Tetrahedron Letters No. 10, pp. 651-659, 1963. Pergamon Press Ltd.
Printed in Great Britain.

# HOMOGENEOUS CATALYSIS IN THE HYDRATION OF ACETYLENES

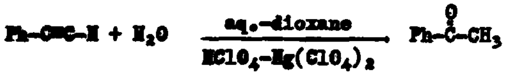
William L. Budde and Raymond E. Dessy

Department of Chemistry, University of Cincinnati, Cincinnati 21, Ohio

(Received 26 October 1962; in revised form 15 January 1963)

In connection with a detailed study of the role of mercury in the well-known mercury salt-acid catalysed hydration of acetylenes, it was necessary to survey the effect of the relative amounts of acid, mercuric salt, substrate and water on the course of the reaction. These studies, reported here in part, have yielded some unexpected results which are of mechanistic and synthetic interest.

Under consideration was the conversion of phenylacetylene to acetophenone. In general, the reaction was accomplished by pipetting 5.00 ml. of a dioxane solution of mercuric perchlorate which contained various amounts of water and perchloric acid into 5.00 ml. of a dioxane solution of phenylacetylene.



$$\text{Ph-C}\equiv\text{C-H} + H_2O \xrightarrow[\text{HClO}_4\text{-Hg(ClO}_4)_2]{\text{aq.-dioxane}} \text{Ph-}\overset{O}{\overset{\|}{C}}\text{-CH}_3$$

In those runs designed to explore the effect of acid and water concentrations, the reactant concentrations were 0.05 M phenylacetylene (0.5 mmoles), 0.05 M mercuric perchlorate (0.5 mmoles), from 0.25 to 1.0 M perchloric acid (2.5-10 mmoles) and from 0.8 to 11.5 M water (8-115 mmoles). The character of the reaction varied depending upon the $(H_2O)/(HClO_4)$ ratio. At relatively low ratios, i.e., 3-4, the reaction solution became instantaneously bright yellow, then gradually the color decayed to a pale yellow.

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, in certain instances, could be redissolved by shaking. If the concentration of water exceeded the concentration of acid by a factor of 8-10 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.[1]

A series of determinations was made over the previously indicated range of water concentrations and at perchloric acid concentrations of 0.25 M, 0.5 M and 1.0 M. Plots of per cent yield versus water concentration for each series of reactions are shown in Fig. 1.

Yields in systems employing relatively low water concentrations were quite reproducible. For the system 0.05 M in phenylacetylene, 0.05 M in mercuric perchlorate, 0.5 M in perchloric acid and 1.41 M in water, five separate runs 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 hrs.); 51.4 (16 hrs.); 55.7 (24 hrs.); 52.4 (60 hrs.). In heterogeneous reactions individual yields could not be reproduced readily; nevertheless, as the water concentration was gradually increased an unmistakable

---

[1] It appears significant that the mercuric perchlorate solutions which resulted in the clean reactions consistently showed ultraviolet absorption maxima at somewhat longer wave lengths and with increased intensity compared to those catalyst solutions of higher water content: $\lambda_{max}$ mμ (ε), 246-247 (8400) in dioxane/2.82 M water/1.0 M perchloric acid; 239-240 (3150) in dioxane/6.0 M water/1.0 M perchloric acid. Apparently the state of solvation of the mercuric ion as indicated by its ultraviolet absorption spectrum is an important factor in the reaction.

All reactions were allowed to proceed 45.0 minutes at 22°, quenched with 200 ml. of water which contained sufficient sodium hydroxide to neutralize the perchloric acid, filtered, extracted with carbon tetrachloride and analyzed gas chromatographically utilizing 2-octanone as an internal standard.

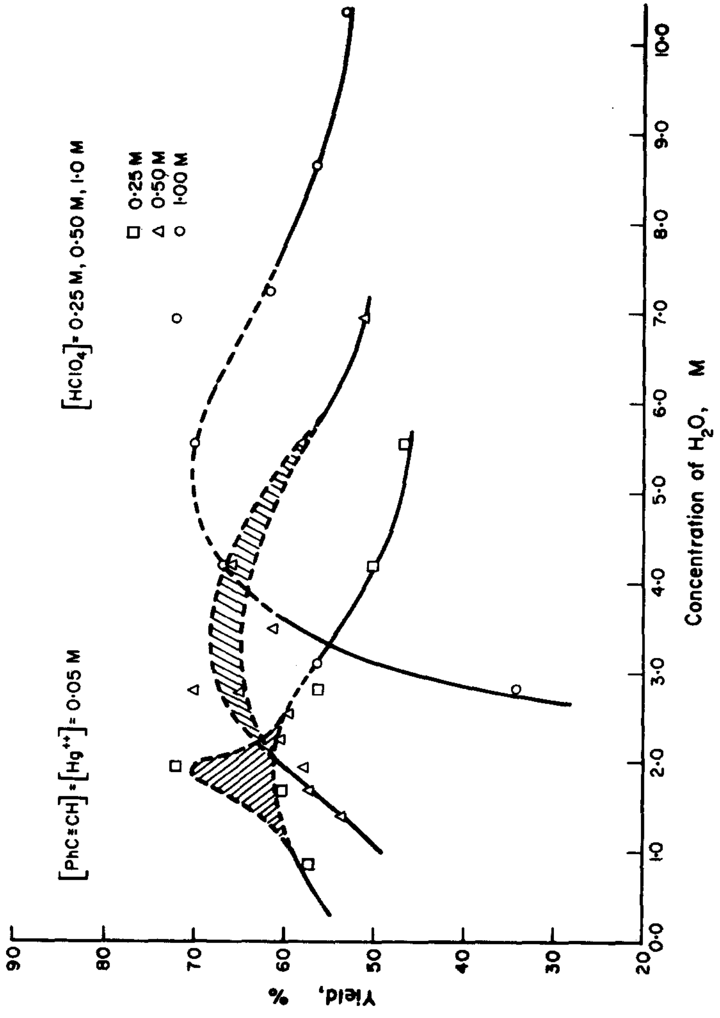


**Fig. 1** Yield of acetophenone as a function of water concentration.

pattern was established: first a gradual increase in yield followed by a tailing off at higher water levels.

The homogeneous reaction described above was selected for more detailed study. Progressive shortening of the reaction time in this system led to the conclusion that the final composition of the reaction solution was rapidly established: per cent yield (reaction time), 59 (20 hrs.); 53.8 (45.0 min.; av. of four determinations); 50.2 (20.0 min.); 49.4 (15.0 min.); 50.2 (10.0 min.); 45.8 (5.0 min.); 42 (2.0 min.).

The effect of progressively increasing the concentration of phenylacetylene on the concentration of acetophenone (usually taken as that produced in 45.0 min.; in most cases separate runs allowed to proceed for 24 hrs. produced yields within a few per cent) in this system is shown in Fig. 2. The concentration of acetophenone increases sharply, then appears to level off at ~ 0.05 M. Additional experiments in this series were not undertaken because of the occurrence of a heterogeneous 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.

These results suggested that the first step in the hydration reaction is the reversible formation of a 1:1 coordination complex between phenylacetylene and mercuric ion[2] which is responsible for the yellow coloration and which is subsequently attacked by water. Increasing a reactant concentration would increase the equilibrium concentration of this species and

---

[2] (a) H. Lemaire and H. J. Lucas, *J. Am. Chem. Soc.* **77**, 939 (1955), 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; (b) R. L. Adelman, *J. Org. Chem.* **14**, 1057 (1949), has suggested an aceylene-mercuric sulfate complex as an intermediate in the mercuric sulfate catalyzed vinyl acetate-carboxylic acid transvinylation reaction; (c) J. Halpern, B. R. James and A. L. W. Kemp, *J. Am. Chem. Soc.* **83**, 4097 (1961), have suggested a ruthenium (III)-acetylene pi complex as an intermediate in the ruthenium (III) chloride-hydrochloric acid catalyzed hydration of acetylenes in aqueous solutions.

consequently increase the observed concentration of acetophenone. This hypothesis was tested by increasing the mercuric ion concentration in this

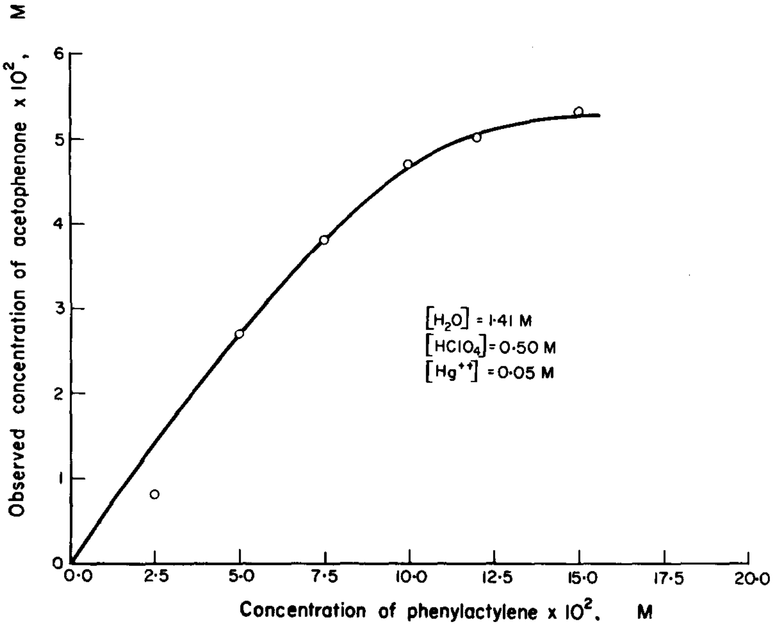


**Fig. 2**

Acetophenone concentration as a function of phenylacetylene concentration.

system to 0.1 M and 0.25 M in separate experiments. The phenylacetylene and perchloric acid concentrations were maintained at 0.05 M and 0.5 M respectively in each but it was necessary, in order to preserve homogeneity, to increase the water concentrations in these experiments to 1.69 M and 3.07 M respectively.[3] The former run resulted in a 38% yield of acetophenone as compared to the ~ 54% yield observed at a phenylacetylene to mercuric ion ratio of one. In the latter experiment no acetophenone could be detected gas chromatographically. This behavior was inconsistent with the hypothesis of the formation of an equilibrium concentration of a 1:1 intermediate.

The color changes observed in reactions employing excesses of mercuric ion are significant. As the first part of the catalyst solution was added to the 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 and 0.5, a broad shoulder was observed initially in the 315-330 mμ range. The intensity of this absorption decreased with time. Neither phenylacetylene nor the mercuric ion absorbed in the 300-400 mμ range. The absorbance at 320 mμ as a function of the 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 correlate well with the qualitative observations described above and strongly suggest that the yellow-colored species is intimately associated with the overall process.[4]

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 rapidly hydrated.

---

[3] As displayed in Fig. 1, an increase in water concentration from 1.41 M to 3.07 M at a perchloric acid concentration of 0.5 M increases the yield of acetophenone.

[4] H. Lemaire and H. J. Lucas, reference 2a, also observed yellow colored solutions. They concluded that the coloration was due to a by-product present in small concentration which was not related to the rate of the reaction but which may possibly be related to the concentration of the 3-hexyne-acetoxymercuric ion complex.

This hypothesis is the only one which is consistant with the observed color changes, the near 50% yields observed at phenylacetylene to mercuric ion ratios of one, the increased production of acetophenone at higher

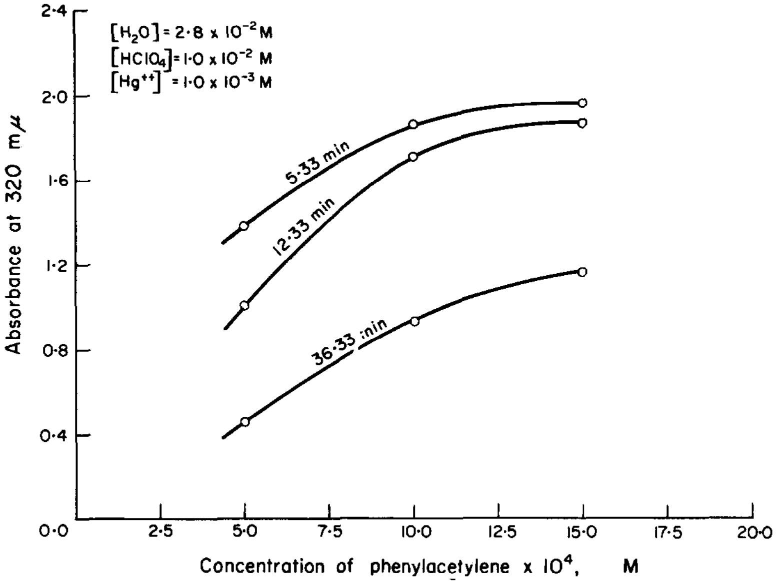


**Fig. 3**

**Absorbance at 320 mμ as a function of phenylacetylene concentration**

phenylacetylene to mercuric ion ratios and the diminished production of acetophenone at phenylacetylene to mercuric ion ratios less than one. Apparently no previous example of a bis-(acetylene)-mercuric ion complex has been reported[5].

The apparent leveling off of the acetophenone concentration at about the concentration of mercuric ion in those experiments in which the phenyl-

---

[5] Additional evidence for the existence of bis-(acetylene)-mercuric ion complexes has been submitted for publication.

acetylene to mercuric ion ratio was increased (Fig. 2) is suggestive of the formation of an acetophenone-mercuric ion complex[6] resulting in a loss of the coordination sites available to phenylacetylene and the diminished production of acetophenone. An alternate explanation is 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. No reduction in yield was observed, even though nearly equivalent amounts of acetophenone and mercuric perchlorate were allowed to equilibrate under reaction conditions for up to two days before addition of phenylacetylene. These results therefore favor the latter explanation[7].

From a synthetic point of view these results suggest that by the proper

---

[6] A loosely formed mercuric chloride-acetophenone complex has been described by L. Paoloni, C.A. 54, 12045$^h$ (1960); Rend. ist super. sanita 22, 813 (1959).

[7] It has not been possible to detect the presence of a carbonyl band in the infrared spectra of the final reaction solutions because of the occurrence of a broad absorption, presumably due to mercuric perchlorate, centered near 1700 $cm^{-1}$.

The ultraviolet spectra of the final reaction solutions very closely resemble the spectrum of a 1:1 mixture of acetophenone and mercuric perchlorate in aqueous perchloric acid-dioxane mixtures which in turn is indistinguishable from the spectrum of acetophenone in pure dioxane ($\lambda_{max} = 240$ mμ , $\varepsilon = 13000$) but easily distinguished from the characteristic phenylacetylene spectrum. Although this data does not appear to support the presence of an acetophenone-mercuric ion complex, it is not conclusive since such a complex would be expected to exhibit a spectrum quite similar to that of the uncomplexed molecule.

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 mixtures where the phenyl proton resonance appears as a single sharp absorption and is shifted by -0.45 ppm relative to the uncomplexed molecule in the same medium. The final reaction solutions show the same absorption at the identical field strength as the acetophenone-mercuric perchlorate mixtures.

Therefore it is 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 is attributed to the heterogeneous character of the reaction at phenylacetylene to mercuric ion ratios greater than two.

control of certain variables the reflux temperatures and long reaction times commonly employed in acetylene hydration reactions may be avoided. Mercuric perchlorate apparently has not been widely utilised as a catalyst; its combination with solvent dioxane appears advantageous. Surprisingly, too high a concentration of water is detrimental to the hydration process. One interpretation of this may be the preferential occupation of the proper co-ordination sites on mercury by water and to the exclusion of acetylene. The most critical factor appears to be the acetylene to mercury ratio; clearly excesses of catalyst are undesirable. Further studies of this and related systems are in progress.

The authors wish to acknowledge a fellowship from the Diamond Alkali Company and a grant from the U.S. Public Health Service, National Institutes of Health, U.S.P.H.-RG-9022. One of them (R.E.D.) wishes to acknowledge the support and encouragement in the form of an Alfred P. Sloan Fellowship.