*Anal.* Calcd. for $C_8H_{18}$: C, 84.21; H, 15.79. Found: C, 84.10; H, 15.87.

The product isolated was completely stable toward permanganate and nitrating mixture. The yield of isooctane, 2,2,4-trimethylpentane, was less than in some of the other experiments because aluminum chloride is a very strong polymerizing catalyst.

EXPERIMENT 11.—Aluminum chloride alone completely polymerized isobutene under the conditions of the experiments and produced a viscous oil.

## Summary

1. A new simultaneous reaction of hydropolymerization was discovered and studied in the case of amylene and isobutene.

RIVERSIDE, ILLINOIS RECEIVED SEPTEMBER 24, 1936

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 568]

# The Hydration of Unsaturated Compounds. V. The Rate of Hydration of Acetylene in Aqueous Solution of Sulfuric Acid and Mercuric Sulfate[1]

BY R. H. FRIEMAN,[2] E. R. KENNEDY AND H. J. LUCAS

In the usual commercial process of hydrating acetylene to acetaldehyde in the presence of mercuric sulfate and sulfuric acid, there is present an insoluble or slightly soluble amorphous substance, a mercury organic compound or compounds. It is probable that the composition of these precipitates varies with conditions, as pointed out by Whitmore.[3] As to whether these precipitates are intermediates in the hydration process, the evidence is conflicting. Whitmore points out that the hydration of the triple bond may merely be catalyzed by mercuric ions in acid solution, as in the case of piperonylacetylene.[4] It has been postulated that organo-mercury compounds are intermediates.[5]

**The Analytical Method.**—The procedure finally developed for the analysis of acetylene in aqueous solution, based upon the methods of Davis, Crandall and Higbee[6] and of Eberz and Lucas[7] follows. Into a 300-ml. conical flask having a ground glass stopper with sealed-in stopcock, is pipetted 25.00 ml. of 0.0500 *N* potassium bromate–bromide solution and the flask is evacuated to about 25 mm. with a water aspirator. Then 5 ml. of 6 *N* sulfuric acid is added, the mixture is allowed to stand for two to three minutes, and then in order are pipetted in, 10 ml. of 0.2 *M* mercuric sulfate, 25 ml. of water, and finally 2 to 10 ml. of the sample to be analyzed, a dilute aqueous solution of acetylene. The last is thoroughly rinsed into the flask from a special pipet of the type described by Eberz and Lucas[7] and the flask, still under vacuum and wrapped in a black cloth to exclude light, is shaken mechanically for five to seven minutes. At this time, 5 ml. of 2.0 *N* sodium chloride and 10 ml. of a freshly prepared 20% potassium iodide solution are added. The shaking is continued for another five to seven minutes, the black cloth is removed, the vacuum is then broken, 50 to 100 ml. of water is added to dilute the solution, and titration is made with 0.03 *N* sodium thiosulfate solution. A blank is run at the same time, omitting only the sample.

**Discussion of the Analytical Method.**—The simple bromate–bromide method of determining unsaturation is not satisfactory for the triple bond, as pointed out by Davis, Crandall and Higbee[6] in the case of acetylene, because of the interference due to oxygen, and by Mulliken and Wakeman[8] in the case of liquid alkynes, for which the analytical results were low. The former authors showed that aluminum, nickel and mercury salts are an aid in the quantitative determination of acetylene. In the present work it has been found that the bromination of acetylene proceeds rapidly and smoothly if the molal ratio of mercuric sulfate to the total halide present is greater than unity, but under these conditions the iodine end-point with starch is uncertain. The addition of sodium chloride overcomes this difficulty, making reproducible results possible.

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[1] For the preceding paper in this series, see Eberz, Welge, Yost and Lucas, THIS JOURNAL, **59**, 45 (1937).

[2] Mr. Frieman died suddenly of a heart attack on January 13, 1935.

[3] Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co., N. Y., 1921, p. 118, cites numerous references.

[4] Manchot and Hass, *Ann.*, **399**, 150 (1913).

[5] Vogt and Nieuwland, THIS JOURNAL, **43**, 2071 (1921); Hennion, Vogt and Nieuwland, *J. Org. Chem.*, **1**, 159 (1936).

[6] Davis, Crandall and Higbee, *Ind. Eng. Chem., Anal. Ed.*, **3**, 108 (1931).

[7] (a) Eberz and Lucas, THIS JOURNAL, **56**, 1232 (1934); (b) Lucas and Eberz, *ibid.*, **56**, 460 (1934).

[8] Mulliken and Wakeman, *Ind. Eng. Chem., Anal. Ed.*, **7**, 59 (1935).

The accuracy of the method has been demonstrated by (a) varying the time of bromination, in order to test the possibility of substitution, and (b) varying the ratio of acetylene to bromine in order to determine upper and lower limits. It was found that the same volume of thiosulfate solution was required to back titrate equal volumes of a given aqueous acetylene solution, when the time of bromination was 4, 8, 12, 16, 20 or 24 minutes. This indicates that no substitution takes place. In Fig. 1, in which per cent. of bromine reacted is plotted against the molal ratio of acetylene to bromine, a 45° angle line is drawn, which is the theoretical curve, on the assumption that one-half of the moles of bromine reacted represent the moles of acetylene. An analysis was made of four different aqueous acetylene solutions, in order to establish the acetylene content. These results do not appear on the plot, since they would automatically fall upon the curve. Volumes of the four solutions, different from those taken for the analysis, were then analyzed and the results plotted. It is apparent that the values fall upon the theoretical curve when the initial molal ratio of bromine to acetylene is four or more, *i. e.*, at least twice the theoretical amount, but deviate when this ratio is less. Even when the bromine is in very large excess, *viz.*, one hundred to one, the results are comparable, showing again that no substitution takes place. Because of the good agreement over a wide range of conditions, it is believed that the analytical method is reliable. This procedure of testing the method was resorted to when it was found that pure acetylene was not available, as discussed under purification. The method was not always reliable in the presence of acetaldehyde, as discussed under interference of acetaldehyde.

**Materials.**—Mercuric sulfate solutions were prepared from C. P. mercuric oxide and C. P. sulfuric acid. Acetaldehyde was prepared by the depolymerization of paraldehyde and was distilled three times through a fractionating column. Solutions of acetaldehyde of known concentration in water were made up by weight. The acetylene was taken from a "Prestolite" cylinder.

**Purification of Acetylene.**—The acetylene supposedly was purified by passing through solutions in spiral wash bottles, *viz.*, sodium bisulfite, for removing acetone coming from the cylinder, copper sulfate (made acid by the addition of a few drops of sulfuric acid), for removing phosphine, chromic anhydride in 50% (by volume) sulfuric acid, for oxidizing impurities, especially phosphine, and finally sodium hydroxide. The gas then passed through towers packed with solids, *viz.*, calcium chloride, calcium hypochlorite (H. T. H.), and flake sodium hydroxide.[9] The acetylene from this system was still impure for it absorbed more than the theoretical amount of bromine (a variable amount, usually about 114% of the theoretical), its vapor density was 26.60 (against a theoretical value of 26.02), and an aqueous bromine solution, through which a large volume of the gas had been passed, gave a positive phosphomolybdate test for phosphate. Slow passage of the gas through the purifying apparatus enhanced the purity of the gas, for the lowest value of the vapor density, 26.30, was obtained under these conditions. If the per cent. of sulfuric acid in the chromic acid wash bottle was much greater than 50%, there was rather rapid reduction of the chromic acid due to oxidation of the acetylene. Variations in the method of purification, or even a lack of purification, did not alter greatly the bromine value of different samples of gaseous acetylene. The error involved in this determination is 1 to 2% and is due to the difficulty in accurately measuring the small sample of 2 to 3 cc. of gas, and in quantitatively transferring it to the bromine flask.[10] Even though the acetylene contained phosphine, it is believed that the reaction rate data are not influenced by it, since the amount dissolved in the hydrating solutions was so small that a positive phosphomolybdate test could not be obtained.

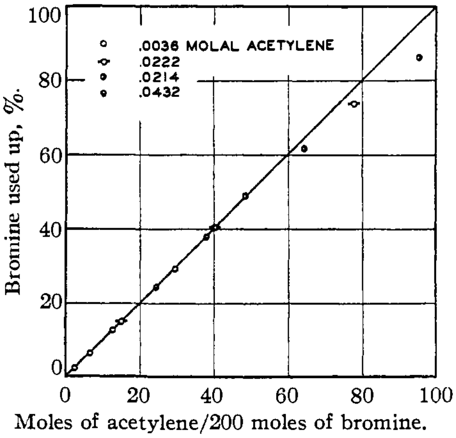

Fig. 1.—Limitations of the analytical method.

**Apparatus and Method.**—The apparatus previously described[7b] was used for this work. The method consisted in passing acetylene into a sulfuric acid solution of known concentration, 5.000 weight formal (*wf.*),[11] until a sufficient amount was dissolved, and adding a measured volume of standard mercuric sulfate in 5.000 *wf.* sulfuric acid, all at 25°. After shaking, the resulting clear solution[12] was quickly transferred to the apparatus, kept at 25 ± 0.04°, from which samples were removed for analysis at intervals of twenty to forty minutes.

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[9] This train was believed to embody the best features of numerous purification methods described by others. See Mathews, THIS JOURNAL, **22**, 106 (1900); Kahutani and Yamada, *C. A.*, **25**, 1655 (1931); Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," D. Van Nostrand Co., New York, 1931, p. 171; Livingston and Schiflett, *J. Phys. Chem.*, **36**, 750 (1932).

[10] The weight of acetylene was calculated by the use of the *P–V–T* relation given in "International Critical Tables," Vol. III, McGraw-Hill Book Company, Inc., N. Y., 1928, p. 3.

[11] Or 4.167 formula weights per liter (*vf.*).

[12] If any cloudiness developed the liquid was discarded.

**Interference of Acetaldehyde with the Analytical Method.**—The reaction product, acetaldehyde, interferes with the acetylene analysis. It is not possible to correct for this effect, because of the variability of results when aldehyde solutions are added to the analytical mixture. There appeared to be a qualitative relationship between the amount of bromine used up and the age of the added aldehyde solution; moreover, this amount appeared to increase more rapidly as the concentration of the acid was raised. It is probable that the variations in the amount of bromine used up by added acetaldehyde, which in some cases were as much as 100%, were due to its partial conversion to other products, such as paraldehyde, aldol and crotonic aldehyde. The error due to the interference of aldehyde with the analytical procedure was estimated to be of the same order of magnitude as the precision of measurement by the time the acetylene was about one-fourth reacted. In the initial stages of the hydration, where the concentration of aldehyde (and consequently the bromine reactive substance) was very small, the analytical procedure was regarded as reliable.

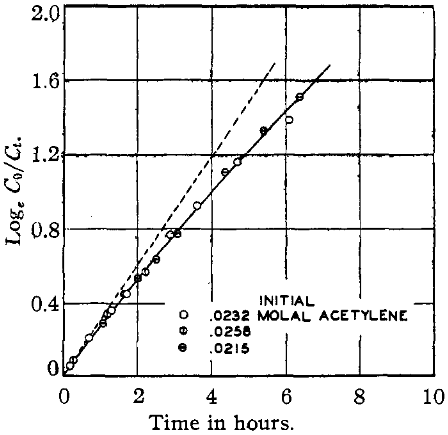

Fig. 2.—Hydration of acetylene in 5.00 weight formal sulfuric acid and 5.00 × $10^{-5}$ weight formal mercuric sulfate.

**The Initial Hydration Rate.**—In order to obtain the initial slope of $\log_e C_0/C_t$ against $t$ (in hours), it was necessary to extrapolate to zero time. The data and the initial slopes of fourteen experiments are shown in Table I. When the mercuric sulfate is 5.00 × $10^{-5}$ *wf.*, and when no aldehyde has been added, the values of the initial reaction rate constants (taken from the initial slopes) lie between 0.285 and 0.322, with 0.290 as the average. The satisfactory agreement here, over a five-fold change in initial acetylene concentration, shows that the initial rate is first order with respect to the acetylene concentration. The similarity of different runs is shown by plotting $\log_e C_0/C_t$ against $t$, as in Fig. 2, which gives the results of three typical experiments, *viz.*, 4, 5 and 6. Here the data of all three fall upon the solid curve; the dotted straight line is the average initial slope of eight experiments. It is evident that the rate subsequent to the initial one does not obey the first order equation, but apparently is dependent upon some higher power, which proved to be the four-thirds power.

TABLE I

HYDRATION EXPERIMENTS IN 5.00 WEIGHT-FORMAL SULFURIC ACID

| Run | $k$ initial, hrs.$^{-1}$ | Initial concentration $C_2H_2$ *vf.* | Initial concentration $CH_3CHO$ *vf.* | Initial concentration $HgSO_4$ *wf.* × $10^5$ |
|---|---|---|---|---|
| 1 | 0.292 | 0.0225 | zero | 5.00 |
| 2 | .285 | .0252 | zero | 5.00 |
| 4 | .302 | .0232 | zero | 5.00 |
| 5 | .288 | .0215 | zero | 5.00 |
| 6 | .285 | .0285 | zero | 5.00 |
| 7 | .260 | .0123 | zero | 5.00 |
| 13 | .322 | .0052 | zero | 5.00 |
| 14 | .293 | .0245 | zero | 5.00 |
| Average | .290 | | | |
| 3 | .186 | .0229 | zero | 4.00 |
| 10 | .415 | .0275 | zero | 6.00 |
| 9 | zero | .0470 | zero | zero |
| 8 | .201 | .0257 | 0.042 | 5.00 |
| 11 | .198 | .0248 | .083 | 5.00 |
| 12 | .285 | .0275 | .083 | 6.00 |

The initial hydration rate is second order with respect to the concentration of mercuric sulfate, for the plot of the initial rate constant against the square of the mercuric sulfate concentration gives a straight line, as shown in Fig. 3. This must pass through the origin, because sulfuric acid alone, in the absence of mercuric sulfate, did not cause hydration of acetylene. It is worthy of note that dependence of rate upon the square of the mercuric sulfate holds when aldehyde is present (experiments 11 and 12, Table I).

The dependence of the rate upon the concentration of the sulfuric acid was not studied. The rate appears to be dependent upon a higher than first power acid concentration because, in 1 *wf.* sulfuric acid (0.963 *vf.*), the hydration proceeds too slowly to be measured.

**The Effect of Acetaldehyde upon the Hydration Rate.**—The apparent four-thirds power relationship between the reaction rate constant during the course of the hydration, and the acetylene concentration, a relationship which is true of experiments 4, 5 and 6, held in some other cases.

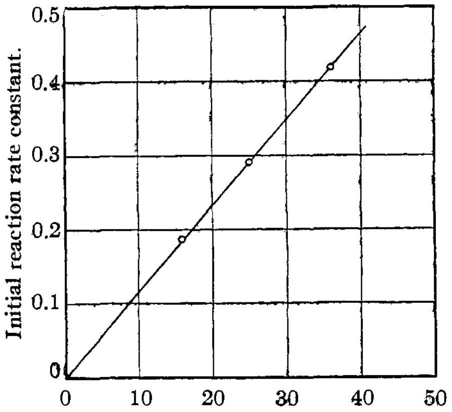

Fig. 3.—Relationship of initial rate constant to the concentration of mercuric ion.

However, it is not typical of all the experiments, for example, those in which the initial acetylene concentration was low (7 and 13) and those in which recently distilled aldehyde was added (8, 11 and 12). Figure 4, in which is plotted the curve for experiment 8 (solid line), indicates a first power relationship to the acetylene. However, the slope of this line is below the value when no aldehyde has been added, shown by the broken line. The effect is not due to interference with the analytical procedure, for the time hardly permitted the formation of the substance responsible for the interference. On the other hand, erratic data and no smooth curves resulted when aldehyde solutions in sulfuric acid which had stood for two to three days, were used instead of a freshly prepared solution. There was no dependence upon the first power relationship in these cases. Since erratic results were associated with some runs in which freshly prepared aldehyde solution was added (for instance, the constants are practically identical in experiments 8 and 11, in which the initial aldehyde concentrations differed by a factor of 2), the best basis for considering the effect of acetaldehyde lies with those experiments which had no acetaldehyde originally. Assuming that the acetaldehyde concentration at the time, *t*, is given by the acetylene which has undergone hydration up to that time, the rate varies approximately as the inverse three-halves power of the aldehyde concentration in those experiments in which the four-thirds power relationship to acetylene held.

The four-thirds power dependence of the rate upon the acetylene concentration, characteristic of such runs, the apparent inverse three-halves power relationship to acetaldehyde concentration, the drop in the initial rate constant when aldehyde is added initially, and the first power relationship of the rate to acetylene concentration under these conditions, probably depend upon the formation of a complex between mercuric ion and acetaldehyde.[13,14]

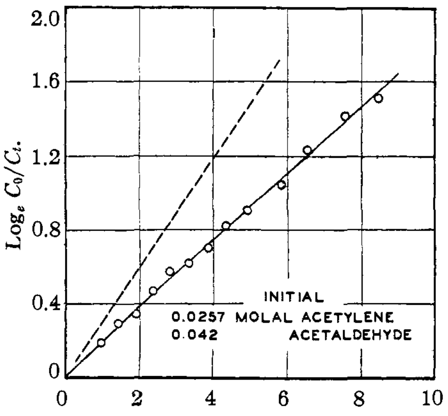

Fig. 4.—Influence of added acetaldehyde upon the hydration of acetylene.

**Discussion of the Hydration Mechanism.**—Since the homogeneous hydration rate of acetylene is first order with respect to the acetylene concentration, and second order with respect to the mercuric sulfate (or acid sulfate) concentration, the simplest interpretation of the reaction mechanism is the assumption that an intermediate complex, from one molecule of acetylene and two molecules of mercuric sulfate (or bisulfate), is the substance which undergoes hydration:

$$C_2H_2 + 2Hg(HSO_4)_2 \rightleftarrows C_2H_2Hg_2(HSO_4)_4$$

$$C_2H_2Hg_2(HSO_4)_4 + H_2O + nH_3O^+ \longrightarrow CH_3CHO + 2Hg(HSO_4)_2 + nH_3O^+$$

It is probable that mercuric bisulfate is the reactive substance, since in the strongly acid solution bisulfate ions predominate over sulfate ions. The assumed higher than first power dependence of the hydration rate upon sulfuric acid is in part accounted for by the presence of the two bisulfate radicals in the complex. Because of the additional catalytic effect of hydrogen ion,

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(13) Denigès, *Ann. chim. phys.*, [7] **18**, 396 (1899), describes a compound of mercuric sulfate and acetaldehyde, $CH_3CHO\cdot HgSO_4\cdot 2HgO$, which is destroyed by hydrochloric acid with regeneration of the aldehyde.

(14) The referee has suggested that the effect may be due to the fact that mercuric ion suffers reduction in the presence of oxygen.

one might reasonably expect a third power, or even higher, dependence. The importance of bisulfate ion in the hydration of acetylene is shown by the work of Vogt and Nieuwland,[5] whose best catalytic mixtures were saturated solutions of potassium (or similar) bisulfate in contact with mercuric sulfate.

One could propose a plausible mechanism for the hydration reaction, based upon the above equation, but the information at present available is still insufficient to permit of a definite decision.

## Summary

Acetylene undergoes homogeneous hydration to acetaldehyde in aqueous solutions in the presence of mercuric sulfate and sulfuric acid. The initial rate of hydration is first order with respect to the acetylene concentration and second order with respect to the mercuric sulfate concentation, while the rate at time *t* has an apparent four-thirds power dependence upon the acetylene. This last is believed to result from the formation of a complex between mercuric sulfate and acetaldehyde.

A probable mechanism of the hydration involves the formation of an intermediate complex between one molecule of acetylene and two molecules of mercuric bisulfate, and the reaction of this complex with water, in the presence of an acid, to form vinyl alcohol, which rearranges to acetaldehyde.

The bromate–bromide method of determining unsaturation is applicable to aqueous solutions of acetylene, provided there is present a soluble mercuric salt whose molal ratio to total halide is greater than unity.

PASADENA, CALIF. RECEIVED NOVEMBER 30, 1936

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[CONTRIBUTION FROM THE BURROUGHS WELLCOME AND CO., U. S. A., EXPERIMENTAL RESEARCH LABORATORIES]

# Pharmacologically Active Compounds from Alkoxy-β-phenylethylamines

BY WALTER S. IDE AND JOHANNES S. BUCK

Considerable pharmacological data have been accumulated on compounds connected with or prepared from methoxy-β-phenylethylamines. It is therefore of great interest to examine the corresponding ethoxy compounds, for this would allow an exact comparison of the pharmacological effects of the ethoxy and methoxy groups to be made. The authors have therefore prepared seven such β-phenylethylamines and from them several series of compounds (N-methylamines, ureas, *unsym*-methylureas, barbituric acids, isoquinolines, N-methylisoquinolines, benzyl-β-phenylethylamines, and characterizing compounds).

## Experimental

The amines were prepared by the series of reactions used by Buck.[1,2] As starting materials aldehydes with the following substituents were used (hereafter these letters refer to the same substituents):

| | |
|---|---|
| A | 2-Ethoxy- |
| B | 3-Ethoxy- |
| C | 4-Ethoxy- |
| D | 2-Ethoxy-3-methoxy- |
| E | 3-Methoxy-4-ethoxy- |
| F | 3-Ethoxy-4-methoxy- |
| G | 3,4-Diethoxy- |

The aldehydes A, B, C, D and E were prepared by ethylating (ethyl sulfate and sodium hydroxide) the corresponding phenolic aldehydes. Aldehyde F was prepared by methylating 3-ethoxy-4-hydroxybenzaldehyde and aldehyde G by ethylating the same phenolic aldehyde.

The aldehydes, together with a number of intermediates, have been described previously (see references, where *Cf.* indicates a different method of preparation or an indirect reference). New intermediates are given in the table.

### References on Intermediates

Aldehydes

A *Cf.* Perkin, *Ann.*, **145**, 306 (1868); Löw, *Monatsh.*, **12**, 396 (1892).
B *Cf.* Werner, *Ber.*, **28**, 2001 (1895); Subak, *Monatsh.*, **24**, 169 Note (1904).
C *Cf.* Kostanecki and Schneider, *Ber.*, **29**, 1892 Note (1896); Hildesheimer, *Monatsh.*, **22**, 499 Note (1902); Gattermann, *Ber.*, **31** 1151 (1898); *Ann.*, **357**, 347 (1907).
D *Cf.* Davies and Rubenstein, *J. Chem. Soc.*, **123**, 2846 (1923).
E, F, G. Buck and Ide, THIS JOURNAL, **54**, 3302 (1932).

Cinnamic Acids

A *Cf.* Perkin, *J. Chem. Soc.*, **39**, 413 (1881); Fittig and Ebert, *Ann.*, **216**, 146 (1883); Stoermer, *Ber.*, **44**, 645 (1911).
B *Cf.* Werner, *loc. cit.*
C *Cf.* Stoermer and Wodarg, *Ber.*, **44**, 637 (1911).
D Rubenstein, *J. Chem. Soc.*, 652 (1926).
E Schlittler, *Ber.*, **66**, 988 (1933); Slotta and Heller, *ibid.*, **63**, 3029 (1930).

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(1) Buck, THIS JOURNAL, **54**, 3661 (1932).
(2) Buck. *ibid.*, **52**, 4119 (1930).