

AN IMPROVED APPARATUS FOR THE LABORATORY PREPARATION OF KETENE AND BUTADIENE

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Ketene is now commonly prepared by the pyrolysis of acetone. This is accomplished by passing acetone vapors either through a hot tube (1) or over an electrically heated metal filament (2). An apparatus of the latter type which gives very satisfactory results is the improved lamp described in this paper. It serves efficiently also in the preparation of 1,3-butadiene from cyclohexene (3, 2c).

The lamp contains a shorter heating element than is used in the devices previously described. It uses an inexpensive Chromel A filament, which is more efficient than platinum or tungsten. Less carbonization occurs when Chromel A is used. Use of the smaller filament results in a shorter contact time, and a higher percentage yield may be obtained (in the case of ketene).

DESCRIPTION OF APPARATUS

The apparatus consists essentially of a Chromel filament (O in fig. II), suspended from the top portion of ground glass joint H so that the filament may be removed from chamber E whenever desired.

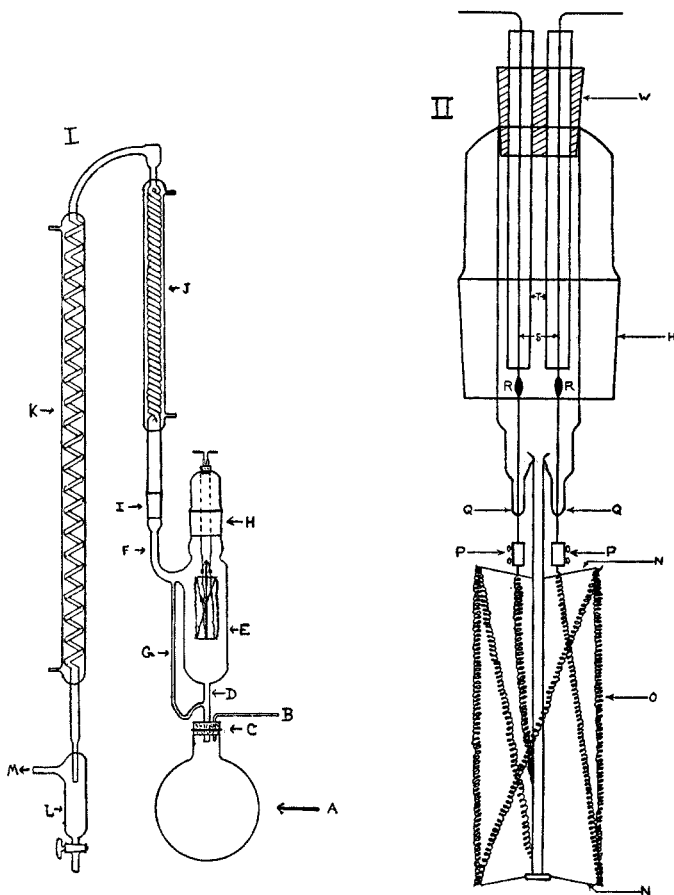
Filament O is prepared from 175 cm. B. and S. gauge 24 Chromel A wire, an alloy of 80% nickel and 20% chromium, by wrapping the wire tightly in a spiral around a rod 3 mm. in diameter, and stretching the coil thus formed to a length of 70 cm. The filament is supported on platinum hooks, N, 15 mm. in length and sealed into the Pyrex glass rod which supports them. The three hooks at the bottom of the rod are spaced 120° apart. Two platinum hooks support the filament at a distance of 11 cm. above the end. The ends of the filament O are connected to tungsten leads by means of the nickel sleeves P, which are 10 mm. in length, 3.5 mm. internal diameter and are equipped with two set screws. The tungsten leads are of B. and S. gauge 24 wire and are sealed into the glass at the points Q, and above these junctions are soldered to B. and S. gauge 24 copper wire (S) at the points R. The copper leads S are insulated by pieces of 6 mm. glass tubing T, which are held by the cork stopper W.

The copper wire leads are connected to a source of 110 volt A.C., preferably through a variable resistance, such as a Variac transformer. A satisfactory fixed

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resistance may be made of Chromel wire wound around a porcelain form. The proper length of resistance wire necessary to keep the filament heated at a dull red must be determined by experiment.

All the glass used in the apparatus is Pyrex. The ground glass joint H is a 55/50 standard taper. Chamber E is constructed from a 25 cm. length of glass tubing of 70 mm. internal diameter. Connecting tube D is 12 mm. tubing, side arm F is 15 mm. tubing and reflux return tube G is 6 mm. tubing. Joint I is a 19/38 standard taper.



Condensers J and K may be of any efficient type. In the apparatus illustrated J is a double spiral condenser 50 cm. long, and K is a single spiral 90 cm. in length. The two are connected at the tops by a glass seal. The liquid trap L sealed to the lower end of condenser K is constructed of 35 mm. tubing and is 125 mm. long, with a stopcock for removal of liquid from the trap. The ketene or butadiene is conducted away through the tube M, of 8 mm. diameter.

OPERATION

The reagent (acetone or cyclohexene) is placed in A, a 2-liter, round-bottomed flask which is attached to the lamp by means of a rubber stopper C. Through this stopper extends a piece of 6 mm. glass tubing B which may be used to introduce more reagent when needed. It must be closed when the apparatus is being operated. The introduction into A of sufficient glass wool to extend a few cm. above the surface of the liquid serves to prevent bumping.

After M is connected to the proper apparatus, the stopcock on L is closed and the liquid in A is heated until it refluxes gently from condenser J. Five minutes refluxing should be allowed to drive the air from chamber E. The current may then be passed through filament O, which should be heated to a dull red glow (temperature 700–750°).

After the starting operations the apparatus needs little attention. Occasionally condensed liquid must be removed from trap L, the amount collecting there being dependent upon the temperature of the water in condensers J and K. If J and K allow too much acetone or cyclohexene to pass, a trap surrounded by ice water may be placed between M and the reaction flask.

At the end of a run the following operations must be carried out rapidly in this order: (1) the source of heat is removed from flask A, (2) the filament current is turned off, and (3) the stopcock on L is opened.

CALIBRATION

The amount of ketene produced per hour may be determined either by weighing the acetanilide produced on passing the effluent gas stream through excess aniline for a measured period of time, or by passing the gas stream through standard alkali with subsequent titration of the unused alkali. By the second method the apparatus described was found to deliver 0.45 mole of ketene per hour. In a continuous run of ten hours 4.53 moles of ketene was produced with a net consumption of but 350 ml. of liquid from flask A. If the residual liquid and condensate were pure acetone, this would represent a 95% yield, but the figure is too high, for although the liquid is chiefly acetone, it also contains small amounts of acetic anhydride, acetic acid and acetylketene. The lamp should be operated for fifteen minutes to expel air from the system before starting to calibrate the apparatus.

To determine the yield of butadiene, the gas from M may be absorbed in a solution of bromine in carbon tetrachloride and the resulting butadiene tetrabromide weighed, or it may be liquefied at -80° and distilled (at about -5°) by means of a Davis column (4). By the first method the present apparatus was found to produce 0.28 mole of butadiene per hour. The unrecovered cyclohexene was 0.45 mole, which represents a 62% yield.

By increasing the filament temperature to 800–850°, a flow of 0.55 mole of butadiene per hour may be obtained. The yield under these conditions, however, is only 32%. Hershberg and Ruhoff (2c) report that Chromel C, a nickel-iron-chromium alloy, is superior to Chromel A for butadiene production. They obtained a 65–75% yield under conditions giving 0.46–0.55 mole per hour.

In a similar apparatus constructed with an uncoiled filament made of 150 cm. B. and S. gauge 22 platinum wire, the flow of ketene (5) per hour was 0.1 mole, and the flow of butadiene (6) was 0.11 mole.

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glass joint be used in the top of the lamp, and to Professor N. L. Drake for his suggestion that coiled Chromel A wire be tried as a filament.

SUMMARY

A lamp is described which is capable of delivering 0.45 mole of ketene per hour from acetone, or 0.28 mole of 1,3-butadiene per hour from cyclohexene. The lamp contains a coiled, electrically-heated Chromel filament.

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