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APPARATUS FOR THE PREPARATION OF KETENE BY THE PYROLYSIS OF ACETIC ANHYDRIDE

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Earlier workers have noted (1–9) that acetic anhydride can be pyrolyzed at atmospheric pressure to ketene and acetic acid; however, experimental details are limited. Ketene produced by the method suggested in this article is essentially pure and is not contaminated with by-product gases as in the case of acetic acid or acetone as source materials. Often this is advantageous in work involving ketene as an intermediate.

It was found that at temperatures of 600° (Run 4, Table I), or above, decomposition products (*e.g.* carbon dioxide, methane) were obtained. Such temperatures, while possibly increasing the conversion per pass of acetic anhydride to ketene, lower the purity of the ketene produced through formation of by-product gases. At temperatures in the neighborhood of 500° no by-product gases are obtained, and there is close agreement between the ketene found in the gas stream and the by-product acetic acid formed. Mass spectrometric analysis showed acetic anhydride ($<0.2\%$) as the only impurity present in the recovered ketene in a measurable amount.

Some typical data are recorded in Table I. Although conversions per pass for the better runs are low (23–30%) efficiencies are very high (95–97%), and recycling of recovered acetic anhydride will permit good yields of ketene.

Careful analysis of the data given in Table I will show that the conversion increases with increasing mass rate (decreasing contact time) which is not ordinarily the case for flow type reactors. This anomaly can possibly be explained by the increased rate of gas-liquid separation at the higher mass rates, thereby, affording less time for recombination of the ketene and by-product acetic acid.

EXPERIMENTAL

Apparatus. The apparatus used is shown in Fig. 1. Acetic anhydride is stored in the reservoir, A, and fed through a metering pump, B, to an electrically-heated flash evaporator, C. The evaporator is constructed of 25 mm. Pyrex tubing containing a piece of 18 mm. Pyrex tubing sealed off at both ends and spirally wound with B&S 14 gauge stainless steel or Chromel A wire; this provides an annular space small in cross-sectional area and large in heating surface. Vapors leave the evaporator at about 150° and enter the pyrolysis chamber, D, where they are rapidly heated to 500–510°. The pyrolysis chamber is constructed of 19 mm. Vycor tubing with a 9 mm. Vycor thermowell, E, extending through its 540 mm. length. Heat is supplied electrically through Chromel A tape wrapped over a thin asbestos layer. If desired an additional winding of tape can be superimposed over the first and its heating action controlled through an electronic temperature controller. The reaction mixture passes into a short (10×100 mm.) condenser which is packed with $\frac{3}{16}$ in. glass helices and cooled by some low temperature coolant (*e.g.* acetone, chloroform-carbon tetrachloride, or methylene chloride) kept at -30 to $-50°$. Since the rate of recombination of ketene and acetic acid is rapid, the gas-liquid mixture is separated rapidly in two small cyclone separators (G, H) in series. The discharges of these cyclones are made of large bore (2 mm.)

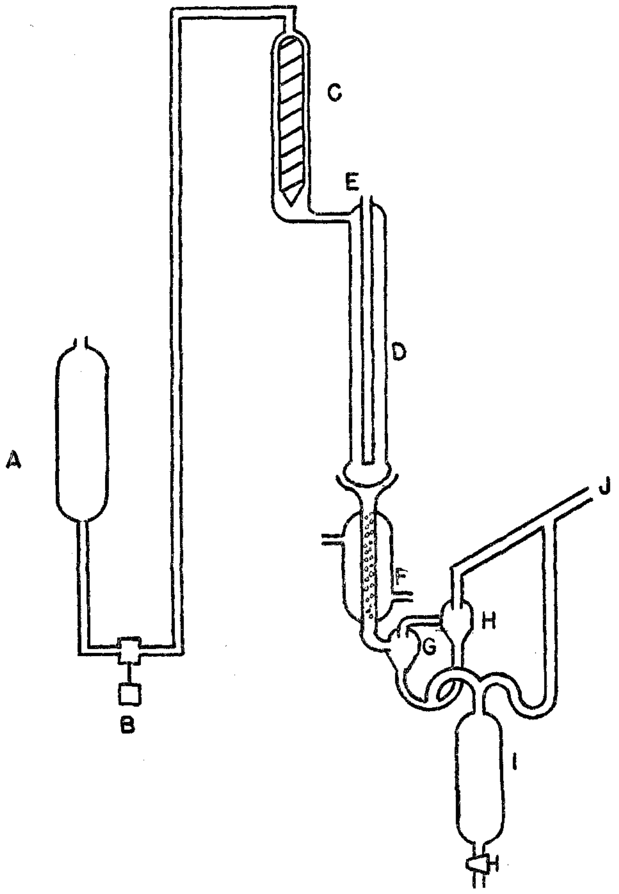
TABLE I

PREPARATION OF KETENE

RUN	Ac_2O CHARGE	MASS RATE[b]	TEMP.,[h] °C.	AcOH PRODUCED	KETENE PRODUCED	CONV.,[c] %	EFF.,[d] %
	g. moles/hr.	*g./cc./hr.*		*g. moles/hr.*	*g. moles/hr.*		
4[a, e, f]	2.08	2.50	590–600	0.639	0.688	31.6	95.0
9[g]	3.41	4.08	500–510	.725	.708	20.8	86.3
12[f]	5.07	6.10	500–510	1.35	1.30	25.6	94.7
13[a, f]	6.17	7.41	500–510	1.75	2.01	30.5	95.9
15[a, f]	4.73	5.67	500–510	1.03	1.19	23.4	97.5

[a] Calculations of conversion and efficiency based on the mean average between AcOH and ketene produced. [b] Mass rate in g. of Ac_2O per cc. of reactor volume per hour. [c] Moles of ketene per mole of acetic anhydride fed. [d] Moles of ketene per mole of acetic anhydride reacted. [e] There was 4.0 l./hr. of by-product gases formed. [f] Ketene absorbed in standard KOH. [g] Ketene absorbed in glacial acetic acid. [h] Thermocouple temperatures not corrected for radiation effects.

FIG. 1



capillary tubing to reduce gas-liquid contact area. Unreacted acetic anhydride and by-product acetic acid are drained through a U-tube trap into the receiver, I. Substantially pure ketene is removed at J.

Analysis. Acetic anhydride and acetic acid were analyzed for by standard procedure (10).

SUMMARY

Ketene, free of by-products, can be conveniently prepared by the controlled pyrolysis of acetic anhydride in a hot tube at 500–510°. Rapid separation of the reaction products is essential to prevent recombination. Depending upon rates of flow, conversions vary from 17% to 31% with corresponding efficiencies of 80 to 96%.

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