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S. A. BALLARD ET AL

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PRODUCTION OF ISOPHORONE AND RELATED PRODUCTS

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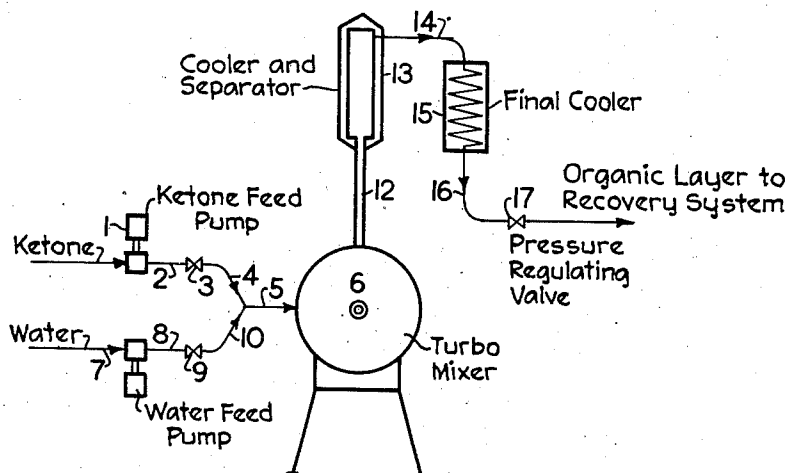


Fig. 1

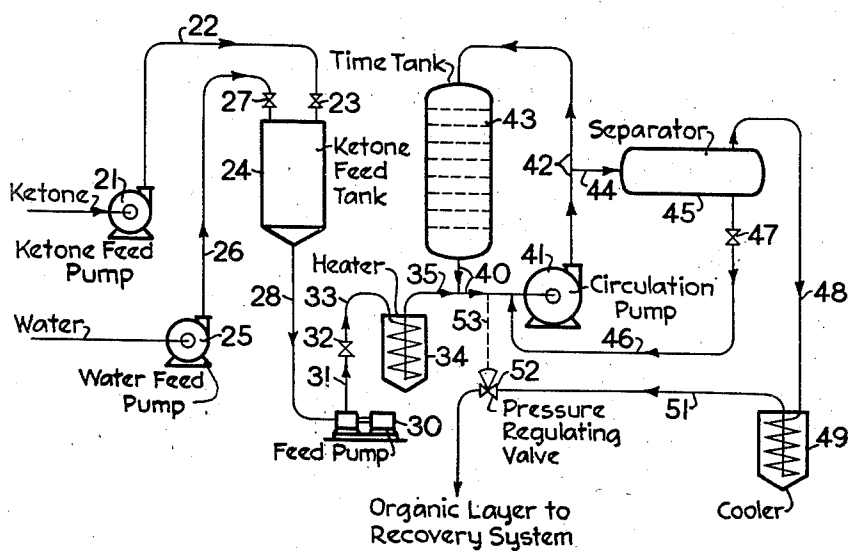


Fig. 2

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UNITED STATES PATENT OFFICE

2,399,976

PRODUCTION OF ISOPHORONE AND
RELATED PRODUCTS

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ment Company, San Francisco, Calif., a cor-
poration of Delaware

Application January 28, 1943, Serial No. 474,060

10 Claims. (Cl. 260—586)

This invention relates to a process for the pro-
duction of isophorone and related products. More
particularly, the invention pertains to a method
of manufacture wherein a saturated ketone of
from 3 to 5 carbon atoms undergoes condensation
with cyclization in the presence of a dilute aque-
ous solution of an alkali metal hydroxide to pro-
duce an unsaturated alicarbocyclic ketone like
isophorone or homo-isophorones.

It is an object of the present invention to pro-
vide a process applicable in effecting the con-
densation of saturated ketones containing from
3 to 5 carbon atoms in a continuous manner.

Another object is to provide a process for pro-
ducing isophorone or homo-isophorones from sat-
urated ketones containing between 3 and 5 car-
bon atoms.

A further object is to provide a process wherein
a saturated ketone containing from 3 to 5 car-
bon atoms is effectively cyclized to isophorone or
homo-isophorones while the non-cyclic isomers
of the same number of carbon atoms or higher
condensation products than the primary unsat-
urated alicarbocyclic ketone product are formed in
only small amounts.

An additional object is to provide a method of
manufacture of isophorone and certain homo-
isophorones which permits the catalyst to be
maintained at substantially initial activity with-
out deterioration over very long periods of time.

The primary object of the invention is to pro-
vide a process for the manufacture of isophorone
which is highly efficient and economical.

The preparation of isophorone by condensation
of acetone is well known and a number of cata-
lysts have been described for effecting the reac-
tion in the liquid phase. Fittig (Ann. 110, 36) and
Bredt and Rübel (Ann. 289, 10) obtained a small
amount of isophorone by treating acetone with
quicklime. The use of sodium ethylate is de-
scribed by Kerp (Ann. 290, 137) for preparing iso-
phorone. German Patent No. 134,982 discloses
the condensation of acetone to give a low yield of
isophorone by the use of sodamide. Calcium car-
bide has been suggested as a liquid phase cata-
lyst, but gives largely very high condensation
products. U. S. Patent No. 2,183,127 shows a
vapor phase method of condensing acetone in
which isophorone is obtained by contacting ace-
tone vapors with calcium oxide, hydroxide or car-
bide.

The preparation of homo-isophorones from cer-
tain homologues of acetone has also been de-
scribed. Ekeley and Howe (J. A. C. S. 45, 1922)
show the condensation of methyl ethyl ketone

to homo-isophorones by long standing at room
temperature in the presence of sodium ethylate,
while diethyl ketone was condensed similarly by
Ekeley and Carpenter (J. A. C. S. 46, 448) at a
low temperature to give the corresponding homo-
isophorones. U. S. Patent No. 2,148,103 describes
condensation of methyl propyl and higher ketones
in the presence of solid alkali metal oxides, hy-
drides, amides or alcoholates, the water of re-
action being distilled from the reaction mixture
and catalyst as fast as formed.

The treatment of several lower ketones is de-
scribed by Franke and Köhler (Ann. 433, 314)
wherein the ketones were permitted to stand at
room temperature in the presence of aqueous al-
kalies or alcoholic alkalies. In copending appli-
cations, Serial No. 257,200, filed February 18, 1939,
and Serial No. 318,506, filed February 12, 1940, in
which one of us is a co-inventor, there is de-
scribed and claimed a method of condensing ke-
tones in the presence of concentrated aqueous
solutions of alkali metal hydroxides and remov-
ing the water of reaction as formed by distillation.

While these prior art methods are effective in
yielding the desired unsaturated alicarbocyclic ke-
tone, they each have certain inherent disadvan-
tages which preclude their suitability for large
technical scale manufacture of isophorone or
homo-isophorones. These will be apparent from
consideration of the problems encountered in con-
densation of acetone to isophorone; the problems
being similar with higher ketone condensation.

The treatment of acetone with a condensation
catalyst causes a number of condensation reac-
tions to occur—i. e., the treatment does not result
in a single and unique reaction of condensation.
For formation of isophorone to be realized, severe
conditions of treatment have been employed by
the use of strong anhydrous alkaline substances
or concentrated solutions of certain of them.
While the formation of isophorone is realized with
such catalysts, the use of these strong condensing
agents causes the formation of high condensation
products like high-boiling condensates, resinous
substances and even tarry materials, in some in-
stances. When the principal product desired is
isophorone, the formation of the high condensate
by-products is responsible for a major loss of yield
of the isophorone in the processes.

In the vapor phase method of condensing ace-
tone, the catalyst soon becomes coated with a
deposit of carbonaceous materials which reduce,
or eventually destroy, its activity. The catalyst
coated with a deposit of this nature must either
be discarded or subjected to a reactivation treat-

ment for removal of the deposit and restoration of the activity, either alternative of which is detrimental to the efficiency of the process.

Water is one of the products of reaction in the formation of isophorone from acetone. The formation of each molecule of isophorone liberates two molecules of water. In the older methods of preparing isophorone outlined above in which acetone was treated with an anhydrous catalyst, the formed or liberated water of reaction caused the catalyst to soon become ineffective or destroyed it and when a concentrated solution was employed, the formed water soon diluted the catalyst solution to an inoperative state under the conditions utilized. Thus in the liquid phase condensation in the presence of sodamide, sodium alcoholate or calcium carbide, the formed water reacts with the catalyst to destroy it. The continual dilution of the concentrated solutions of alkalies, when such were used as catalyst, results in a continually changing reaction medium with respect to the alkalinity thereof, even though all other conditions or variables are maintained constant and, under these conditions, the catalyst solution becomes in time too weak to cause the desired cyclic condensation reaction to isophorone to occur. Later improvements in the art provided distillation as a means of removing the water of reaction as fast as formed. However, the use of concentrated solutions of condensing agents coupled with distillation to remove the formed water is hampered by the formation of high-boiling by-products which represent irretrievable loss of yield to a useful material, owing to the high alkalinity of the catalyst solution. These high-boiling by-products are of little value and no known method is available for conversion of them to useful products, so that it was of utmost importance to find a method of keeping their formation low.

We have now discovered that acetone is condensed to isophorone in the presence of a dilute aqueous solution of an alkali metal hydroxide when liquid acetone is brought into intimate contact with the catalyst solution at a temperature above about 130° C. and that the use of the dilute catalyst solution enables those high-boiling by-products to be maintained at a low value. A temperature above about 130° C. is considerably above the normal boiling temperature of acetone and the acetone is maintained in a liquid state by the use of sufficient pressure to prevent boiling of the reaction mixture. With other variables constant, we have found that the condensation using a dilute aqueous solution of an alkali metal hydroxide gives a low formation of higher condensation products as compared to the amount of these substances formed when a concentrated aqueous solution is employed, with the result that the yield of the isophorone or homo-isophorone is considerably improved by the process of the present invention.

We have now further discovered that the water formed by reaction is removable from the reaction mixture by, in effect, extracting it with the product mixture, and this feature enables operation to be conducted in a continuous manner which is highly efficient. Two phases exist in the reaction mixture, an aqueous catalyst phase and an organic phase. In operation of the process, all of the acetone fed into the reaction zone does not condense to isophorone or other lower or higher condensation products. Water has no appreciable solubility in the majority of the condensation products, but it is completely miscible

with and soluble in acetone. Since the organic phase contains a preponderance of acetone therein, water is appreciably soluble in this phase and by continuously withdrawing a part of the phase from the reaction zone, the water of reaction is removed therefrom. The operation of the process depends for success upon the ability of the organic phase to dissolve water and the controlling substituent therein is the reactant ketone, since the condensation products do not appreciably promote such solubility. Saturated ketones containing from 3 to 5 carbon atoms possess the property of appreciably dissolving water and they are thus operative in the process.

In substance, the process of our invention comprises continuously introducing and commingling a saturated ketone containing between 3 and 5 carbon atoms in the liquid state with a dilute aqueous solution of an alkali metal hydroxide, the reaction zone being maintained at a temperature preferably between 150° C. and 200° C. and under at least sufficient pressure to prevent boiling therein, and continuously withdrawing a portion of the organic phase from the reaction zone, the concentration of hydroxide in dilute aqueous solution being maintained substantially constant by the water of reaction being carried out of the reaction zone with the effluent organic phase and, if more water than that formed in the reaction is extracted, by feeding the needed water into the reaction zone along with the input ketone.

In order that the condensation reaction of a ketone to form the unsaturated alicarbocyclic ketone (isophorone or homo-isophorone) be possible, it is necessary that at least one hydrogen atom be linked directly to each alpha carbon atom of the ketone. The ketones employed as reactants in the process of the invention are acetone, methyl ethyl ketone, methyl propyl ketone, diethyl ketone and methyl isopropyl ketone and each of these open-chain saturated ketones possesses the required structure in having at least one hydrogen atom (some have two and some have three) linked directly to each alpha carbon atom. Acetone is a preferred reactant in that it is most reactive of the ketones, the others requiring, in general, higher reaction temperatures and longer times of residence in the reaction zone for best results.

The temperature maintained in the reaction zone is from about 130° C. to the critical temperature of the ketone reactant. Since the desired reaction is effected in the liquid phase, the upper limit is determined by the critical temperature of the ketone employed as reactant. In the case of acetone, the critical temperature is about 235° C.; with methyl ethyl ketone, it is about 261° C.; and with methyl propyl ketone it is about 282° C. The process is preferably executed at a temperature between 150° C. and 200° C., excellent results being obtained with acetone in the neighborhood of 170° C.

The pressure required to be maintained will vary with the particular operating temperature and the particular ketone reactant employed in the process. As is well-known, the pressure needed will be higher for higher operating temperatures, and since the materials in the reaction zone are kept entirely in the liquid phase in the process, although the operating temperature is above the normal boiling temperature of some constituents therein, the pressure employed is considerably above atmospheric pressure, and at least equal to the sum of the partial pressures

of each of the components present in the reaction zone. Ordinarily a pressure of say 15 lbs. per square inch above the required minimum is maintained so as to satisfactorily prevent any boiling in the reaction zone which might occur, owing to even minor fluctuations of temperature in the execution of the process.

The catalyst is a dilute aqueous solution of an alkali metal hydroxide. By a dilute aqueous solution is meant one containing between 15 per cent and 35 per cent by weight of the alkali metal hydroxide with respect to the aqueous solution. Expressed differently, the dilute aqueous solution contains a weight ratio of water to alkali metal hydroxide between 5.66:1 and 1.86:1. In the operation of the process the concentration of hydroxide in aqueous solution is maintained substantially constant at a value within the indicated range. With other variables constant, the ability of the organic phase to extract water, including the water formed by the reaction, is primarily a function of the amount of ketone reactant present in the organic phase, and this is determined by the time of residence of the ketone in the reaction zone. In general, the longer the time of residence in the reaction zone, the lesser will be the amount of unreacted ketone in the organic phase, a portion of which is withdrawn continuously in an amount equal to the material fed to the reactor. (The time of residence is in time units and equal to the volume of organic phase present in the reactor divided by the volume of ketone per unit time fed to the reactor.) With the use of shorter residence times, larger amounts of water are extracted with the effluent organic phase and, in some cases, the aqueous catalyst phase would tend to become concentrated. This difficulty is avoided by continuously feeding water in with the ketone fed to the reactor. The amount of water fed into the reaction zone is determined by the residence time, the temperature of reaction, the concentration of hydroxide used in the aqueous phase and the particular ketone employed. The use of acetone as the reactant requires more water to be introduced than with the higher ketones and in some cases, especially with the higher ketones, no water need be added.

Any alkali metal hydroxide is suitable for use in the aqueous catalyst phase. Ordinarily, because of cheapness and ready availability, sodium hydroxide is a preferred catalyst although lithium, rubidium, or cesium hydroxides are employed, if desired. The most preferred catalyst is potassium hydroxide which, although somewhat more expensive than sodium hydroxide, has greater activity than the hydroxide of sodium. Since substantially no catalyst is consumed in the process in contradistinction to prior art methods requiring comparatively large requirements of catalyst, our method has practically no cost for catalyst other than the original price. The life of the catalyst solution appears to be indefinite and the only loss is a few hundredths of a per cent carried out with the effluent organic phase.

In the process, the organic phase is intimately contacted or commingled with the aqueous catalyst phase. Any means for churning and mixing the two phases is satisfactory. A suitable reactor is a turbo mixer which is a closed vessel fitted with revolving paddles. Another suitable means of obtaining the required agitation and turbulence is to pump, at preferably high velocity, the mixture of two phases through a time tank fitted with

baffles, perforated plates or the like, the exit of the tank connecting to the intake of the pump.

The volume ratio of the two phases in the reaction zone has little effect as a variable in the results obtained, provided it is kept within reasonable limits of say 5 to 1 either way. Excellent performance of the process is obtained with equal volumes of organic phase to aqueous phase in the reactor or reaction zone, this being the preferred ratio.

The process of the invention is illustrated in the accompanying drawing by Figure 1 which gives a simple arrangement of suitable apparatus for executing the process. Figure 2 shows a combination of more preferred equipment for operation of the process.

In Figure 1, the liquid ketone reactant is pumped into the system by ketone feed pump 1 through pipe 2 to input control valve 3, entering the reactor 6 which is a turbo mixer having an internally rotating paddle wheel and fitted with heating means such as an internal steam coil (not shown) through pipes 4 and 5. If needed, water is pumped into the system by means of water feed pump 7, passing through pipe 8 to control valve 9 and into the reactor by means of pipes 10 and 5. Before starting operation of the system, reactor 6 is filled with the desired quantity of the dilute aqueous solution of an alkali metal hydroxide. One-half of the volume of the reactor is filled with the dilute aqueous catalyst solution when the preferred ratio of one volume of organic phase to one volume of aqueous phase is used. The reaction mixture of catalyst solution, unconverted ketone and products is withdrawn upwards from the reactor 6 through conduit 12 to combined cooler and separator 13 wherein the material is partially cooled and stratification of the organic phase and aqueous phase occurs. The upper layer in cooler and separator 13 is the organic phase; the lower layer being the aqueous phase which returns to turbo mixer 6 by means of pipe 12. Liquid organic phase passes from cooler and separator 13 by means of pipe 14 to final cooler 15 from which the material flows through pipe 16 to pressure regulating valve 17. Pressure regulating valve 17 controls the pressure on the system in combination with feed pumps 1 and 7 so that the material in the system is maintained in the liquid state during operation of the process. The effluent organic layer passes from pressure regulating valve 17 to the recovery system (not shown).

A considerable number of constituents are present in the effluent organic phase fed to the recovery system. In the case of condensation of acetone, the major constituent will be unreacted acetone along with which will be mesityl oxide, diacetone alcohol, the desired isophorone, phorone and higher condensation products. When ketones containing 4 carbon atoms or 5 carbon atoms are employed as reactants, the constituents will be similar homologues and owing to the more complex structure of the 4 and 5 carbon atom ketones, isomers of particular constituents will be present. For example, in the condensation of methyl ethyl ketone, according to the process of the invention, four structural isomers of the homo-isophorone are possible, excluding stereo and optical isomers. The formation of products like mesityl oxide, phorone, and higher unsaturated condensation products form water as a product of reaction, as does isophorone, which water is removed from the reaction zone

in the invented process by the effluent organic phase.

The recovery of the effluent organic phase with isolation of the isophorone or homo-isophorones is handled in several ways. Mesityl oxide and diacetone alcohol are in themselves commercially valuable products and by subjecting the effluent mixture to fractional distillation, these along with the unconverted acetone and other constituents can be separated. Fractional distillation in a continuous manner requires a plurality of columns and when lower condensation products like mesityl oxide and diacetone alcohol are not desired to be isolated as products, the crude organic mixture may be subjected to the selective reversion process described and claimed in copending application of McAllister and Bailey, Serial No. 404,512, filed July 29, 1941. That process enables the crude organic mixture to be treated so that products like mesityl oxide and diacetone alcohol are selectively reverted back to parent acetone without changing isophorone present in the mixture. The recovered acetone obtained by any method can be returned as feed to the condensation process. Those higher condensation products which are not revertible to the parent ketone by a now known method or are not of particular value in themselves are obtained in minimum amount by the process of the invention, and since the lower products can be reverted to the parent ketone as indicated, the only loss of yield of the unsaturated alicarbocyclic ketone, isophorone or homo-isophorones, is in these higher products.

A more elaborate arrangement of apparatus and flow of the process is shown in Figure 2. Ketone reactant, by means of pump 21, pipe 22 and control valve 23, is fed to feed tank 24 which is an intermediate storage vessel for feed to the reaction system. Water, if needed, is supplied to tank 24 through pump 25, pipe 26 and control valve 27. The feed is withdrawn from tank 24 through line 28 to pump 30 which pumps the feed into the reaction and supplies the necessary pressure needed to keep the materials in the reaction system in the liquid state and prevent boiling therein. From pump 30, the feed is passed through pipe 31 to feed control valve 32 and, by means of pipe 33, to heater 34 which supplies the heat needed to maintain the reaction zone at the desired temperature. The feed passes from heater 34 by pipe 35 which is tapped into pipe 40. The reaction zone is a circulating system consisting of pipe 40, circulation pump 41 of large capacity, pipe 42 and time tank 43 which is fitted with baffles, perforated plates or the like to promote turbulence and violent agitation of the reaction mixture. Before commencing operation of the process, the reaction system is filled with the desired quantity of dilute aqueous solution of the alkali metal hydroxide. The reaction mixture is withdrawn from the circulating system through pipe 44 tapped into pipe 42 and the material is fed to separator 45 where stratification of the organic phase and the aqueous phase occurs. The aqueous phase is returned from separator 45 by means of pipe 46 to pipe 40 in the suction side of pump 41 in the circulating system. Valve 47 connected in pipe 46 is used to control the level of the phases in separator 45. The effluent organic phase passes from separator 45 through pipe 48 to cooler 49 where the phase is cooled and from which the material passes through line 51 to a conventional pressure regulating valve

52 which controls the pressure on the system and is actuated through connection 53 tapped into pipe 40 of the circulating system. The effluent organic layer is taken from valve 52 and run to the recovery system (not shown). The recovery and separation of the products is done in the same manner as described in the system of flow shown in Figure 1.

When effecting the condensation of ketones containing four or five carbons under certain conditions (long residence time, towards the upper limit of the hydroxide concentration, etc.) it is sometimes found that the aqueous catalyst solution tends to become diluted from the particular and desired caustic concentration by the inability of the effluent organic phase to extract sufficient water from the reaction zone. This excess water is removable from the system by several expedients. Thus in the system shown in Figure 2, a unit is inserted in line 46 through which catalyst solution is returned from separator 45 back to the reaction zone, in which unit, removal of water with concentration of the aqueous hydroxide phase is effected. For this purpose, the unit is a continuous evaporator wherein the caustic solution is concentrated and the concentrated solution then returned continuously into the reaction zone. If desired, a continuous liquid phase extraction unit can be used in which a liquid extractant like a butyl alcohol which will remove water and concentrate the caustic solution is suitable. Another method which is effective in obtaining the desired result with the process is to increase the ability of the organic phase to extract water from the aqueous phase in the system by continuously feeding in a lower alcohol such as methyl alcohol, ethyl alcohol, normal propyl alcohol or isopropyl alcohol into the reaction zone. Such a substance is inert in the reaction zone, but greatly assists the organic phase to extract water from the aqueous phase so that the concentration of hydroxide in the aqueous solution will remain constant and not become diluted by failure of the organic phase to extract or remove sufficient water from the reaction zone.

In starting up the process in either arrangement of apparatus shown in Figure 1 or Figure 2, the aqueous catalyst solution is introduced into the reaction zone and the air therein is displaced by pumping in the ketone reactant. No withdrawal of the organic phase from the reaction zone is permitted until the desired amount of reaction has occurred after which withdrawal is started and fresh feed introduced. During the starting up period, pressure is maintained on the system by means of the pumps so that the materials therein are in the liquid state. After starting, the process soon settles down to a steady state.

The saturated ketone employed as reactant and condensed to the mono-unsaturated alicarbocyclic ketone is ordinarily the sole reactant fed to the system in the process of the invention. Mixed isomeric products are obtained by using a plurality of the individual saturated ketones containing 3 to 5 carbon atoms.

For the purpose of further illustrating the process of the invention, the following examples are given, but it is to be understood that the invention is not to be construed as limited to any details given therein.

Example I

Acetone was condensed continuously in the presence of a dilute aqueous solution of sodium

hydroxide, the hydroxide concentration in aqueous solution being maintained at about 25 per cent throughout the run. The acetone was processed in apparatus similar to that shown in Figure 1. Acetone was continuously introduced at a rate of about 840 cc. per hour along with 60 cc. per hour of water which maintained the caustic concentration constant. Equal volumes of organic layer to catalyst layer were used in the reaction zone and the temperature therein was maintained at 170° C. The size of the mixer was such that the residence time of the acetone therein was about 37 minutes. The effluent organic phase was flowed from the reaction system to a fractionating column in which the unreacted acetone was stripped from the mixture. The residue was permitted to accumulate and was later distilled to separate the constituents thereof.

The composition of the organic layer from the reactor during the run was as tabulated below:

Constituent	Weight percentage
Acetone.....	79.0
Mesityl oxide.....	3.6
Diacetone alcohol.....	1.6
Isophorone.....	4.0
Heavy ends.....	1.1
Water of condensation.....	2.1
Water of injection.....	8.6

Of the acetone converted, the distribution of the constituents in weight percentage of the acetone converted was as given in the following table:

Constituent	Weight percentage
Total products.....	13.6
Mesityl oxide.....	4.7
Diacetone alcohol.....	1.8
Isophorone.....	5.5
Heavy ends.....	1.6

In this run, a 78 per cent yield of isophorone was obtained in the product containing 9 or more carbon atoms.

Example II

A series of runs were made wherein acetone was condensed with a dilute aqueous solution of potassium hydroxide. A temperature of about 170° C. was employed in each run using an apparatus similar to that shown in Figure 1. The conditions and results of the runs are shown in the accompanying table, the two variables of the different runs being the residence time and the concentration of potassium hydroxide maintained in the aqueous phase. A phase ratio of 1:1 was used and the pressure maintained on the reactor was about 300 lbs. per sq. in.

Conditions:

KOH conc., weight per cent	18	22	28	32
Residence time, min.	30	40	10	30
Acetone feed rate, cc. per hr	1040	780	3120	1040
Water feed rate, cc. per hr	129	81	270	40
Weight per cent water in feed	14.5	12.3	10.5	4.96

Composition of product—weight per cent:

Acetone	79	70.9	79.0	76.7
Mesityl oxide	1	2.7	3.3	4.1
Diacetone alcohol	1.5	5.5	2.6	4.0
Isophorone	3	4.8(5)	2.1(4)	5.5(0)
Heavy ends	0.5	1.6(8)	0.4(2)	1.9(3)
Water of condensation	1	2.3	1.3	2.9
Water injected	14	12.1	11.3	4.9

Weight per cent acetone converted to:

Total products	19	19.4	11.1	19.3
Mesityl oxide	4	3.6	4.5	5.1
Diacetone alcohol	7	6.3	3.0	4.2
Isophorone	6	7.0	3.0	7.3
Heavy ends	2	2.5	0.6	2.7

Isophorone yield:

Weight per cent isophorone in C ₉ and higher	79	74.3	83.7	74.0
Weight per cent KOH in product		0.041	0.062	

Example III

Acetone was condensed in the presence of dilute aqueous potassium hydroxide in an apparatus similar to that shown in Figure 2. The run was continued for 178 hours and the catalyst was in no way deteriorated at the end of this time. The aqueous catalyst solution was maintained with 30.3 per cent potassium hydroxide therein. The temperature of operation in the reactor was 169° C. under a pressure of 290 lbs. per sq. in. and the phase ratio of organic phase to aqueous phase was 1.2:1. The conditions and results of the run are tabulated below:

Conditions in reactor:

Acetone fed to reactor, g. p. h.	175.9
Water fed to reactor, g. p. h.	18.8
Residence time, min.	17.5
Wt. per cent water in effluent organic layer	14.1
Wt. per cent KOH in effluent organic layer	0.024

Mol per cent acetone converted to:

Mesityl oxide	5.9
Isophorone	6.3
Heavy ends	1.6

Percentage yields in isophorone and heavy ends:

Isophorone	79.8
Heavy ends	20.2

This application is a continuation-in-part of our co-pending application, Serial No. 396,192, filed May 31, 1941.

We claim as our invention:

1. A process for producing an isophorone which comprises continuously introducing a saturated ketone of 3 to 5 carbon atoms into a reaction zone and intimately contacting said ketone with a dilute aqueous solution containing between 15 and 35 per cent by weight of an alkali metal hydroxide with respect to the hydroxide and water therein at a temperature of from 130° C. to the critical temperature of said ketone while maintaining sufficient pressure in said reaction zone to keep the entire contents therein in the liquid state,

continuously withdrawing from said reaction zone a portion of liquid organic phase containing water extracted from said dilute aqueous solution by the contacting therewith, and continuously introducing into said reaction zone sufficient water with respect to the water removed therefrom in said effluent organic phase to maintain the concentration of the hydroxide in said dilute aqueous solution substantially constant.

2. A process for producing isophorone which comprises continuously introducing acetone into a reaction zone and intimately contacting said ketone with a dilute aqueous solution containing between 15 and 35 per cent by weight of an alkali metal hydroxide with respect to the hydroxide and water therein at a temperature of from 130° C. to the critical temperature of acetone of about 235° C. while maintaining sufficient pressure in said reaction zone to keep the entire contents therein in the liquid state, continuously withdrawing from said reaction zone a portion of liquid organic phase containing water extracted from said dilute aqueous solution by the contacting therewith, and continuously introducing into said reaction zone sufficient water with respect to the water removed therefrom in said effluent organic phase to maintain the concentration of the hydroxide in said dilute aqueous solution substantially constant.

3. A process for producing an isophorone which comprises continuously introducing and commingling a 3 to 5 carbon atom saturated ketone with a dilute aqueous solution of an alkali metal hydroxide at a temperature between 150° C. and 200° C. while maintaining the reaction mixture in the liquid state by application of sufficient pressure to prevent boiling thereof, continuously withdrawing from the reaction mixture a portion of liquid organic phase containing water extracted from said dilute aqueous solution by the commingling therewith, and continuously introducing into the reaction mixture sufficient water with respect to water withdrawn therefrom in said effluent organic phase so as to maintain the concentration of said hydroxide in said dilute aqueous solution substantially constant at a value between 15 and 35 per cent by weight.

4. A process for producing isophorone which comprises continuously introducing and commingling acetone with a dilute aqueous solution of an alkali metal hydroxide at a temperature between 150° C. and 200° C. while maintaining the reaction mixture in the liquid state by application of sufficient pressure to prevent boiling thereof, continuously withdrawing from the reaction mixture a portion of liquid organic phase containing water extracted from said dilute aqueous solution by the commingling therewith, and continuously introducing into the reaction mixture sufficient water with respect to water withdrawn therefrom in said effluent organic phase so as to maintain the concentration of said hydroxide in said dilute aqueous solution substantially constant at a value between 15 and 35 per cent by weight.

5. A process for producing isophorone which comprises continuously introducing and commingling acetone with a dilute aqueous solution of sodium hydroxide at a temperature between 150° C. and 200° C. while maintaining the reaction mixture in the liquid state by application of sufficient pressure to prevent boiling thereof, continuously withdrawing from the reaction mixture a portion of liquid organic phase containing water extracted from said dilute aqueous solution by

the commingling therewith, and continuously introducing into the reaction mixture sufficient water with respect to water withdrawn therefrom in said effluent organic phase so as to maintain the concentration of said hydroxide in said dilute aqueous solution substantially constant at a value between 15 and 35 per cent by weight.

6. A process for producing isophorone which comprises continuously introducing and commingling acetone with a dilute aqueous solution of potassium hydroxide at a temperature between 150° C. and 200° C. while maintaining the reaction mixture in the liquid state by application of sufficient pressure to prevent boiling thereof, continuously withdrawing from the reaction mixture a portion of liquid organic phase containing water extracted from said dilute aqueous solution by the commingling therewith, and continuously introducing into the reaction mixture sufficient water with respect to water withdrawn therefrom in said effluent organic phase so as to maintain the concentration of said hydroxide in said dilute aqueous solution substantially constant at a value between 15 and 35 per cent by weight.

7. A process for producing an isophorone which comprises continuously introducing into a reaction zone and intimately contacting therein a saturated ketone of 3 to 5 carbon atoms with a dilute aqueous solution of an alkali metal hydroxide at a temperature of from 130° C. to the critical temperature of said ketone; continuously transferring a portion of the reaction mixture from said reaction zone to a stratification zone wherein said transferred reaction mixture separates into an aqueous phase and an organic phase, sufficient pressure being maintained in said reaction zone and in said stratification zone to keep the entire contents therein in the liquid state; continuously returning stratified aqueous phase from said stratification zone to said reaction zone; continuously withdrawing from said stratification zone stratified liquid organic phase containing water extracted from said dilute aqueous solution by the contacting therewith; and continuously introducing into said reaction zone sufficient water with respect to the water withdrawn in said effluent organic phase to maintain the weight ratio of water to said alkali metal hydroxide in said dilute aqueous solution substantially constant at a value between 5.66:1 to 1.86:1.

8. A process for producing isophorone which comprises continuously introducing into a reaction zone and intimately contacting therein acetone with a dilute aqueous solution of an alkali metal hydroxide at a temperature of from 130° C. to the critical temperature of acetone of about 235° C.; continuously transferring a portion of the reaction mixture from said reaction zone to a stratification zone wherein said transferred reaction mixture separates into an aqueous phase and an organic phase, sufficient pressure being maintained in said reaction zone and in said stratification zone to keep the entire contents therein in the liquid state; continuously returning stratified aqueous phase from said stratification zone to said reaction zone; continuously withdrawing from said stratification zone stratified liquid organic phase containing water extracted from said dilute aqueous solution by the contacting therewith; and continuously introducing into said reaction zone sufficient water with respect to the water withdrawn in said effluent organic phase to maintain the weight ratio of water to said sodium hydroxide in said dilute aqueous solution substantially constant at a value between 5.66:1 to 1.86:1.

9. A process for producing isophorone which comprises continuously introducing into a reaction zone and intimately contacting therein acetone with a dilute aqueous solution of sodium hydroxide at a temperature of from 130° C. to the critical temperature of acetone of about 235° C.; continuously transferring a portion of the reaction mixture from said reaction zone to a stratification zone wherein said transferred reaction mixture separates into an aqueous phase and an organic phase, sufficient pressure being maintained in said reaction zone and in said stratification zone to keep the entire contents therein in the liquid state; continuously returning stratified aqueous phase from said stratification zone to said reaction zone; continuously withdrawing from said stratification zone stratified liquid organic phase containing water extracted from said dilute aqueous solution by the contacting therewith; and continuously introducing into said reaction zone sufficient water with respect to the water withdrawn in said effluent organic phase to maintain the weight ratio of water to said sodium hydroxide in said dilute aqueous solution substantially constant at a value between 5.66:1 to 1.86:1.

10. A process for producing isophorone which

comprises continuously introducing into a reaction zone and intimately contacting therein acetone with a dilute aqueous solution of potassium hydroxide at a temperature of from 130° C. to the critical temperature of acetone of about 235° C.; continuously transferring a portion of the reaction mixture from said reaction zone to a stratification zone wherein said transferred reaction mixture separates into an aqueous phase and an organic phase, sufficient pressure being maintained in said reaction zone and in said stratification zone to keep the entire contents therein in the liquid state; continuously returning stratified aqueous phase from said stratification zone to said reaction zone; continuously withdrawing from said stratification zone stratified liquid organic phase containing water extracted from said dilute aqueous solution by the contacting therewith; and continuously introducing into said reaction zone sufficient water with respect to the water withdrawn in said effluent organic phase to maintain the weight ratio of water to said potassium hydroxide in said dilute aqueous solution substantially constant at a value between 5.66:1 to 1.86:1.

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