[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

KETENE FROM ACETIC ACID

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The thermostability of acetic acid was noted many years ago by Cahours[1] and by Berthelot.[2] Nef,[3] however, was the first to study its decomposition in a detailed manner. He reported methane, carbon dioxide, carbon monoxide, ethylene, hydrogen, carbon and acetone as reaction products when the acid vapors were passed over pumice at 500°. Still more recently, these substances and also acetic anhydride were observed by Peytral,[4] who passed acetic acid through an 11-cm. platinum tube at 1150°. She postulated three reactions to explain the results

$$\begin{aligned} 2CH_3CO_2H &\longrightarrow H_2O + (CH_3CO)_2O \\ CH_3CO_2H &\longrightarrow CO_2 + CH_4 \\ 2CH_3CO_2H &\longrightarrow 2CH_2O + 2CO + C_2H_4 \end{aligned}$$

The acetic anhydride reaction has recently been made the subject of patents.[5] The peculiarity of such anhydride formation may not be self-evident. However, almost no other monocarboxylic acid behaves in this manner. Some unusual feature, therefore, must be present in this case.

To provide an interpretation of the mechanism of pyrolysis of acetic acid, the "methane system" has proved useful and interesting. Just as the hydroxyl group serves in the *water system*, or the amino group in the *ammonia system*, so the methyl group is the analog in the *methane system*. On this basis carbonic acid, acetic acid and acetone are structurally similar. The known equations for the decomposition of carbonic acid and of acetone,[6] namely, $HO{-}CO{-}OH \longrightarrow H_2O + O{=}C{=}O$, and $CH_3{-}CO{-}CH_3 \longrightarrow CH_4 + CH_2{=}C{=}O$, provide a basis for the analogy that acetic acid should break down primarily both into "carbon dioxide + methane" and into "ketene + water." Thus

$$\begin{aligned} CH_3{-}CO{-}OH &\longrightarrow H_2O + CH_2{=}C{=}O \\ CH_3{-}CO{-}OH &\longrightarrow CH_4 + O{=}C{=}O \end{aligned}$$

In confirmation of this prediction, search for ketene in the reaction products of the acetic acid pyrolysis revealed its presence in appreciable amounts. Ketene unquestionably is the precursor of acetic anhydride, because of its reaction with acetic acid

$$CH_2{=}C{=}O + CH_3CO_2H \longrightarrow (CH_3CO)_2O$$

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[1] Cahours, *Compt. rend.*, **19**, 771 (1844); **20**, 51 (1845).

[2] Berthelot, *Ann. chim. phys.*, [3] **33**, 295 (1851); **53**, 187 (1858).

[3] Nef, *Ann.*, **318**, 221 (1901).

[4] Peytral, *Bull. soc. chim.*, **31**, 113 (1922).

[5] British Patent 194,719, March 10, 1923; U. S. Patent 1,570,514, Jan. 19, 1926; *Chem. Abstracts*, **17**, 3509 (1923); **20**, 768 (1926) and others.

[6] Hurd, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. IV, p. 39.

Furthermore, it serves to explain the origin of the ethylene and the carbon monoxide: $2CH_2{=}C{=}O \longrightarrow C_2H_4 + 2CO$.

Experimental Part

Estimation of Ketene.—The following plan was adopted for the determination of the "acetic acid, acetic anhydride, ketene" mixture which was produced by passing acetic acid through a heated tube. The hot effluent vapors were conducted upward through a vertical bulb condenser to remove the bulk of the acid and the acetic anhydride. Remaining traces of these substances were condensed in two ice-cooled U-tubes, which were connected in series at the top of the condenser.[7] From the second U-tube, the gases were conducted into a flask containing an excess of a measured volume of aniline, wherein the available ketene content was quantitatively removed as acetanilide. This value for ketene is certainly lower than the true value because of the fact that some ketene is removed in the condensers either by simple solution or by reaction either with water or with acetic acid.

A series of experiments was carried out to demonstrate that the acetanilide originated largely or entirely from the ketene. In the first place, it was ascertained that acetic acid mixes with aniline with almost no diminution in volume. Thus 9 cc. of aniline and 1.1 cc. of acetic acid gave 10.1 cc. of mixture. Since the increase in volume in the aniline flask was negligible when the ketene vapors (generated from 85 to 600 cc. of glacial acetic acid) were admitted, this is evidence that negligible quantities of acetic acid were introduced. In no case was the increase more than 1 cc. Secondly, it was definitely established by the following tests that acetic acid does not convert aniline in the cold into acetanilide under the conditions of the experiment. (a) One cc. of acetic acid was mixed with an excess of aniline and left for two hours. Then the acid was neutralized with a dilute solution of sodium bicarbonate, extracted with ether, the ether evaporated and the aniline distilled to 200°. There was no trace of residual acetanilide. (b) A repetition of (a) with similar results, except that 20 cc. of acid and 20 cc. of aniline were used. (c) Similar to (b) except that 5 g. of acetanilide was purposely admixed at the start. At the conclusion of the experiment 4.8 g. of acetanilide was recovered. Finally, since acetanilide may be formed by the interaction of acetic anhydride and aniline in the cold, it was proved that the quantity of acetic anhydride which could have been present was quite insufficient to produce the acetanilide which was isolated. To prove this, the acetic acid and acetic anhydride condensate from Run 4 below was analyzed for the anhydride content by Whitford's method,[8] and was found to contain 0.11 g. of acetic anhydride per cc. of the condensate. Since the total increase in volume of the aniline through which the ketene passed was only one cc., the maximum amount of acetanilide caused by acetic anhydride would be 0.27 g. Presumably even less than this would be formed from this source since acetic anhydride possesses a lower vapor pressure than acetic acid and would tend, therefore, to remain more completely in the condensate. Actually, 4 g of acetanilide was isolated in this run. In Run 6 no acetic anhydride could be detected, yet 3.5 g. of acetanilide was isolated. Its origin must have been from ketene.

Reagents and Apparatus.—Glacial acetic acid was purified by crystallization. The acid was frozen at 15°, filtered off. melted and distilled. The fraction boiling between 115 and 118° was taken. A sample of this fraction melted at 17°. The aniline was also freshly distilled.

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[7] From 600 cc. of original acetic acid in one run at 800°, 480 cc. was recovered by the condenser, 4 cc. by the first U-tube and none by the second.

[8] Whitford, This Journal, **47,** 2939 (1925).

The apparatus for the pyrolysis was essentially similar to that previously described[9] for the preparation of ketene from acetone. A quartz tube was generally used because of the high temperature required (800°), although similar results were also obtained with a Bohemian glass tube. Porcelain chips were used as packing in both. The temperature was recorded inside the tube by a thermocouple which was sheathed by a small pyrex tube. The quartz reaction tube was heated by the longest unit (16 inches) of an ordinary 3-segmented electric combustion furnace. The acetic acid vapors flowed first through the hot reaction tube, then through a vertical bulb condenser and two ice-cold U-tubes, and finally through a flask which contained 30 cc. of aniline. The remaining gases were inflammable (probably CH_4, CO, C_2H_4) and also contained carbon dioxide (white precipitate with lime water), but they were not otherwise examined.

Pyrolysis.—It was established that little or no decomposition of acetic acid occurred as it was vaporized (by rapid boiling) and passed through a tube at 600° or at 700°. Thus, at 700°, from an original 100 cc. there was almost complete recovery and no trace of acetanilide (*via* ketene) was isolable. At 800°, however, the acid decomposed and ketene was evident in the products. The results of six selected representative experiments are summarized in Table I.

TABLE I

PYROLYSIS OF ACETIC ACID AT 800°

Orig. acetic acid, cc.	Recov. vol., cc.	Acid consumed, cc.	Acetanilide, g.	Equiv. % yield of ketene
100	80	20	0.6	1.2
100	75	25	0.7	1.2
85	60	25	2	3.4
600	440	160	4	1.1
600	480	120	2.5	0.9
400	280	120	3.5	1.2

The aniline was searched for acetanilide in the following manner. It was washed with a dilute solution of sodium bicarbonate and extracted with ether. Both aniline and ether were distilled off up to 200°, and the residue was dissolved in boiling water, filtered and allowed to cool. These acetanilide crystals were collected on a filter, dried and weighed. In general, the percentage yield of available ketene was 1–2%. Unquestionably, as explained above, the true yield of ketene was greater than this.

Summary

At 800° or higher acetic acid undergoes a reaction of dehydration into ketene as well as a reaction of demethanation into carbon dioxide. These are the primary reactions, but the reactivity of ketene sponsors other effects. Such secondary processes include addition with water or with acetic acid (giving acetic acid and acetic anhydride, respectively) or

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[9] Hurd and Cochran, THIS JOURNAL, **45**, 515 (1923); Hurd, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1925**, Vol. IV, p. 39.

pyrolysis into carbon monoxide and ethylene. The concept of the "methane system" has been adapted to explain these results.

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TREMETOL, THE COMPOUND THAT PRODUCES "TREMBLES" (MILKSICKNESS)

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Tremetol is the active principle of two plants, richweed and rayless goldenrod, both of which cause the disease known as trembles. This disease is also known as milksickness, especially by the medical profession. Richweed or white snakeroot (*Eupatorium urticaefolium*) is responsible for the disease in the Central States; rayless goldenrod or jimmy weed (*Aplopappus heterophyllus*,) occurs in the Southwestern section of the United States, where it produces the same disease.

Extensive pharmacological study, the results of which have been published in other places[1] has demonstrated that the active constituent of these plants is a substance to which the name tremetol has been applied. This paper contains the results of the chemical study of tremetol.

To prepare tremetol the following procedure has been used successfully. The plant material should be fresh in the case of richweed; rayless goldenrod is still poisonous when dried but appears gradually to lose toxicity. Old dried richweed does not produce trembles. The plant is comminuted and extracted with alcohol. The solvent is distilled from the extract, best under diminished pressure, and the greenish fatty residue is extracted with boiling water as long as anything dissolves. The insoluble material is collected and thoroughly extracted with boiling 50% alcohol. The solvent is removed from this solution and the thick resinous mass that separates is allowed to cool and harden, when the watery portion of the residue may be poured off it. The resinous mass is now thoroughly extracted with boiling 30% alcohol and the solution is filtered hot from the insoluble matter. On cooling the filtrate crude tremetol ester separates. A further crop may be obtained by evaporating the alcohol from the mother liquors. The combined crops are now hydrolyzed by boiling with 5% alcoholic potash for four hours, the alcohol is distilled off and the residue is dissolved in water. The free tremetol is extracted from this solution with successive portions of ether. The ether solutions are united, concentrated to convenient volume and washed, first with dilute sodium hydroxide solution and then with water, to remove possible phenols and resin acids. The purified ether solution is now mixed with 4 volumes of petroleum ether, filtered from any precipitate and allowed to evaporate. The solution in ether and reprecipitation with petroleum ether should be repeated twice to insure purity. On removal of the solvent tremetol remains as a straw-yellow, thick oil of pleasant aromatic odor distantly reminiscent of clove and nutmeg. Should solid, waxy particles separate, the substance has not been thoroughly separated from a sterol that accompanies it in richweed

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[1] *J. Agric. Res.*, **35**, 547–576 (1927); *J. Am. Med. Assocn.*, **91**, 234–6 (1928); *J. Am. Vet. Med. Assocn.*, (n. s.) **26**, 603–605 (1928). A report on rayless goldenrod is in course of publication.