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PROCESS FOR PREPARING KETENE

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This invention relates to new methods for preparing ketene by the decomposition of acetone. Briefly, the invention consists in subjecting acetone to a temperature between about 200° and 400° C. in the presence of intensely ionizing radiations. The object of the invention is to provide conditions whereby the thermal decomposition threshold for acetone may be lowered, whereby improved yields of ketene are obtained. Another object is to reduce undesired side reactions. Other objects will be apparent from the following description.

It is known that actetone, when subjected to temperatures of about 600° C., will undergo pyrolysis to produce ketene, as in the following equation:

$$CH_3—CO—CH_3 \rightarrow CH_2=C=O+CH_4$$

However, the yields obtainable in this process are fairly low, ranging from about 11% to 17.5% (Ber., 43, page 2821 (1910); J.A.C.S., 45, page 518 (1923)). It has also been reported that the reaction will not take place at temperatures below 455° C. (J.A.C.S., 45, page 517 (1923)), and that any temperatures below 600° C. result in sharply diminished yields (ibid., page 519). Since ketene is a highly unstable product it would obviously be desirable to provide methods whereby this product could be produced at lower temperatures, thereby reducing losses of the initially formed ketene, and retarding side reactions.

I have now found that the decomposition of acetone to ketene is remarkably sensitive to the effects of ionizing radiations. For example, when a sample of liquid acetone was subjected to a temperature of about 150° C., while enclosed in a vessel containing a cobalt-60 radiation source, a detecable amount of ketene was produced in eight hours. When the same experiment was repeated at 20° C. no detectable amount of ketene was produced. At reaction temperatures below about 100° C., the effect of ionizing radiations is substantially nil; at temperatures of about 100° to 200° C., such radiations will effect a slow reaction. At temperatures of 200°–400° C., the effect of irradiation becomes of more practical interest; under these conditions, conversions to ketene ranging between about 10% and 30% may be obtained in periods of time ranging between about one second and 60 minutes. Those skilled in the art will understand that the lower temperatures require longer contact times and/or a higher intensity of ionizing radiations. Conversely, at the higher temperature levels, the contact time and/or the intensity of radiation may be correspondingly diminished.

Suitable sources of ionizing radiations include natural and synthetic radioactive isotopes, atomic reactors and the products thereof, particle accelerators and the like. If radioactive isotopes are employed, the desired isotope may be incorporated into metal billets, granules or powder, and then placed in intimate contact with the acetone at the desired temperature. In a continuous process, a tubular reactor is preferably used which is embedded in an isothermal heater, the tube itself containing a substantial proportion of the radioactive isotope. It is preferred

to use radiation consisting predominantly of gamma rays, i.e. electromagnetic waves in the 0.010 to 1.40 angstrom unit wave length range. Gamma rays possess greater powers of penetration than either alpha or beta radiations, and hence where strong gamma emitters are used, the radiation source need not be as evenly distributed within the reaction zone as is the case where alpha or beta ray emitters are used. In the case of tubular reactors, strong gamma ray emitters such as cobalt-60 may be used to construct tubular reactors having an inside diameter of about 0.10 to 4.0 inches. Where a strong beta emitter such as tin-123 is used, smaller reactors should be used in order to provide for adequate penetration of radiations into the reaction zone.

It is preferred to employ a source of radiation of sufficient strength to produce between about 10^4 and 10^8 roentgens per hour per cubic centimeter within the reaction zone.

Isotope	Half-life	β radiation, Mev.	γ radiation, Mev.
Na 22	2.6 y.	0.58	1.3
Mn 54	310 d.		0.85
Co 60	5.3 y.	0.31	1.1–1.3
Zn 65	250 d.	0.32	0.45–1.0
Y 88	105 d.	0.83	0.9–2.76
Zr 95	65 d.	0.39	0.8
Rh 102	210 d.	1.3	0.46
Ag 110	225 d.	0.59	0.6–1.5
Sn 123	130 d.	1.3	0
Cs 134	2.3 y.	0.65–0.9	0.6–0.79

In one modification of the process, liquid acetone at slightly below its critical temperature of 235° C. may be enclosed in a pressure vessel including the radiation source. A pressure relief valve is provided above the surface of the liquid responsive to the vapor pressure in the vessel. When ketene is produced it is automatically withdrawn as gaseous product by the opening and closing of the relief valve, and is thereby continuously removed from the reaction zone.

As is well known ketene is vary unstable, and hence cannot be preserved as such. Usually, the pyrolysis gases are utilized directly in various acetylation processes, as for example to produce acetamide with ammonia, ethyl acetate from ethanol, or acetyl chloride from hydrogen chloride. Sometimes the gases are used directly for the acetylation of cellulose. Alternatively, the ketene may be dimerized to produce its more stable dimer boiling at 127.4° C. In the process of this invention, the recovery of ketene from unreacted acetone is simplified in all cases because the reaction gases are cooler, and hence it is in many instances unnecessary to cool the gases at all before using them in the desired acetylation process. The remaining acetone may then be recycled with little or no preheating. The invention may perhaps be more readily understood from the following example, which however is not intended to be limiting in scope:

Example

A reactor is constructed comprising a 36-inch tube (1-inch I.D.) of aluminum-clad radioactive cobalt. The radioactive tube comprises a minor proportion of cobalt-60 as the major radiation source, and is produced by subjecting a natural cobalt tube to neutronic bombardment in an atomic reactor until the desired intensity of radiation is induced. The radiation intensity at the center of the finished tube is about 10^5 roentgens per hour per cubic centimeter.

The reactor tube is then immersed in a lead bath held at a constant temperature of about 350° C. Liquid acetone is vaporized, preheated to about 350° C., and passed through the reactor tube at atmospheric pressure, and at a rate calculated to provide about 30 seconds residence

time. It is found that a substantial conversion to ketene takes place, and the yield, based on acetone consumed, is in excess of 30%.

When the foregoing experiment is repeated at 100° C., there is no detectable conversion to ketene. Similarly, when the experiment is repeated at 350° C. in an inert tubular reactor, the conversion is nil.

Those skilled in the art will understand that reactors containing radioactive sources must be handled with due care, and adequate shielding of e.g. lead or concrete must be provided in order to protect the operator.

From the foregoing it will be apparent that the process of this invention is considerably more efficient than the purely thermal process known in the art. The invention is not to be considered as limited to the use of any particular source of radiation, but is conceived as being broadly operable in the presence of any ionizing radiations of the herein specified intensity. It is intended that the true scope of the invention be embraced by the following claims.

I claim:

1. A method for preparing ketene from acetone which comprises heating acetone for about one second to sixty minutes at a temperature between about 200° and 400° C. in the presence of gamma radiations of about 0.45 to 2.76 mev. energy level, and recovering ketene from the resulting product, the intensity of said gamma radiations within the reaction zone being between about 10^4 and 10^8 roentgens per hour per cubic centimeter.

2. A process as defined in claim 1 wherein said gamma radiation is produced by a cobalt-60 radiation source.

3. A process as defined in claim 1 wherein said reaction is carried out at a temperature below the critical temperature of acetone, with the acetone in liquid phase, and wherein gaseous ketene is continuously removed from the reaction zone as formed.

4. A process for preparing ketene which comprises passing acetone vapors through a radioactive tubular reactor at a temperature between about 200° and 400° C. and a residence time between about one second and sixty minutes, and recovering ketene from the products, said tubular reactor being composed of metallic material comprising a radioactive element emitting gamma rays of 0.45 to 2.76 mev. energy level at an intensity sufficient to provide between about 10^4 and 10^8 roentgens per hour per cubic centimeter within the reaction zone.

5. A process as defined in claim 4 wherein said radioactive element is cobalt-60.

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