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## HYDROLYSIS OF ISOBUTYL CHLORIDE

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This invention concerns an improved method of hydrolyzing isobutyl chloride, whereby isobutyl alcohol, tertiary butyl alcohol, and isobutylene are produced simultaneously. It also concerns procedure for controlling the relative yields of said products from the hydrolysis.

Isobutyl chloride is known to be more difficultly hydrolyzable than are most alkyl halides. For instance, Freund, J. pr. (2) 12, 25, reported that isobutyl chloride was not hydrolyzed to an appreciable extent when heated with water in a sealed tube at 100° C. for 12 hours. Niederist, Ann. 186, 388, found that isobutyl iodide was only partially hydrolyzed when heated with water in a sealed tube at 120° C. for 40 hours. By separating the unreacted isobutyl iodide remaining after such treatment and retreating it in the same manner he succeeded in hydrolyzing the major portion of the iodide. He reported isobutyl alcohol to be the product of his hydrolysis. Niederist did not describe the hydrolysis of isobutyl chloride, but stated that it behaved similarly to the iodide when treated in like manner.

We have now found that isobutyl chloride can readily be hydrolyzed by heating the same under pressure to a temperature above 95° C. with an aqueous base and that isobutyl alcohol, tertiary butyl alcohol, and isobutylene are the products from such hydrolysis. We have also found that the relative yields of the several products may be varied by changing the kind of base used, the relative proportions of the reactants, etc. We have further found that by acidifying the hydrolyzed reaction mixture and continuing to heat the same under pressure, the yield of tertiary butyl alcohol can be increased considerably and the yield of isobutylene reduced.

To the accomplishment of the foregoing and related ends, the invention consists in the method hereinafter fully described and particularly pointed out in the claims, the following description and examples setting forth in detail only certain of the various ways in which the principle of our invention may be employed.

The hydrolysis of isobutyl chloride is carried out by heating the compound under pressure to a temperature above 95° C. with an aqueous solution or suspension containing approximately its chemical equivalent or more of an inorganic base, e. g. a hydroxide of sodium, potassium, calcium, barium, lead, or iron; a carbonate of sodium, potassium, calcium, or barium, etc. The hydrolysis may be carried out at temperatures as high as 500° C., but is preferably carried out between 120° and 350° C. The hydrolysis may be carried out in any of the usual types of high pressure reactors, for instance, in a tubular autoclave.

The relative yields of isobutyl alcohol, tertiary butyl alcohol, and isobutylene from the hydrolysis are dependent upon the particular conditions under which the reaction is carried out and may be varied. In general, it may be stated that under otherwise similar operating conditions:—

(1) The use of a soluble metal hydroxide, e. g. sodium or potassium hydroxide, rather than one which is only sparingly soluble, e. g. calcium hydroxide, as the hydrolyzing agent results in an increased yield of isobutyl alcohol and decreased yields of tertiary butyl alcohol and isobutylene;

(2) The use of an alkali metal carbonate or bicarbonate, rather than an alkali metal hydroxide, as the hydrolyzing agent results in an increased yield of tertiary butyl alcohol and a decreased yield of isobutylene;

(3) An increase in the ratio of water to isobutyl chloride in the reaction mixture results in an increase both in the yield of tertiary butyl alcohol and in the rate at which the hydrolysis occurs; and

(4) A change in the reaction temperature does not ordinarily result in any great change in the respective yield of the several products, but as the reaction temperature is raised above 300° C. there is usually a noticeable decrease in the yield of the alcohol products and increase in the yield of isobutylene, and such changes in yields become more pronounced as the temperature is raised.

In hydrolyzing isobutyl chloride to produce isobutyl alcohol as the principal product, we prefer to heat the isobutyl chloride under pressure to a temperature above 120° C. with at least 3 times its weight of a not more than 3 normal aqueous solution of an alkali metal base, e. g. a hydroxide, carbonate, or bicarbonate of sodium or potassium.

Isbutylene is produced in maximum yield when a relatively insoluble base, e. g. a hydroxide of calcium, barium, magnesium, iron, etc., is used as the hydrolyzing agent and the reaction is carried out at a high temperature, particularly above 300° C.

Tertiary butyl alcohol is produced in maximum yield from the hydrolysis when a mild base, e. g. calcium hydroxide, sodium carbonate or bicarbonate, etc., is used as the hydrolyzing agent, the molecular ratio of water to isobutyl chloride in the reaction mixture is high, e. g. above 30, and the reaction is carried out below 300° C.

The time required to complete the hydrolysis varies from less than one minute to several hours, depending upon the temperature at which the hydrolysis is carried out, the kind and proportion of base employed, etc. The completeness of the hydrolysis may readily be determined at any time by withdrawing an aliquot portion of the reaction liquor and analyzing it for inorganic chlorides. When inorganic chloride is found to have been formed in amount chemically equivalent to the isobutyl chloride employed, the hydrolysis is complete.

Following the hydrolysis, the isobutylene contained in the reaction mixture may, if desired, be partially converted to tertiary butyl alcohol by adding a strong acid, e. g. hydrochloric, sulphuric, nitric, benzene-sulphonic acid, etc., or a salt such as aluminum chloride, stannic chloride, etc., which hydrolyzes to form a strong acid, to the mixture and continuing to heat the latter under pressure, preferably at a temperature between about 75° and 150° C. The acid is preferably added in amount sufficient to neutralize any base present and to form, with the water present in the hydrolysis mixture, an aqueous acid solution having a strength from 0.02 to 2 normal, but a larger or smaller proportion of acid may be used if desired.

After the reaction according to any of the above procedures is completed, the reactor is cooled and gaseous isobutylene is released therefrom and collected in a suitable receiver. The liquid mixture is then fractionally distilled to separate the isobutyl and tertiary butyl alcohol products as relatively concentrated aqueous solutions thereof. Either of said alcohols may, of course, be dehydrated completely by known procedure, e. g. by distilling the same in the presence of calcium oxide.

The following table, which shows a number of experiments wherein isobutyl chloride was hydrolyzed by the present method, illustrates the changes in yields of the several products which result from certain changes in the conditions under which the hydrolysis is carried out. Each experiment was carried out by heating a reaction mixture, having the composition stated in the table, in a closed reactor with agitation at the temperature and for the time also stated in the table. After the heating operation was completed, the reactor was cooled and isobutylene was released therefrom and collected in a gas receiver. An aliquot portion of the reaction liquor was analyzed to determine the inorganic chloride content thereof. From the inorganic chloride content of the liquor, the percentage of the isobutyl chloride employed which was reacted was calculated in the usual manner. Such percentage is referred to in the table as the "conversion". The main body of reaction liquor was then fractionally distilled, whereby a small additional quantity of isobutylene was evolved and collected, and the alcohol products were separated as relatively concentrated aqueous solutions thereof. The yields of product stated in the table are the per cent of theoretical yield, based on the quantity of isobutyl chloride reacted.

In the foregoing table, comparison between runs 1–4, wherein aqueous calcium hydroxide is used as the hydrolyzing agent, shows that in general an increase in the ratio of water to isobutyl chloride in a reaction mixture results in an increase in the yield of tertiary butyl alcohol and a decrease in the yield of isobutylene, but that as said ratio becomes higher the change in yields resulting from a further unitary change in ratio is less pronounced. A comparison of runs 5 and 6 shows that when an aqueous sodium hydroxide solution is used as the hydrolyzing agent an increase in the ratio of water to isobutyl chloride likewise results in an increase in the yield of tertiary butyl alcohol and a decrease in the yield of isobutylene. Similar results are obtained when other inorganic bases are used.

In runs 3 and 4, wherein calcium hydroxide was used as a hydrolyzing agent at widely different temperatures, but under otherwise comparable operating conditions, and in runs 6 and 7 wherein sodium hydroxide was employed at widely different temperatures, it will be noted that a change in reaction temperature does not greatly alter the respective yields of the several products. However, as the reaction temperature is raised above 300° C., the yield of isobutylene is usually increased to a noticeable extent and the yields of the alcohol products, particularly tertiary butyl alcohol, are reduced. Such changes become more pronounced as the reaction temperature is raised.

A comparison of run 6 with runs 2, 10, and 11 shows that by employing a water-soluble metal hydroxide, e. g. sodium hydroxide, as the hydrolyzing agent rather than a metal hydroxide which is relatively insoluble in water, e. g. a hydroxide of calcium, lead, or magnesium, the yield of isobutyl alcohol becomes increased while the yields of tertiary butyl alcohol and isobutylene are each lowered.

From a comparison of runs 8 and 9 with runs 2, 6, 10, and 11, it will be noted that by using an alkali metal carbonate or bicarbonate as the hydrolyzing agent, rather than a metal hydroxide under otherwise similar operating conditions, each of the alcohol products are formed in high yield and the yield of isobutylene is lowered.

Regardless of the exact procedure employed in carrying out the hydrolysis reaction, the yield of tertiary butyl alcohol can be increased at the expense of the isobutylene product by acidifying the hydrolyzed mixture with a strong acid, e. g. sulphuric or hydrochloric acid, preferably in amount sufficient to form a 0.02 to 2 normal

*Table*

| Run No. | Reaction mixture | | | | | | Time of heating hours | Temperature °C. | Conversion per cent | Yields | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Isobutyl chloride moles | Base | | $H_2O$ moles | Mole ratio of $H_2O$/isobutyl chloride | Chemical equivalents of base per mole of isobutyl chloride | | | | Isobutyl alcohol | Tertiary butyl alcohol | Isobutylene |
| | | Kind | Moles | | | | | | | | | |
| 1 | 6 | $Ca(OH)_2$ | 3.24 | 66.7 | 11.1 | 1.08 | 4 | 185 | 96.5 | 19.0 | 8.6 | 66.4 |
| 2 | 4 | $Ca(OH)_2$ | 2.16 | 88.8 | 22.2 | 1.08 | 4 | 170 | 95.2 | 21.8 | 21.7 | 53.3 |
| 3 | 2 | $Ca(OH)_2$ | 1.08 | 88.8 | 44.2 | 1.08 | 4 | 165 | 98.1 | 21.7 | 27.0 | 45.5 |
| 4 | 4 | $Ca(OH)_2$ | 2.10 | 205.5 | 51.4 | 1.05 | 0.25 | 220 | 97.5 | 23.6 | 26.6 | 43.7 |
| 5 | 6 | NaOH | 7.2 | 66.7 | 11.1 | 1.20 | 4 | 180 | 98.7 | 42.1 | 6.2 | 46.1 |
| 6 | 4 | NaOH | 4.32 | 88.8 | 22.2 | 1.08 | 4 | 155 | 91.5 | 43.2 | 9.1 | 41.4 |
| 7 | 4 | NaOH | 4.32 | 88.8 | 22.2 | 1.08 | 0.08 | 300 | 97.9 | 37.7 | 10.4 | 43.2 |
| 8 | 8 | $K_2CO_3$ | 4.32 | 177.7 | 22.2 | 1.08 | 4 | 165 | 97.2 | 43.1 | 27.0 | 30.0 |
| 9 | 8 | $NaHCO_3$ | 8.64 | 177.7 | 22.2 | 1.08 | 4 | 165 | 88.3 | 45.1 | 29.2 | 19.3 |
| 10 | 4 | $Pb(OH)_2$ | 2.16 | 88.8 | 22.2 | 1.08 | 4 | 175 | 98.0 | 23.9 | 21.5 | 52.3 |
| 11 | 4 | $Mg(OH)_2$ | 2.16 | 88.8 | 22.2 | 1.08 | 4 | 175 | 99.5 | 20.4 | 18.5 | 53.6 |

aqueous acid solution in said mixture, and thereafter heating the mixture under pressure between 75° and 150° C. Such mode of increasing the yield of isobutylene product is illustrated by the comparative experiments described in the following example.

*Example*

(*a*) A mixture of 8 moles of isobutyl chloride, 8.4 moles of sodium hydroxide, and 205.5 moles of water was heated in a bomb, with agitation, at 220° C. for 10 minutes. The bomb was then cooled and gaseous isobutylene was released therefrom and collected. A 5 cubic centimeter sample of the reaction liquor was analyzed for inorganic chlorides, it being found that 99.5 per cent of the isobutyl chloride was reacted. The main body of reaction liquor was then fractionally distilled, whereby a small additional quantity of isobutylene was collected and the alcohol products were separated as relatively concentrated aqueous solutions thereof. The per cent of theoretical yields of the several products, based on the quantity of isobutyl chloride reacted, were as follows:—isobutyl alcohol, 39.9 per cent; tertiary butyl alcohol, 7.5 per cent; and isobutylene, 45.2 per cent.

(*b*) A mixture of isobutyl chloride, sodium hydroxide, and water in the proportions stated in the above experiment (*a*), was heated in a bomb, with agitation, at 220° C. for 10 minutes. The bomb was then cooled and sufficient sulphuric acid was injected into the same under pressure to neutralize any unreacted sodium hydroxide remaining therein and to form, with the water in the reaction mixture, a 0.16 normal aqueous sulphuric acid solution. The acidified mixture was heated with stirring between 100° and 107° C. for 2 hours. The bomb was then cooled, gaseous isobutylene was released, and the reaction liquor was discharged. A 5 cubic centimeter portion of the liquor was analyzed for chloride content, it being found that 97.7 per cent of the isobutyl chloride had been reacted. The main body of reaction liquor was then fractionally distilled to separate the products contained therein. The per cent of theoretical yields of the several products, based on the isobutyl chloride consumed in the reaction, were:—isobutyl alcohol, 41.6 per cent; tertiary butyl alcohol, 30.7 per cent; and isobutylene, 10.7 per cent.

In the experiments described in the above example it will be noted that by acidifying the hydrolyzed reaction mixture and again heating it under pressure, the yield of tertiary butyl alcohol was increased by more than 4 times and the yield of isobutylene was reduced to a corresponding extent.

The isobutylene produced by our method is sometimes contaminated with normal butylenes and diisobutylene, which may also be formed in the hydrolysis, but the combined yield of said by-products is usually low, e. g. below 7 per cent of theoretical.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:—

1. The method which comprises heating a mixture of isobutyl chloride, water, and a metal base to a reaction temperature above 100° C. at superatmospheric pressure and thereafter separating isobutylene, isobutyl alcohol, and tertiary butyl alcohol from the reacted mixture.

2. The method which comprises heating isobutyl chloride with at least its molecular equivalent of a metal base in the presence of water at superatmospheric pressure to a reaction temperature above 100° C. and thereafter separating isobutylene, isobutyl alcohol, and tertiary butyl alcohol from the reacted mixture.

3. In a method wherein a mixture of isobutyl chloride, water, and an inorganic base is reacted under pressure at an elevated temperature to form isobutyl alcohol, tertiary butyl alcohol, and isobutylene, the steps for increasing the yield of tertiary butyl alcohol which consist in acidifying the reacted mixture with a compound selected from the class consisting of strong acids and salts capable of undergoing hydrolysis to form strong acids and heating the acidified mixture at super-atmospheric pressure to a temperature between about 75° and about 150° C.

4. In a method for making isobutylene, the steps which consist in heating a mixture of isobutyl chloride, water, and a slightly soluble metal hydroxide to a reaction temperature above 100° C. at superatmospheric pressure and thereafter separating isobutylene from the reacted mixture.

5. In a method for making isobutylene, the steps which consist in heating a mixture of isobutyl chloride with an aqueous mixture containing approximately its chemical equivalent of a slightly soluble metal hydroxide to a reaction temperature above 100° C. at superatmospheric pressure and thereafter separating isobutylene from the reacted mixture.

6. In a method for making isobutyl alcohol and tertiary butyl alcohol simultaneously, the steps which consist in heating a mixture of isobutyl chloride with at least 30 times its molecular equivalent of water and approximately its chemical equivalent of a water-soluble base selected from the class consisting of alkali metal carbonates and bicarbonates at superatmospheric pressure to a reaction temperature above about 120° C. and thereafter fractionally distilling the reacted liquor to separate isobutyl alcohol and tertiary butyl alcohol therefrom.

7. In a method for making tertiary butyl alcohol in good yield, the steps which consist in heating a mixture of isobutyl chloride with at least 30 times its molecular equivalent of water and approximately its chemical equivalent of a base selected from the class consisting of alkali metal carbonates and bicarbonates and slightly soluble metal hydroxides at superatmospheric pressure to a reaction temperature above 120° C. and thereafter fractionally distilling the reacted liquor to separate tertiary butyl alcohol therefrom.

8. In a method of making tertiary butyl alcohol in good yield, the steps which consist in heating a mixture of isobutyl chloride with at least 30 times its molecular equivalent of water and approximately its chemical equivalent of a base selected from the class consisting of alkali metal carbonates and bicarbonates and slightly soluble metal hydroxides to a reaction temperature above about 120° C., thereafter acidifying the mixture with mineral acid to form an aqueous mineral acid solution having a strength of 0.02 to 2 normal, and heating the acidified mixture at superatmospheric pressure to a temperature between about 75° and about 150° C.

9. The method which comprises heating a mixture of isobutyl chloride, water and sodium hydroxide at superatmospheric pressure to a re-

action temperature above 100° C. and thereafter separating isobutylene, isobutyl alcohol and tertiary butyl alcohol from the reacted mixture.

10. The method which comprises heating isobutyl chloride with at least its molecular equivalent of sodium hydroxide and sufficient water to dissolve said hydroxide at superatmospheric pressure to a reaction temperature above 100° C. and thereafter separating isobutylene, isobutyl alcohol and tertiary butyl alcohol from the reacted mixture.

11. The method which comprises heating a mixture of isobutyl chloride, water and calcium hydroxide at superatmospheric pressure to a reaction temperature above 100° C. and thereafter separating isobutylene, isobutyl alcohol and tertiary butyl alcohol from the reacted mixture.

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