolved in a large excess of water, the solution saturated with sodium chloride, and extracted repeatedly with methylene chloride. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and the solvent removed under reduced pressure. The residue, a pale yellow semi-solid, showed an infrared spectrum which was essentially superimposable upon the spectrum of an authentic sample of deoxybenzoin. The yield was 2.1 mmoles (45%) which was converted to the 2,4-dinitrophenylhydrazone, m.p. 200–202°, lit. 204°.

Preliminary Analytical Data.—Preliminary to the actual survey, several runs were made in which the mercuric perchlorate was omitted and several others were made in which known quantities of acetophenone were substituted for phenylacetylene. The results of these experiments are shown below.

PRELIMINARY SURVEY OF PRODUCT AND RECOVERY YIELDS

Run	Ph—C≡C—H concn., <i>M</i>	Hg(ClO ₄) ₂ concn., <i>M</i>	HClO ₄ concn., <i>M</i>	H ₂ O concn., <i>M</i>	Yield, % PhCOCH ₃
1 ^a	0.05	..	0.50	1.4	0
2 ^b	0.05	..	0.50	1.4	47
	PhCOCH ₃				
3	0.0537	0.05	0.50	1.4	95 ^c
4	0.05	0.05	0.50	1.4	94 ^c

^a 45 min. ^b 7.5 days at 22°. ^c % recovery.

It is clear from runs 1 and 2 that the hydration of phenylacetylene in aqueous perchloric acid-dioxane is relatively slow under the conditions of these experiments.

In control experiments (runs 3 and 4) an ~95% recovery was obtained. Undoubtedly some acetophenone was lost; this relatively constant error means that the absolute values of the reported yields may be low by a few per cent; but, as will be seen, the precision in reproducing the yields on which key conclusions were based is reasonably good and as a result comparisons of yields within the group of experiments can be done with a relatively high degree of confidence.

Results and Discussion

A detailed study of the mechanism of hydration of acetylenes by mercuric perchlorate-perchloric acid catalysis in dioxane-water solvent systems has revealed that the catalyst components—mercuric perchlorate, perchloric acid—interact with the dioxane-water solvent system, often slowly, to give the active catalytic species. Ultraviolet spectral studies on the catalyst system suggest that a dioxane-mercuric ion complex is this active component. The addition of an acetylene to an active catalyst system results in the instantaneous production of a yellow complex, the rate of formation of which is associated with the activity of the catalyst system, and whose rate of disappearance is related to the structure of the acetylene employed, and the concomitant production of ketone, as determined by gas chromatography. Spectral data suggest that this is a

2:1 acetylene-mercuric ion complex, which, when attacked by water, yields ketone. Evidence indicates that a ketone-mercuric ion complex forms during the reaction but this is not important in determining overall conversion to ketone since the active catalyst sites remain available. The data supporting these views follow.

A dioxane solution 1.1×10^{-2} *M* in phenylacetylene, 1.3×10^{-2} *M* in mercuric perchlorate, 1.3×10^{-1} *M* in perchloric acid, and 5×10^{-1} *M* in water was prepared by reaction of mercuric oxide with concentrated perchloric acid, dilution with aqueous dioxane, and addition of phenylacetylene. On addition of the latter, a pale yellow solution formed within a few seconds. The coloration dissipated during about 20 min. leaving a clear colorless solution.

Aliquots of the reaction solution were diluted with dioxane after the reaction had proceeded for 2 min., 30 min., and 24 hr. The ultraviolet spectra of these solutions were observed. After 2 min. the spectrum of the reaction solution showed a shoulder centered at 258 $\text{m}\mu$ and doublet maxima, of approximately equal intensity, at 247 and 236 $\text{m}\mu$. The shoulder appeared to be due to the mercuric perchlorate spectrum, since a mercuric perchlorate solution in aqueous perchloric acid-dioxane showed a maximum at 253 $\text{m}\mu$ of about the correct intensity so as to account for it. The positions of the doublet maxima agree exactly with those observed in the spectrum of phenylacetylene (in pure dioxane). The characteristic spectrum of phenylacetylene in the 255–300 $\text{m}\mu$ range is completely masked by the mercuric perchlorate absorption.⁹

After 30 min. and 24 hr. the spectrum of the reaction solution showed a single maximum, at 239 $\text{m}\mu$ (the intensity was approximately the same for each). Since acetophenone dissolved in a mercuric perchlorate solution in aqueous perchloric acid-dioxane showed a strikingly similar absorption at 241 $\text{m}\mu$, and gas chromatographic analysis confirmed the production of acetophenone, it was reasonable to conclude that phenylacetylene was being hydrated rapidly in the presence of mercuric perchlorate *via* an intermediate which produced a yellow-colored solution. The 280- $\text{m}\mu$ band of acetophenone was completely masked by the mercuric perchlorate absorption.

Catalyst Structure.—As mentioned, mercuric perchlorate solutions in aqueous perchloric acid-dioxane show an ultraviolet absorption spectrum. It appears significant that the mercuric perchlorate solutions which resulted in the most intensely yellow-colored reaction solutions with phenylacetylene consistently showed absorption maxima at longer wave lengths and with increased intensity compared to those catalyst solutions of higher water content. Several examples are shown in Table I.

All of the mercuric perchlorate solutions utilized in reactions with alkynes in this work were prepared by making up, from mercuric oxide and perchloric acid, relatively concentrated solutions, *i.e.*, 0.10 *M*, and then carrying out the reactions and/or spectral dilutions after equilibration at 22° for various amounts of time. As shown by a comparison of the spectral properties of the catalyst solutions listed in Table I, the length of equilibration does not affect the absorption spectrum when the catalyst solutions are prepared as specified above, nor does the length of equilibration (as shown in the discussion of the results of run 11) affect the yields of acetophenone when the catalyst solutions are prepared in this manner.

(9) R. A. Friedel and M. Orchin, "Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1951.

TABLE I^a
 ULTRAVIOLET SPECTRA OF CATALYST SYSTEMS

Run ^b	Hg(ClO ₄) ₂ concn., M	HClO ₄ concn., M	H ₂ O concn., M	Time, hr.	λ _{max} , mμ	ε _{max}
11	0.10	1.0	2.8	15	246	8250
57 ^c	.10	1.0	2.8	15	247	8250
36-41	.10	1.0	2.8	15	247	8600
45	.10	1.0	2.8	4.5	247	8400
16	.10	1.0	5.6	15	241	3150
17	.10	1.0	7.0	15	240	2650
20	.10	1.0	14.0	15	239	2800
42	.50	1.0	6.1	50	239	1920

^a In order to obtain the spectra of the catalyst solutions, a 0.10-ml. aliquot was diluted to 100.0 ml. with dioxane which contained sufficient perchloric acid and water so that the concentration of these factors was unchanged. All spectra were taken immediately after dilution. ^b These run numbers refer to run in which the respective catalyst solutions were utilized. ^c Also 0.1 M in LiClO₄.

If, on the other hand, relatively dilute, *e.g.*, 1×10^{-2} M, solutions were prepared by reaction of small amounts of mercuric oxide with perchloric acid and diluting directly to the concentrations required for spectral analysis, a slow reaction was observed with the gradual formation of the absorption peak in the 240-250 mμ range. Only a limited number of observations of this reaction were made; the available data are summarized in Table II.

 TABLE II
 ULTRAVIOLET SPECTRA OF DILUTE CATALYST SYSTEMS AS A
 FUNCTION OF TIME^a

Run	Hg(ClO ₄) ₂ concn., M	HClO ₄ concn., M	H ₂ O concn., M	Time, hr.	λ _{max} , mμ	ε _{max}
29	2.5×10^{-3}	3×10^{-1}	55.5	1	270 ^b	240
				24	276 ^c	440
				168	276	440
30	2.5×10^{-3}	2.5×10^{-1}	5.5	1	244 ^d	2360
				24	244 ^d	2520
				48	244 ^d	2760
				240	244 ^d	3560
31	2.5×10^{-3}	2.5×10^{-1}	0.63	1	247	5440
				24	251	7560
				216	253	8720
				504	254	8200
32	2.5×10^{-3}	2.5×10^{-2}	4.5	1	244 ^e	1600
				24	244 ^e	1600
				48	244 ^e	1840
				72	244 ^e	1760

^a All spectra were obtained by dilution with pure dioxane by a factor of ten. Re-equilibration of the dilute solutions was assumed to be slow; this was checked, in the case of run 31, after 504 hr., by making several dilutions by factors of 10, 14.5, 20, and 33.3. A plot of A_{max} vs. concentration was linear. ^b Very broad. ^c Broad. ^d Shoulder. ^e End absorption.

An examination of runs 29 through 31, where the solvent was changed from pure water to almost pure dioxane, verifies that the formation of the absorption peak is clearly time dependent under these relatively dilute conditions.

Runs 30 and 32 show the effect of increasing the acid concentration at approximately constant water concentration: the rate of increase in intensity is higher at higher acid concentrations.

From these limited data it appears reasonable, since aqueous mercuric perchlorate shows an almost insignificant absorption, to conclude that the absorption band is not due to transitions within the hydrated mercuric ion. Three possibilities remain: (a) the absorption band is due to mercuric perchlorate ion pairs in dioxane, a solvent of very low dielectric constant; (b) the absorption band is due to the formation of a dioxane-

 TABLE III
 $\text{Ph}-\text{C}\equiv\text{C}-\text{H} \xrightarrow[\text{HgClO}_4, \text{HClO}_4]{\text{H}_2\text{O, dioxane}} \text{PhCOCH}_3$

Run	Ph-C≡C-H concn., M	Hg(ClO ₄) ₂ concn., M	HClO ₄ concn., M	H ₂ O concn., M	Yield, %
5	0.05	0.05	0.25	0.85	57
6	.05	.05	.25	1.7	60
7	.05	.05	.25	2.0	73
8	.05	.05	.25	2.8	56
9	.05	.05	.25	4.2	50
10	.05	.05	.25	5.6	46
11	.05	.05	.50	1.4	54 ^a
12	.05	.05	.50	1.7	58
13	.05	.05	.50	2.0	58
14	.05	.05	.50	2.2	60
15	.05	.05	.50	2.6	59, 60
16	.05	.05	.50	2.8	65, 70
17	.05	.05	.50	3.5	60, 61, 63
18	.05	.05	.50	4.2	66
19	.05	.05	.50	5.6	58
20	.05	.05	.50	7.0	50, 52
21	.05	.05	1.0	2.8	34
22	.05	.05	1.0	3.1	56
23	.05	.05	1.0	4.2	67
24	.05	.05	1.0	5.6	70
25	.05	.05	1.0	7.0	72
26	.05	.05	1.0	7.3	62
27	.05	.05	1.0	8.7	57
28	.05	.05	1.0	11.4	53

^a Average of five (51, 52, 54, 56 (2)).

mercuric ion complex; and (c) the absorption is due to a solvent-dependent charge transfer band of the perchlorate anion. The results obtained with the catalyst solution utilized in run 57 (Table I), in which addition of lithium perchlorate produced no observable effect on the spectrum of the system, might tend to favor (b) as the source of the absorption band. The effect produced by increasing the acid concentration is consistent with the protonation and subsequent expulsion of a coordinated water molecule. It is noteworthy that in concentrated solutions of relatively low water content mercuric perchlorate crystals containing loosely bound dioxane are produced. A dioxane-mercuric perchlorate complex of the composition $\text{Hg}(\text{H}_2\text{O})_2(\text{dioxane})_4(\text{ClO}_4)_2$ has been reported.¹⁰

Ketone Production.—In those runs designed to explore the effect of acid and water concentrations on acetophenone production, the reactant concentrations were 0.05 M phenylacetylene, 0.05 M mercuric perchlorate, from 0.25 to 1.0 M perchloric acid, and from 0.8 to 11.5 M water.

The character of the reaction varied depending upon the (H₂O)/(HClO₄) ratio. At relatively low ratios, *i.e.*, 3-4, the reaction solution became instantaneously bright yellow, then gradually the color decayed. At higher ratios, *i.e.*, 4-10, the coloration was accompanied by the gradual formation of small amounts of a finely divided black precipitate which could be redissolved by shaking. If the concentration of water exceeded the concentration of acid by a factor of 8 to 10 or greater, an immediate white precipitate appeared on mixing and a greatly diminished yellow coloration was observed. During the course of the reaction this white precipitate dissolved, yielding a pale yellow homogeneous solution.

For the homogeneous system, designated as run 11, 0.05 M in phenylacetylene, 0.05 M in mercuric perchlorate, 0.50 M in perchloric acid, and 1.4 M in water, a progressive shortening of the reaction time, in runs 36, 11, and 37-41, lead to the conclusion that the final

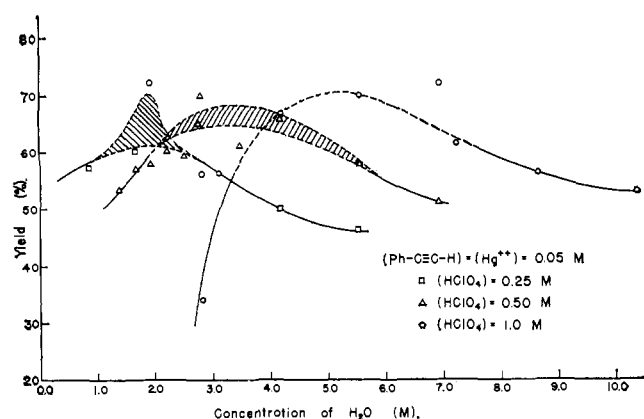


Figure 1.

yield of acetophenone in the reaction solution was rapidly established: per cent yield (reaction time), 59 (20 hr.); 54 (45.0 min.; av. of five determinations); 50 (20.0 min.); 49 (15.0 min.); 50 (10 min.); 46 (5.0 min.); 42 (2.0 min.). All of the yield data in this work are therefore based on 45-min. runs, except where noted.

Plots of percentage yield vs. the water concentration, at perchloric acid concentrations of 0.25, 0.50, and 1.0 M, are shown in Fig. 1 derived from data in Table III. Yields in systems employing relatively low water concentrations were quite reproducible. For example, in run 11, five separate determinations utilizing different stock solutions of phenylacetylene, different catalyst solutions which had been allowed to equilibrate for varying amounts of time, and work-up procedures which differed in the amount of time lapsing between the quenching of the reaction and the actual work-up produced the following results: per cent yield (age of catalyst solution), 54 (2.5 hr.); 56 (9 hr.); 51 (16 hr.); 56 (24 hr.); 52 (60 hr.); the standard deviation is 2%.

In the heterogeneous reactions, yields could not always be reproduced; nevertheless, as the water concentration was gradually increased an unmistakable pattern was established under each of the three acid concentrations: first, a gradual increase in yield followed by a tailing off at higher water levels.

The gradual increase in yield with increasing water concentration is not unexpected for a hydration reaction. The tailing off at higher water levels is surprising; a possible interpretation of this will be presented in the following sections, although the source and consequences of the heterogeneity at high $(\text{H}_2\text{O})/(\text{HClO}_4)$ ratios is difficult to ascertain.

In order to obtain more information about the hydration reaction and such intermediates which may exist, the homogeneous reaction was selected for more detailed study.

The effect of progressively increasing the concentration of phenylacetylene on the concentration of produced acetophenone at constant mercuric perchlorate concentration is shown in Fig. 2. The data required for the plot are given in Table IV, runs 44, 11, and 45-48. Plotting concentration of produced acetophenone vs. phenylacetylene added initially, one notes that the formation of acetophenone increases sharply at first and then appears to reach a plateau. Additional experiments in this series were not undertaken because of the occurrence of a heterogeneous (white or black transient precipitates during reaction) system at phenylacetylene to mercuric ion ratios greater than two. A steadily intensifying yellow coloration was observed in the reaction solution as the phenylacetylene to mercuric ion ratio was increased.

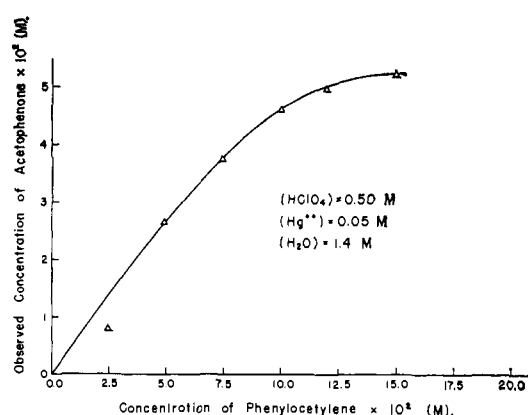
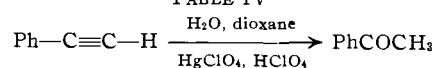


Figure 2.

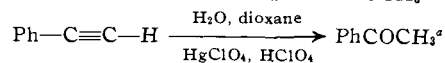
The plateau in the acetophenone concentration at about the concentration of mercuric ion in these experiments might suggest the formation of an acetophenone-mercuric ion complex resulting in a loss of the coordination sites available to phenylacetylene and the diminished production of acetophenone. A loosely bound acetophenone-mercuric chloride complex has been described by Paoloni.¹¹ An alternate explanation is

TABLE IV^a

Run	Ph-C≡C-H concn. M	Ph-C≡C-H concn. mmoles	Hg(ClO ₄) ₂ concn. M	Hg(ClO ₄) ₂ concn. mmoles	PhCOCH ₃ produced, mmoles	Yield, %
42 ^b	0.05	0.50	0.25	2.50	0	0
43 ^c	.05	.50	.10	1.00	0.194	39
44 ^{a,d}	.025	.50	.05	1.00	.163	33
11 ^{a,e}	.05	.50	.05	0.50	.270	54
45 ^a	.075	.75	.05	.50	.378	50
46 ^a	.10	1.00	.05	.50	.471	47
47 ^{a,f}	.12	1.20	.05	.50	.509	42
48 ^{a,f}	.15	1.50	.05	.50	.525	35

^a All reactions in dioxane for 45.0 min. at 22°; $\text{HClO}_4 = 0.50 M$, $\text{H}_2\text{O} = 1.4 M$. ^b $\text{H}_2\text{O} = 3.1 M$. ^c $\text{H}_2\text{O} = 1.7 M$. ^d 10-Min. reaction time. ^e Average of five determinations. ^f Heterogeneous.

that, because of the heterogeneous character of the reaction at phenylacetylene to mercuric ion ratios of two or larger, acetophenone production is greatly reduced. The former possibility was checked by conducting several reactions in the presence of added acetophenone. The results are shown in Table V.

TABLE V^aEFFECT OF ADDED SALTS OF PhCOCH_3 

Run	Additive	Concn., M	Yield, %
11 ^b	None		54
54 ^c	Acetophenone	0.05	49
55 ^{c,d,e}	Acetophenone	.043	54
56 ^{c,f}	Acetophenone	.04	50
57	LiClO_4	.05	54
58 ^c	LiCl	.05	53

^a $\text{Ph}-\text{C}\equiv\text{C}-\text{H} = 0.05 M$, $\text{Hg}(\text{ClO}_4)_2 = 0.05 M$, $\text{HClO}_4 = 0.50 M$, $\text{H}_2\text{O} = 1.4 M$; all reactions for 45.0 min. at 22°. ^b Average of five determinations. ^c The yield was adjusted by reducing the observed amount of acetophenone by the amount of the additive. ^d Additive equilibrated for 45 hr. with mercuric perchlorate solution before reaction. ^e Average of two determinations. ^f Additive equilibrated for 65 hr. with mercuric perchlorate solution before reaction.

(11) L. Paoloni and G. B. Marine-Bettolo, *Chem. Abstr.*, **54**, 12045h (1960); *Rend. ist. super. sanita*, **22**, 813 (1959).

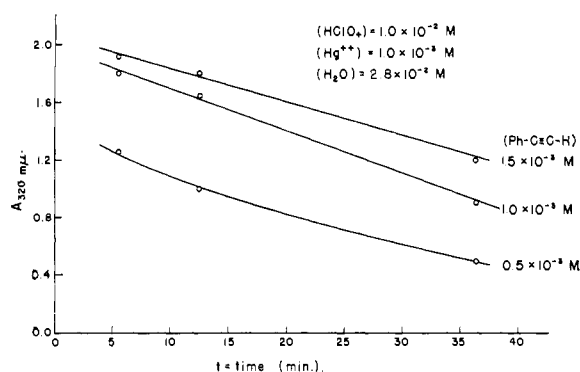


Figure 3.

As seen from a comparison of run 11 with runs 54–56, no reduction in yield was observed; in runs 55 and 56, nearly equivalent amounts of acetophenone and mercuric perchlorate were allowed to equilibrate under reaction conditions for up to 2 days before the addition of phenylacetylene. These data therefore favor the latter explanation.

Repeated attempts were made in an effort to detect the presence of a carbonyl band in the infrared spectra of the final reaction solutions, but these were consistently frustrated by the occurrence of a broad band centered near 1700 cm^{-1} . This band does not appear in the spectrum of dioxane, phenylacetylene, or perchlorate salts.¹² It was therefore assumed to be related to one of the bending modes of water.¹³

Some evidence of complexation may be inferred from the proton n.m.r. spectrum of mixtures of acetophenone and mercuric perchlorate in aqueous perchloric acid-dioxane. In dioxane 1.20 *M* in perchloric acid, 4.0 *M* in water, and 0.11 *M* in acetophenone, the phenyl protons of acetophenone show a single sharp absorption at -0.88 p.p.m. relative to chloroform as an external reference. In a similar solution but also 0.12 *M* in mercuric perchlorate, this absorption appeared at -1.33 p.p.m. After standing 1 day, a reaction solution, with all constituents at the same concentrations as above, showed a sharp absorption at -1.32 p.p.m.

On the basis of these experiments it was concluded that although an acetophenone–mercuric ion complex may exist, it does not inhibit the mercuric ion catalysis of the hydration reaction; the leveling off in acetophenone production was attributed to the heterogeneous character of the reaction at phenylacetylene to mercuric ion ratios of two or greater.

These results are consistent with the hypothesis that the first step in the hydration reaction was the reversible formation of a coordination complex between phenylacetylene and mercuric ion which was responsible for the yellow coloration and which was attacked subsequently by water. This hypothesis was tested further by increasing the mercuric ion concentration in the system to 0.10 and 0.25 *M* in runs 43 and 42. The phenylacetylene and perchloric acid concentrations were maintained at 0.05 and 0.50 *M*, respectively, in each, but it was necessary, in order to preserve homogeneity, to increase the water concentrations in these experiments to 1.7 and 3.1 *M*, respectively. As displayed in Fig. 1, an increase in water concentration from 1.4 to 3.1 *M* at a perchloric acid concentration of 0.5 *M* increases the yield of acetophenone; but, in these experiments the former run 43 resulted in a 38% yield of acetophenone as compared to the 54% yield observed at a

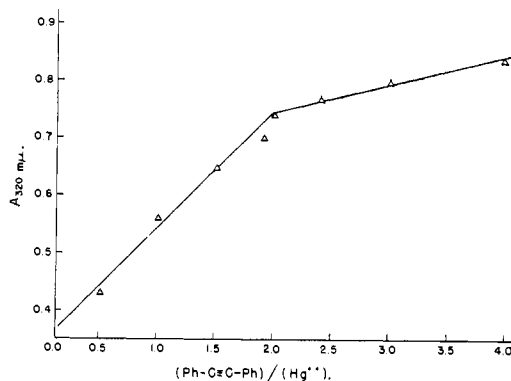


Figure 4.

phenylacetylene to mercuric ion ratio of one. In the latter run, 42, no acetophenone could be detected gas chromatographically. Clearly this behavior was inconsistent with the hypothesis of the formation of a 1:1 intermediate complex.

One possible interpretation of these facts is that initially a bis-(phenylacetylene)–mercuric ion complex is preferentially formed, and that this is the only species in which phenylacetylene is hydrated rapidly. This conclusion is the only one which is consistent with the observed color changes, the near 50% yields observed at phenylacetylene to mercuric ion ratios of one, the production of acetophenone at higher phenylacetylene to mercuric ion ratios, and the diminished production of acetophenone at phenylacetylene to mercuric ion ratios less than one.

Intermediate Complex.—The color changes observed in reactions employing excesses of mercuric ion are significant and aid in interpretation of the role of the yellow-colored complex in the reaction and its structure. As the first part of a catalyst solution was added to a phenylacetylene solution, a brilliant yellow coloration was observed; but, as the mercuric ion concentration began to exceed the phenylacetylene concentration the solution became rapidly colorless. Quantitative measurements of these color changes were made spectrophotometrically. In order to make the observations directly, it was necessary to reduce the concentrations of the reactants across the board by a factor of 100. For systems employing phenylacetylene to mercuric ion ratios of 1.5, 1.0, and 0.5, a broad shoulder was observed initially in the 315–330 $m\mu$ range which tailed into the visible—the source of the yellow color. The intensity of this absorption decreased with time. Neither phenylacetylene nor mercuric ion absorbed in the 300–400 $m\mu$ range. The absorbance at 320 $m\mu$ as a function of phenylacetylene concentration for various times is shown in Fig. 3.

As the ratio of phenylacetylene to mercuric ion was increased, the intensity of absorption increased just as the concentration of acetophenone increased with increasing phenylacetylene concentration (Fig. 2). These observations strongly suggest that the yellow-colored species is intimately related to the hydration reaction.

The effect of reductions in yields of acetophenone at relatively higher water concentrations (Fig. 1, Table III) may now, on the basis of these conclusions and the assumption of an intermediate phenylacetylene–mercuric ion complex, be attributed tentatively to the preferential occupation of the proper coordination sites on the mercuric ion by water and to the exclusion of phenylacetylene, using the following logic.

If a competition exists between water and phenylacetylene and if the yellow-colored solutions are attributed correctly to a phenylacetylene–mercuric ion intermediate, then increases in water concentration

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should decrease the concentration of the intermediate and consequently the intensity of absorption due to the presumed intermediate. Several observations of the initial rates of increase in absorbance, measured arbitrarily at 340 $m\mu$, as a function of water concentration are shown in Table VI.

TABLE VI^a
 $\text{H}_2\text{O, dioxane}$
 $\text{HgClO}_4, \text{HClO}_4 \rightarrow \text{PhCOCH}_3$

Time, min.	System absorbance values at 340 $m\mu$		
	H_2O concn., ^b 0.2 <i>M</i>	H_2O concn., ^c 0.5 <i>M</i>	H_2O concn., ^d 3 <i>M</i>
4.5	0.39	0.20	0.10
12.5	1.17	0.78	.39
19.5	1.47	1.06	.55
27.5	1.64	1.28	.61

^a $\text{Hg}(\text{ClO}_4)_2 = 1.3 \times 10^{-3}$ *M*, $\text{Ph}-\text{C}\equiv\text{C}-\text{H} = 1.1 \times 10^{-3}$ *M*, $\text{HClO}_4 = 1.3 \times 10^{-2}$ *M*. ^b Run 33. ^c Run 34. ^d Run 35.

Clearly, increased water concentration strongly inhibited the formation of the yellow-colored species or, as an alternate interpretation, increased the rate of its reaction so that its accumulation was inhibited. In view of the previous presentation of acetophenone yields as a function of water concentration, the former explanation appears more likely and strongly suggests again that the intermediate causing the absorption is intimately connected with the hydration reaction.

Similar reasoning could be used to explain the shift of the family of curves in Fig. 1 to higher (H_2O) as (HClO_4) is increased. The HClO_4 competes with HgClO_4 for the water present, which is necessary for the consummation of the hydration reaction. Thus as (HClO_4) is increased, a higher initial water concentration is required.

Qualitatively it was observed that hexyne-1 also formed a yellow-colored solution when mixed with the appropriate mercuric perchlorate solution, but the coloration dissipated rapidly with time. With diphenylacetylene a similarly yellow-colored solution was produced but the complex, as indicated by the lack of any apparent dissipation of the yellow coloration over an extended period of time, appeared to be relatively inert. When the ratio of diphenylacetylene to mercuric ion was increased, a more rapid reaction occurred; the solution took on a deep amber coloration within a day and produced deoxybenzoin, the expected hydration product of diphenylacetylene. The product was identified by infrared analysis and as the 2,4-dinitrophenylhydrazone.

The relative inertness of the diphenylacetylene-mercuric ion complex provided an ideal opportunity to study its stoichiometry. Relatively concentrated solutions of various mixtures of diphenylacetylene and mercuric perchlorate were prepared and permitted to equilibrate for short periods of time; aliquots were then diluted with dioxane which contained sufficient perchloric acid and water so that the concentrations of these factors were unchanged. Then, according to the method of Yoe and Jones,¹⁴ the measured absorbance of the dilutions at 320 $m\mu$ was plotted against the diphenylacetylene to mercuric ion mole ratio. The plot is shown in Fig. 4.

The break in the slope of the absorbance curve at a mole ratio of two diphenylacetylenes to one mercuric ion indicated a bis-(diphenylacetylene)-mercuric ion complex. That the absorbance increased by only an additional 13.5% on addition of two additional equivalents of diphenylacetylene suggested that a relatively high

formation constant was associated with the over-all process.

In one experiment a solution 0.05 *M* in mercuric ion, 0.10 *M* in diphenylacetylene, 0.50 *M* in perchloric acid, and 1.4 *M* in water was permitted to equilibrate for a short time and then quenched in the same manner as described for the phenylacetylene reaction. A recovery of greater than 62% of pure diphenylacetylene was obtained, indicating complex formation is reversible.

Measurements of the absorbance were carried out at 320 $m\mu$ because, as with the phenylacetylene-mercuric ion complex, the diphenylacetylene-mercuric ion complex showed a broad shoulder in the 315-330 $m\mu$ region. This similarity in the spectra of the two species suggested that the same stoichiometry, *i.e.*, a bis-(alkyne)-mercuric ion complex, could be assigned to the phenylacetylene-mercuric ion complex. Thus the previous conclusion, made on the basis of hydration product yields, was supported.

The proton n.m.r. spectrum of diphenylacetylene is modified by complexation with mercuric ion. In dioxane, 1.20 *M* in perchloric acid, 4.0 *M* in water, and 0.12 *M* in diphenylacetylene, the phenyl protons of diphenylacetylene show a single sharp absorption at -0.92 p.p.m. relative to chloroform as an external reference. In a similar solution, but also 0.12 *M* in mercuric perchlorate, this absorption appeared at -1.38 p.p.m., or a net shift of -0.46 p.p.m. to the low field side of chloroform for the complexed ligand relative to the uncomplexed ligand. The chemical shifts measured from the solvent dioxane absorption peak were within 1 c.p.s. of those measured from the external chloroform reference. The spectrum of the bis-(diphenylacetylene)-mercuric ion complex was reproduced identically several times over a period of 3 days, testifying to the relative inertness of the complex. When the diphenylacetylene concentration was increased to 0.5 *M*, the phenyl resonance again appeared at -1.38 p.p.m. but no absorption due to the uncomplexed ligand was observed. Such a simple spectrum is expected if the complexed diphenylacetylene ligands are exchanging rapidly with the uncomplexed ligands of the solution. But under these circumstances the position of the absorption peak is expected to be concentration dependent. This seemingly contradictory result is being explored further.

A comparable effect has been observed recently by Schug and Martin,¹⁵ who reported that the α -proton resonance of *cis*-2-butene is shifted -0.65 p.p.m. on complexation with silver ion.

Summary and Conclusions

It has been shown that phenylacetylene is hydrated *via* a bis-(phenylacetylene)-mercuric ion intermediate in aqueous perchloric acid-dioxane mixtures. Similar complexes were observed with 1-hexyne and diphenylacetylene, the latter being considerably less reactive than the others. The structure of these complexes is unknown. Although unlikely in this case, the possibility of alkyne dimerization to a substituted cyclobutadiene-mercuric ion complex must be considered. This result has been observed with palladium(II) chloride¹⁶ and cobaltocene.¹⁷ Other possibilities include structures resembling a substituted mercuracyclopentadiene¹⁸ (mercurole) and, the most likely, a

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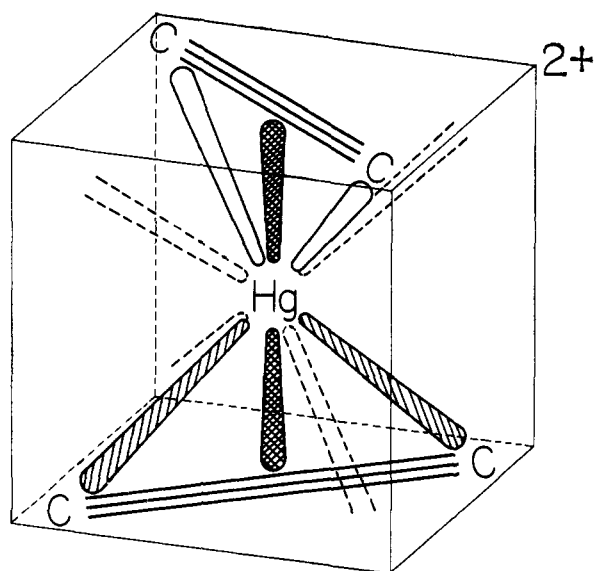


Figure 5.

bis-alkyne π -complex in which the character of the alkyne is essentially retained.

It is suggested that this might involve μ -bonding between the metal ion and the acetylenes, utilizing sp -hybrid orbitals from the mercuric ion, with d_{π} - p_{π} backbonding from the metal ion to the π -antibonding orbitals of the acetylenes also being present (Fig. 5).

Lemaire and Lucas⁷ have presented evidence for a 3-hexyne-acetoxymercuric ion complex as an intermediate in the mercuric acetate-perchloric acid-catalyzed addition of acetic acid to 3-hexyne in glacial acetic acid, and Adelman¹⁹ has suggested an acetylene-mercuric sulfate complex as an intermediate in the mercuric sulfate-catalyzed transvinylation reaction. Recently, Halpern and co-workers²⁰ suggested a ruthenium(III)-acetylene π -complex as an intermediate in the ruthenium(III) chloride-hydrochloric acid-catalyzed hydration of acetylenes in aqueous solutions. Lemaire and Lucas observed, in certain instances, yellow-colored solutions; but, they concluded that the coloration was due to a by-product present in small concentration which was not related to the rate of the addition reaction but which may possibly be related to the concentration of the 3-hexyne-acetoxymercuric ion complex. It appears significant that they observed that the development of the color was strongly inhibited by water and that the development of the color was most favored where the concentration of perchloric acid was equal to or exceeded the concentration of mercuric acetate.

Meriwether and co-workers²¹ have reported that refluxing of certain bis-(carbonyl)-bis-(phosphine)-nickel(0) complexes with disubstituted acetylenes in a hydrocarbon solvent or acetonitrile with inert gas sweeping led to the formation of intense yellow-colored solutions with the concurrent evolution of carbon monoxide. The coloration, due to a species with an absorption band at $290\text{ m}\mu$, was stable for long periods of time but disappeared on exposure to air. It was suggested,

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because of the similarity of their ultraviolet spectra to the spectra of a series of bis-(phosphine)-monoacetylene-platinum(0) complexes isolated by Chatt and co-workers,²² that these species were the less stable nickel analogs. The assigned stoichiometry of the platinum complex was not supported by any experimental evidence; no stoichiometric investigation of the nickel complex was reported. The apparent similarity of the ultraviolet spectra of these two series of complexes with the spectra of the bis-(alkyne)-mercuric ion complexes and the fact that mercury(II) is isoelectronic in the valence shells with both platinum(0) and nickel(0) is interesting.

It is also intriguing that the bis-alkyne intermediate was identified first with a mercuric salt of a very strong acid—with an anion of feeble complexing tendency—but dissolved in an organic solvent of low water content. Years ago, Nieuwland²³ pointed out that mercuric perchlorates, fluoroborates, nitrates, arenesulfonates, and sulfates in aqueous solution were effective catalysts; but, that the halides, acetates, and phosphates were ineffective. Suggestions concerning the use of organic solvents in hydration reactions, utilizing conventional mercuric sulfate catalysis, have been made previously and used with some success.²⁴ A reinvestigation of certain of the extensive number of reactions reported to be catalyzed by mercuric fluoroborate would seem worthwhile.

Further studies into the detailed mechanism of catalysis of hydration will require additional studies into the precise nature of the mercuric ion in mixed aqueous acidic-organic solvents. Westheimer,²⁵ in a study of the mechanism of mercuration of aromatic compounds, has suggested that mercuric perchlorate exists as tetrahedral $[\text{Hg}(\text{H}_2\text{O})_3\text{ClO}_4]^+$ in aqueous systems. On the other hand, apparently octahedral complexes of mercury have been isolated.²⁶ The configuration of the ionic mercuric salts is, in general, unknown in aqueous, much less mixed aqueous organic solvents where changes in configuration and other properties are expected. Perhaps the recently developed Hg_0 function, analogous to the H_0 function, will aid in the exploration of this area. This relates to the activity of mercuric ion as water is withdrawn from it and is derived from observed rates of mercuration of benzene.²⁷ The analogy to the present system is obvious.

Acknowledgments.—The authors wish to thank the Sloan Foundation (R. E. D.) and the Diamond Alkali Co. (W. B.) for fellowship support, and to acknowledge the support of the National Science Foundation (NSFG-14182), the Petroleum Research Fund (PRF-1080-A4), the Army Research Office (Durham) (ARO 31-124), the U. S. Office of Scientific Research (AFOSR-49-638-824), and the National Institute of Health (NSPH-RG-9022).

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