[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

OPTIMUM CONDITIONS FOR THE PREPARATION OF KETENE FROM ACETONE

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Inasmuch as ketene has been found to be an effective acetylating agent for various types of compounds, this study of conditions governing its production was undertaken. Ketene is prepared by the pyrogenic decomposition of acetone. The following work concerned itself with the variables which were considered to influence the yield, the more important of which were the temperature of the furnace, the rate of flow of acetone, and the rate of decomposition of acetone.

During the investigation, it was found that the glass combustion tube in which the ketene is formed could not be replaced by an iron pipe. Instead of ketene production, there was always formation of carbon due, no doubt, to the catalytic dehydration by certain metallic oxides in the pipe. It is quite conceivable that ketene was formed, and that the following equation represents its decomposition: $CH_2{=}C{=}O \longrightarrow H_2O + 2C$.

Apparatus

The apparatus which was found to be most successful for the production of ketene was patterned after that described by Hurd and Cochran.[1]

It differed, however, in several important details. First, instead of a dropping funnel with a pear-shaped bulb, a graduated, cylindrical dropping funnel (125 cc.) was used. This allowed the volume of spent acetone to be read at any time during the process. Second, a graduated cylinder in which to collect the distillate was used in place of Hurd and Cochran's container "D," for similar reasons. Third, with a spiral (or bulb) condenser, it was found possible to eliminate the two U-tubes. Fourth, corks were eliminated from the ends of the combustion tube, and from the upper end of the condenser, by drawing these tubes out to the diameter of the glass tubes with which they were to be joined. Connection was then made with rubber tubing, after taking the necessary precaution to have the ends of the glass tubes in contact. The two corks, one in the round-bottomed flask and the other at the bottom of the condenser, were as free from holes as possible. They were well softened, and were painted with water glass inside and outside and left in place one day before use. The small cork in the dropping funnel gave no trouble. It was chosen carefully and was softened, but was not painted with water glass. Fifth, the gas combustion furnace was replaced by an electrically heated furnace,[2] the temperature of which was registered by a pyrometer with a standardized Chromel-Alumel thermocouple. The central tube of this furnace was of Alundum, 3 × 80 cm.; the Pyrex combustion tube and the thermocouple were placed in it.

Ketene was estimated by one of two methods. One was to pass the gases through an excess of standard alkali solution, and to titrate the ex-

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[1] Hurd and Cochran, THIS JOURNAL, **45**, 519 (1923).

[2] Built by W. A. Van Winkle and described in his Doctor's Thesis, University of Illinois, 1919. Any electric combustion furnace would be satisfactory.

cess with standard acid. With an efficient bubbler, only a negligible trace of acetanilide was found when the gases from the the hydroxide were passed into an ethereal solution of aniline. However, the supplementary reaction vessel containing aniline, or containing a known amount of standard alkali, was always used. The second method was to convert the ketene to acetanilide by passing the gases through a solution of aniline in ether or through a considerable excess of pure aniline. Here, also, a second reaction flask collected only traces of ketene.

Results

Quantitative data for about 50 runs were obtained between the temperatures 630° and 740°. For lack of space, it is impossible to record them all. Five representative runs are given in Table I.

Table I

Representative Runs

Temp. °C.	Min.	Cc. used	Cc. cond.	Cc. decomp.	Cc. of NaOH 5.414 N	Cc. of HCl 2.602 N	Ketene %
630	31	50	39.5	11.5	49.74	91.78	19.6
665	48	125	104	21	48.30	63.93	33.2
695	42	81	31	50	50.02	19.35	32.3
695	25	125	94.5	30.5	48.33	28.22	45.1
735	16	79	29	50	47.40	11.06	33.4

The best yields of ketene were obtained in the temperature range 695–705°. This is 100–200° higher than the temperature first advocated by Schmidlin and Bergman,[3] although it is in close agreement with the temperature, 710°, recently announced by Staudinger and Hauser.[4]

In all, 23 runs were made between 695° and 705°, giving yields[5] of ketene which varied between 22.9 and 48%. The yields in more than two-thirds of the cases were above 35%. The lowest yield was obtained when more than 87% of the acetone introduced was decomposed into gaseous products; the highest yield, when about 9% was decomposed.

There is a rough relationship which can be drawn between the percentage of acetone decomposed and the percentage yield of ketene. The reason for it undoubtedly lies in the fact that ketene vapor is prevented from decomposition, once it is formed, by sweeping it rapidly from the furnace with acetone vapor. In the experiments in which over half of the acetone was decomposed, regardless of other factors, the highest yield obtained was 34.4%, and the highest yield was only 27.4% when four-fifths or more of the acetone was decomposed. When less than half, or better yet, when less than 40% of the acetone was decomposed, the yields were much better.

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[3] Schmidlin and Bergman, *Ber.*, **43**, 2821 (1910).

[4] Staudinger and Hauser, *Helvetica Chim. Acta*, **4**, 887 (1921).

[5] In one run, a yield of 64.8% of ketene was obtained, but this result could not be duplicated.

In many cases it was possible to duplicate results to a nicety. Such, for example, were the yields of 45.0 and 45.1% obtained under similar conditions. One of these cases is cited in Table I. A similar result is shown in the yields of 25.0 and 25.1% at 735°, when acetone entered at the rate of 3 cc. per minute, with about 85% of it undergoing decomposition. Although many such cases were encountered, there were also many in which the yields did not check so closely under similar conditions. With a pyrogenic reaction such as this, it would be surprising were this not the case. It may be said, however, that most of the results of experiments carried out under similar conditions are comparable. To illustrate the point that anomalous results are encountered, one example will suffice. It was customary to obtain 40% or more of ketene when only one-tenth of the acetone was decomposed. In two cases, however, the yield dropped to about 32%. For practical ketene production, the optimum value for acetone decomposition is between 25 and 40%.

The rate of flow of acetone also influences the yield. The two cases at 695°, cited in the table, illustrate this fact. In the first, the rate of flow of acetone is 1.9 cc. per minute and in the second 5 cc. per minute. The higher yield in the latter case is due in part to this cause, but also in part to the difference in rate of decomposition of the acetone. Here again, no exact numerical relationship can be stated, but in a general way it seems that the best rate of flow is about 5 cc. per minute. Good results were obtained between 2.5 and 7 cc. per minute.

An attempt to correlate the combined effect of these two factors on the yield of ketene was fruitless. The rate of decomposition of acetone did not appear to be a factor in the ultimate yield of ketene. This may be interpreted to mean that whatever effect the percentage of undecomposed acetone may have upon the yield of ketene, it is an effect that is independent of the rate of flow of acetone.

There is a relationship, however, between temperature and rate of flow of acetone. Within limits, a higher temperature may be used without seriously diminishing the yield of ketene, providing the flow of acetone is accelerated accordingly. This observation coincides with that of Mlle. Peytral,[6] who noted that when acetone vapors were passed rapidly through a platinum tube 11 cm. long, at 1150°, a pronounced ketene odor was apparent which was absent when acetone was introduced at a slower rate.

The Pyrex combustion tubes usually lasted for 40 or 50 runs before replacement was necessary. A curious feature was noticed when a tube that had served for 37 runs was removed and broken. Its appearance was stratified, as though it were composed of two concentric tubes, the outer sheath being two or three times as thick as the inner one. This was revealed by a cross-section of the tube at any point where it had been in the

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[6] Peytral, *Bull. soc. chim.*, [4] **31**, 122 (1922).

furnace. The cylindrical cleavage plane was very distinct. There was a dark gray incrustation between the layers, and in many places bubbles had developed between the layers. The same phenomenon was observed in a second combustion tube which was used similarly for about the same length of time.

Summary

An improved apparatus for the preparation of ketene from acetone is described. The temperature, the rate of flow of acetone, and the percentage decomposition of acetone all influence the yield of ketene.

For practical purposes, the following conditions seem best for ketene production: temperature, 695–705°; rate of flow of acetone, 5 cc. per minute, and the decomposition of acetone, between 25 and 40% of that introduced. These conditions give consistent yields of ketene which range between 35 and 45%.

The glass combustion tube becomes stratified after it has served in a number of runs. No ketene results when the glass tube is replaced by an iron pipe. Carbonization occurs instead, at temperatures which would allow ketene production.

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[Contribution from the Research Laboratory of the Eastman Kodak Company, No. 226]

THE PLASTICITY OF CELLULOSE IN CUPRAMMONIUM HYDROXIDE[1]

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In recent years no little interest has been shown in the viscosity of solutions of cellulose in cuprammonium hydroxide. It has been shown by Ost[2] and others[3] that cotton which has been bleached or treated with sodium hydroxide or even hot water will give a solution in cuprammonium hydroxide which has a lower viscosity than will an untreated cotton.

Joyner put forward the hypothesis that the viscosity in Schweitzer's reagent was dependent on a hypothetical substance which he called "cellulose A." Inasmuch as he had proved that the logarithm of the viscosity of cotton in cuprammonium hydroxide was proportional to the total cotton concentration, he assumed that, in a given cotton, the logarithm of the viscosity would be proportional to the "cellulose A" content and that he

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[1] Read at the Ithaca Meeting of the American Chemical Society, September, 1924.

[2] Ost, *Z. angew. Chem.*, **24,** 1892 (1911).

[3] (a) Gibson, Spencer and McCall, *J. Chem. Soc.*, **117,** 479 (1920). (b) Joyner, *ibid.*, **121,** 1511, 2395 (1922). (c) Farrow and Neale, *J. Text. Inst.*, **15,** p. 157T (1924).