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PROCESS FOR OXIDIZING OLEFINS TO ALDEHYDES AND KETONES

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The present invention relates to a process for oxidizing olefins to aldehydes, ketones and acids.

It has already been proposed to oxidize ethylene catalytically by means of an argentiferous catalyst to ethylene oxide, or by means of an oxidation catalyst other than a silver-containing catalyst at a raised temperature to obtain mixtures of formaldehyde, acetaldehyde, formic acid, acetic acid and other products. In these processes, however, acetaldehyde or acetic acid cannot be produced in a yield interesting from an economical point of view. Our experiments have revealed that the oxidation carried out under such conditions in the presence of a noble metal catalyst likewise involves small yields of acetaldehyde, and the relative proportion of formaldehyde obtained generally preponderates.

It is also known that compounds of palladium, platinum, silver, or copper form complex compounds with ethylene. Furthermore, the formation of acetaldehyde was observed in decomposing a potassium-platinum-complex compound. Other unsaturated compounds may favor the complex formation. In this case stoichiometric reactions are concerned yielding the noble metal as such.

It has also been described to reduce palladous chloride by means of ethylene in the presence of water to palladium metal. In this reduction the formation of acetaldehyde was observed. It is also known that palladous chloride dissolved in water can be reduced rapidly and completely to palladium by means of propylene, even if propylene is admixed with nitrogen or air, or by means of isobutylene. It is described that carbon dioxide is not evolved in any one of the aforesaid reductions.

In a number of prior applications various processes are described according to which carbonyl compounds can be obtained from the corresponding olefins in a good yield and, if desired, in a continuous manner by contacting said olefins with an oxidizing agent, a liquid catalyst having an acid to neutral reaction and comprising water, a compound of the noble metals belonging to group VIII of the periodic table and a redox system. In this connection reference is made to the following applications, all relating to a "Process for oxidizing olefins to aldehydes, ketones and acids":

Serial No. 747,116, filed July 8, 1958, by W. Berndt, L. Hörnig, U. Schwenk, W. Riemenschneider, W. Schmidt and O. E. Bänder, Serial No. 750,150, filed July 22, 1958, Serial No. 763,691, filed September 26, 1958 and now abandoned, Serial No. 768,624, filed October 21, 1958, Serial No. 770,007, filed October 28, 1958, now Patent No. 3,076,032, Serial No. 769,912, filed October 27, 1958, Serial No. 769,554, filed October 27, 1958.

In the aforesaid applications the term "carbonyl compounds" is used in its broad sense, i.e. it covers not only aldehydes and ketones but also carboxylic acids such as acetic acid.

It is supposed that in the reaction described in the aforementioned applications the oxidation of the redox system added, i.e. for example the oxidation of immediately formed cuprous chloride to cupric chloride, is the velocity determining step for the entire reaction. Since it is advantageous to accelerate a slow reaction in order to arrive at a high conversion, care must be taken that the redox system undergoes rapid oxidation by the

oxidizing medium, such as oxygen or gases containing oxygen, preferably air. Oxidation may be accelerated by a fine distribution of the oxidizing gases or by operating under a raised partial pressure of oxygen, or by addition of an inorganic oxidation promoter.

It has been stated in the aforesaid applications that sometimes the presence of a salt, such as sodium chloride or potassium chloride, may prove advantageous. For example, these salts—like hydrochloric acid itself or other alkali metal or alkaline earth metal halides such as LiCl, CaCl₂, MgCl₂, or other salts such as FeCl₃, FeCl₂, ZnCl₂, or CuCl₂—improve the solubility of CuCl, which may be formed in the course of the reaction and is only very sparingly soluble in water (0.11% at 80° C.). The solubility of CuCl may also be improved by addition of formic acid. However, the use of these additives for improving the solubility of cuprous chloride has the disadvantage that relatively large amounts thereof are necessary. Accordingly a relatively concentrated solution is formed in which the solubility of oxygen is decreased compared with more diluted solutions. This means that by the application of such additives an increased concentration of one reactant (the cuprous ion) can only be attained by a decrease of the concentration of the other reactant (the oxygen).

I have now found that the aforesaid disadvantages can be avoided if halogenated acetic acids or salts thereof are used as dissolving intermediaries in catalysts containing as essential ingredient copper chloride. In these catalysts cuprous chloride is formed during the reaction which is regenerated to yield cupric chloride by the action of the oxidizing agent. The halogenated acetic acids or the salts thereof have a very strong dissolving action on CuCl and therefore they need only be added in a minor amount, generally 1-50%, by weight calculated upon the amount of copper (CuCl₂·2H₂O) contained in the solution. The reduction of the oxygen solubility in the contact liquid, which is otherwise caused by the presence of the required large amounts of further additives, is therefore only small. Adding halogeno-acetic acid or a salt thereof is especially advantageous in view of the fact that these compounds prevent CuCl from being precipitated during the reaction. Since precipitated CuCl would be no longer available for the reaction and might cause clogging and other difficulties, a reduction in the yield and disturbances are prevented. In view of the fact that CuCl is kept in solution there always appears a high concentration of cuprous ions which are available for a reaction with the more or less great amount of oxygen present. This favors the desired rapid oxidation to the readily soluble CuCl₂—which is presumably the velocity-determining step for the entire reaction—and accelerates the entire reaction.

From among the halogenated acetic acids trichloroacetic acid and also dibromoacetic acid are especially active. The solubility of CuCl in 2.5% aqueous trichloroacetic acid, for example, is more than 50 times the solubility of CuCl in water.

Salts of halogenoacetic acids, mixtures of these salts, or mixtures of these salts with free halogenoacetic acids, may also be used with a similar result. As salts there may be used those with inorganic cations or with organic bases. There may be mentioned more especially, salts of alkali metals, ammonia, alkaline earth metals, for example of sodium, potassium, lithium, magnesium, calcium, barium, iron, copper, palladium, or cerium, and also salts of triethylamine, tripropylamine, di- and/or triethanolamine.

Substituting the aforesaid salts for the free halogenoacetic acids involves the advantage that too strong an acidification and accordingly a decrease in conversion are avoided. The optimum amount of salts to be added is dependent on the composition of the catalyst used in each

individual case. When a contact is concerned containing, per liter of water, 100 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 2 grams of PdCl_2 , it suffices to add 20–25% of trichloroacetic acid or the corresponding amount of salts, the percentage figures being calculated upon the amount of copper, which in turn is calculated as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The addition of the aforesaid substances in preparing carbonyl compounds from olefins involves a smooth reaction and an increased conversion.

The process of the present invention may be carried out with the catalysts and under the conditions broadly described in the above-mentioned applications, for preparing carbonyl compounds from the corresponding olefins, i.e. olefins having the same number of carbon atoms as the carbonyl compounds. These catalysts contain a compound of a noble metal of group VIII of the periodic table, particularly palladium, and a chloride of copper and, if desired, one or more redox systems.

As redox systems there may be present, for example, those that contain in addition to the chloride of copper, compounds of metals which under the reaction conditions employed may appear in various oxidation stages, for example compounds of mercury, cerium, thallium, tin, lead, titanium, vanadium, antimony, chromium, molybdenum, uranium, manganese, iron, cobalt, nickel or osmium, and also inorganic redox systems other than the latter, preferably in admixture with compounds of other of the aforesaid metals specified above, such as sulfite/sulfate, or arsenite/arsenate systems and/or organic redox systems, for example azobenzene/hydrazobenzene, or quinones or hydroquinones of the benzene-, anthracene- or phenanthrene series.

As compounds of the noble metals of group VIII of the periodic table there may be used in the process according to the present invention, for example, compounds of palladium, iridium, ruthenium, rhodium, or platinum, i.e. of metals the stable valence of which is at most 4. Compounds of this series of metals are believed to be capable of forming addition compounds or complex compounds with ethylene. The reaction may likewise be carried out in the presence of a noble metal from which, in the course of the reaction, the reactive compounds are formed.

As oxidizing agent there may be used, for example, oxygen, if desired in admixture with an inert gas. The oxygen may be employed, for example, in the form of air, which is the cheapest oxidizing agent, or in the form of air enriched with oxygen. The use of air is, however, confined to certain limits, if the unreacted gases are circulated, inasmuch as nitrogen concentrates as ballast material.

The reaction may be supported or carried out by addition of an active oxidizer, which are broadly listed in the above mentioned applications.

It is often advantageous to add, prior to or during the reaction, a compound yielding anions under the reaction conditions applied, for example an inorganic acid, preferably a mineral acid, such as sulfuric acid, nitric acid or a volatile acid, such as hydrochloric acid or hydrobromic acid, or a salt such as ammonium chloride, ammonium bromide, zinc chloride, aluminum chloride, iron chloride, chromic chloride, titanium tetrachloride, sodium hydro-sulfate, a halogen such as chlorine, bromine, or bromotrichloride, or a halogen-oxygen compound, for example hypochlorous acid, bromic acid, chlorine dioxide, or thionyl or sulfuryl chloride, or also an organic substance, preferably a saturated aliphatic halogen compound of low molecular weight such as ethyl chloride, propyl chloride, butyl chloride, acetyl chloride, benzoyl chloride, propionyl chloride, phosgene. Such addition enables a possible decrease of anions to be counteracted and the lifetime of the catalyst to be prolonged.

The process of the present invention is carried out in solution at relatively low temperatures. Preferably a pure aqueous solution is used, but the reaction may like-

wise be carried out in aqueous solutions in which the water is diluted with a hydrophilic solvent, such as acetic acid, acetone, methylethylketone or other ketones, ethylene glycol, propylene glycol, glycerol, dioxane or mixtures thereof.

The present process is carried out with special advantage at temperatures within the range between 50 and 160° C., preferably 50 and 100° C., since it is carried out in the liquid phase, it is necessary to operate under a raised pressure if the temperature used is above the boiling point of the catalyst solution. If desired, the process may also be carried out at temperatures outside the ranges indicated above, for example at 170° C. to 180° C., or for example at 40° C., or within a range of, for example, 80° C. to 120° C. Furthermore atmospheric pressure, a raised pressure or reduced pressure may be applied, that is, a pressure of up to 100, preferably of up to 50 atmospheres gauge. The process may be carried out under pressure regardless of whether the temperatures used are above or below 100° C. It is furthermore of importance to carry out the process in an acid to neutral medium. The preferred pH-values are within the range between 0.8 and 3; higher pH-values between, for example, 0.8 and 5 or 2 and 6, or lower pH-values, for example 0.5, may also be used, although such pH-values generally do not involve a special advantage.

In addition to the use of halogenated acetic acids or the salts thereof it is possible to influence the solubility of cuprous chloride to a certain extent by modifying the ratio of olefin to oxygen. The moment at which the olefin to oxygen ratio is modified, can be readily determined by continuously measuring the pH, which may be performed by any known method.

If the pH decreases, it is easily possible to readjust the optimum pH-range by adding either more oxygen or less olefin, or by combining these two steps. If the pH increases, the optimum pH-range can be readjusted inversely. This method of controlling the reaction may also be combined with the above described addition of compounds yielding anions.

Sometimes it may be advisable to provide the pH-measuring device with an automatic connection to the dosing device for the supply of ethylene and oxygen. In this case the pH is once adjusted to the optimum value and the reaction can then be controlled automatically.

In the process of the invention likewise sometimes the presence of a salt, such as sodium chloride or potassium chloride or other salts mentioned above, may prove advantageous.

The reaction may be supported by increasing the ethylene and/or oxygen concentration in the reaction space, for example, by increasing the pressure and/or by the presence of a solvent. The ethylene concentration in the reaction solution may be considerably increased, for example by using higher concentrations of metal salts binding ethylene, for instance copper-, iron-, mercury- or iridium-compounds, especially halides, or the sulfates, the latter especially when mercury is concerned, or by using organic solvents which are preferably miscible with water, for example acetic acid, methylethylketone or other ketones, mono- or polyhydric alcohols, acyclic ethers or dimethyl formamide. The gases may be circulated, if desired, for example a gas containing a few percent of unreacted oxygen.

Due to the presence of oxidizing agents acetic acid may be formed in a small amount in addition to acetaldehyde. If desired, the oxidation of acetaldehyde to acetic acid which is known in the art, may be combined with the reaction described above in order to omit partially or totally the aldehyde stage, or acetaldehyde may be oxidized in a second stage in known manner to acetic acid, for example in the presence of manganese compounds.

Under the conditions specified above under which ethylene yields acetaldehyde, propylene yields preponderantly acetone and propionaldehyde. α - and β -butylene yield

preponderantly methylethylketone, the α -butylene yielding also butyraldehyde, and isobutyraldehyde can be obtained from isobutylene.

In the case where higher olefins are concerned, such as pentene and its homologs, cyclohexene or styrene, the reaction proceeds substantially in a manner analogous to that described and it can be carried out under the same conditions as set forth above. Due to the relatively mild reaction conditions there are almost exclusively obtained those oxidation products which had to be expected in view of their structure, without noteworthy isomerizations or molecule decompositions occurring.

Mixtures of olefins or gases containing olefins or other unsaturated compounds may be reacted in the same manner, provided they are capable of reacting under the reaction conditions, for example diolefins. The reaction of olefins containing 2 to 3 carbon atoms is, however, preferred. Under circumstances, the reaction conditions must be adapted to the compounds used and to their physical properties. The higher boiling points of the reaction products may also require a corresponding modification of the reaction conditions. Diacetyl may be obtained, for example, from butadiene.

The reactants may be diluted by gases inert towards the reaction, for example by nitrogen, carbon dioxide, methane, ethane, propane, butane, isobutane and other saturated aliphatic compounds and furthermore by other compounds such as cyclohexane, benzene or toluene.

The olefins may, however, not only be diluted by one or more of the aforementioned gases, but likewise with carbon monoxide and/or hydrogen, if desired in addition to the aforementioned gases, and increased pressure may be applied. If such gas mixture contains CO, oxygen should be present at least in an amount as is necessary to convert the olefin to aldehyde and carbon monoxide to carbon dioxide. From a mixture of carbon monoxide and olefin, practically the same amounts of carbonyl compounds are obtained as if no carbon monoxide were present. In this reaction the carbon monoxide is partially converted to carbon dioxide.

If hydrogen is present, the major amount of hydrogen remains unaltered, whereas a small portion thereof reacts with formation of water and another small portion with hydrogenation of the olefins. The fact that neither hydrogen nor carbon monoxide affect the process of the invention is of special advantage since accordingly industrial gases, for example refined gases or gases obtained in cracking processes, may be used as starting materials. All expensive gas separations can therefore be dispensed with, although a prepurification or concentration of the olefin may prove advantageous. Carbon monoxide and/or hydrogen may appear in the gas mixture, for example in double the amount of the olefin, and yet the olefin oxidation is not substantially impaired. This statement is, however, not intended to indicate a limit. If these gases are present, the multiple stage process which is sometimes very suitable for the present reactions and which is described in application Ser. No. 750,150, may be applied with special advantage. In this process the olefin, if desired in admixture with a small amount of oxygen, is contacted with the catalyst in one stage, while the oxidizing agent is contacted with the catalyst in a second stage or apparatus. As a result of these measures it is possible to practically avoid a mixing of the gases used with oxygen, so that the former can be used for further purposes after having left the reactor.

For stoichiometric reasons the molar ratio of olefin to oxygen must be 2:1 in the complete oxidation of the olefins to the corresponding aldehydes or ketones. To prevent explosions, it is, however, preferred to use an oxygen deficiency, for example in the range of 2.5:1 to 4:1. Still further it is preferred to work outside the range of explosivity, for example with a content of oxygen of 8-20%, or 8-14% under pressure, and to circulate unreacted gas which consists substantially of non-converted

olefin, if desired in admixture with other inert gases, such as nitrogen and/or with hydrogen and/or carbon monoxide, and which may furthermore contain some oxygen. To this gas oxygen and the olefin such as ethylene are added as they are consumed.

The present process may be carried out for example by contacting the olefin and oxygen or air simultaneously with the catalytic substances. However, it is often very advantageous to contact the olefin and the oxidizing agent separately with the liquid catalyst used as is described above. This latter mode of operating has the advantage, that the compositions of the gas mixture need not be controlled carefully and that even in recirculating the olefin, such as ethylene, air may be used as oxidizing medium without disadvantages being involved.

The regeneration may be brought about by contacting the catalyst with the oxidizing medium, for example oxygen or air, in an amount sufficient to bring about regeneration under known conditions, for example at 50-150° C., and, if desired, under pressures and at temperatures being different from those of the first stage in which the catalyst is contacted with the olefin.

In a frequently useful technical variant of the process of this invention, the desired reaction product, for example acetaldehyde, is separated from the reaction gas, the residual gas which may still contain inert gas and/or hydrogen and/or carbon monoxide and may be free from oxygen but may likewise contain oxygen, is reintroduced into the reactor, suitably into its lower part, and an amount of olefin and, if desired, oxygen corresponding to that consumed during the reaction is introduced into the reactor or the olefin and/or the oxygen are added to the recirculated gas. For the sake of security the oxidizing agent, i.e. preferably oxygen, if desired in admixture with inert gases, such as present in air, is preferably introduced through separate inlets, especially when about stoichiometric amounts of the reactants are applied and no diluting gas is present.

The oxidizing agent is preferably introduced into the circulation conduit of the catalyst. The amount of oxygen introduced may be so modified that even in the catalyst solution the explosivity limit is nowhere surpassed. Such modification is generally not necessary; it is rather sufficient to add the oxygen to the residual gas which escapes from the contact solution, in an amount to keep the composition of this residual gas outside the explosive limits.

In order to obtain especially high space-time-yields, it is also possible to introduce either olefin or oxidizing agent, preferably oxygen, or olefin and oxygen into the reactor at various places arranged one above the other or one behind the other. Preferably the inlets for each reactant are locally separated from the other inlets for the same reactant. It is likewise possible that the amount of oxygen introduced is measured so as to be at all places of the reaction vessel below the lower limits of the explosive range.

In many cases the reaction proceeds likewise smoothly if the catalysts used contain only a small amount of compounds of the noble metals belonging to group VIII of the periodic table. In most cases it is sufficient to use a catalyst in which the ratio of the sum of the redox metals, especially the sum of copper and iron, to the noble metal, especially palladium, is at least 15:1, preferably 25-500:1. It is, however, preferred to use a catalyst containing copper salts, in which the ratio of copper to palladium is above 10:1, for example above 15:1 and preferably 50:1 to 500:1, or even above these ranges. This method of operating is more economic in view of the fact that the expensive palladium salt need only be used in a minor amount; it can be used for converting ethylene and olefins other than ethylene, and may be combined as desired with variants hereinbefore or hereinafter described. This embodiment may also be carried out under elevated pressure.

The reaction of the present invention is favorably influenced by irradiation with rays rich in energy, especially in the case where oxygen is used as oxidizing medium. Preferably ultraviolet light is applied, conveniently by using a mercury quartz lamp. Such radiation, which may also comprise X-rays, activates especially the oxygen, increases its oxidizing activity, and promotes both the reaction with the olefin and a possible oxidative destruction of by-products, for example oxalic acid. These measures increase the conversion, reduce the formation of by-products and considerably prolong the lifetime of the catalyst, the activity of which may subside after a prolonged time.

If mainly aldehydes and ketones are to be prepared it is advantageous to additionally prevent or remove an accumulation of carboxylic acids, for example acetic acid, in the reaction space. This aim may for example be attained by distillation or other means. It is to be noted that the liquid catalysts used in the present reaction may become deplete of halogen in the course of time due to the formation of volatile halogenated by-products, for example methyl chloride or ethyl chloride. For some other reasons it has likewise proved to be advisable in some cases, to keep the molar ratio of copper:halogen and more especially of copper:chlorine within the limits of 1:1 and 1:2, preferably within the limits of 1:1.4 and 1:1.8. The above ratio of copper to halogen should be understood to include the amount of halogen added in the form of iron halide or another halide of cations which do not form neutral reacting salts with hydrohalic acids. The amount of halogen which is present in the form of a neutral salt, for example sodium chloride or potassium chloride, or is capable of being bound to form a neutral salt, need not be considered. For example, if the catalyst contains 3 gram equivalents of alkali metal salts or alkaline earth metal salts of acids other than hydrohalic acids, 5 gram equivalents (mols) of chlorine ions added in the form of iron chloride, and 1 mol of copper ions added in the form of copper acetate, the copper to chlorine ratio is 1:2 according to the definition given above.

The copper to halogen ratio may be regulated by supplying hydrogen halide, especially hydrogen chloride, and/or free halogen or compounds yielding halogen ions under the reaction conditions, such as halogeno-oxygen compounds or organic substances, for example those mentioned above as compounds for supplying anions.

Sometimes it is advantageous to add to the catalyst a quinone which may be substituted by sulfonic acid and/or carboxyl groups. By such an addition the reaction velocity and olefin conversion or—if the rate of conversion remains the same—the throughput is considerably increased. It is supposed that by an addition of the aforesaid compounds the slowest reaction which is the velocity determining step for the entire reaction, e.g. the oxidation of intermediately formed cuprous chloride to cupric chloride is likewise accelerated.

As quinones there may be used, for example, ortho- and/or paraquinones, such as benzoquinones, naphthoquinones, anthraquinones, phenanthrenequinones, or alkyl substitution products of such quinones or the substitution products thereof, which have been referred to above. By adding, for example, the potassium salt of 1,2-naphthoquinone-4-sulfonic acid to a dilute copper chloride catalyst activated with palladium chloride, the conversion is more than doubled as compared with a catalyst free from such addition.

A number of suitable quinones is listed in application Ser. No. 769,554, referred to above.

The quinones or their sulfonic or carboxylic acids or the water-soluble salts of quinone sulfonic acids or quinone carboxylic acids are preferably used in a proportion of up to 10 percent by weight, calculated upon the amount of catalyst, and more preferably in a proportion of between 0.1 and 3% by weight.

The conversion and the space-time-yield of the present reaction depend, for example, on the fine distribution of the gas, on the residence time in the apparatus and the composition of the catalyst, the temperature and the pressure used. The optimum residence time can readily be determined by those skilled in the art.

In the process of this invention care should be taken that the heat evolved during the process (high heat effect: about 60 kcal per mol of aldehyde) is dissipated to the exterior.

The present reaction may be carried out, for example, in vertically arranged reactors, such as tubes provided with frits or oscillatory agitators or other usual reaction towers, for example wash towers, suitably filled with filling material. The reaction may likewise be carried out in reactors which are provided at the head with calming or sedative zones in which foamy portions are separated into the liquid and the gaseous components, and from which the catalyst liquid is reintroduced at the foot of the reactor. Furthermore it is possible to carry out the reaction in a tube through which the contact liquid and the reaction mixture flow at a high velocity. The two last-mentioned embodiments may likewise be carried out in two stages as it is indicated above.

The gases may be atomized, for example through a frit, or in another suitable manner, and too voluminous gas bubbles may be divided into smaller ones, for example by means of an agitator. For this purpose there may also be used a vibro-mixer or a turbo-mixer. All these variants enable the reaction to be carried out continuously.

Condensates which separate from the reacted gas, especially aqueous condensates, may be recirculated.

It is not necessary that the catalysts used are made of fine chemicals; they may likewise be produced from suitable metals of commercial purity.

As anion the catalyst may contain chlorine ions or halogen ions other than chlorine, such as bromine ions, nitrates or chlorate- or perchlorate radicals or mixtures of these anions, for example, with sulfate or acetate radicals. Sometimes it is specially advantageous to use a catalyst which contains perchlorate ions.

The apparatus used in the process of this invention should be made of a material which is not corroded by the catalyst and preferably has a sufficient thermal conductivity. Since the catalysts used contain noble metal compounds, for example palladium compounds, it is less suitable to use the usual metals and alloys as construction material, since there is the risk and that these less noble metals, in the presence of water and at the indicated temperatures, precipitate the noble metal salt used in the catalyst, and that they themselves are converted into salt form.

In order to avoid corrosion in the apparatus used, it is often suitable to use an apparatus lined with titanium or titanium alloys containing at least 30% of titanium, or with tantalum. There may also be used glass vessels or enamelled or rubber-lined vessels. The reaction may also be carried out in brick-lined vessels or, under suitable reaction conditions, in vessels the insides of which are lined with plastic material, for example polyolefins, polytetrafluoroethylene or hardenable unsaturated polyesters or phenol-, cresol- or xylene-formaldehyde resins. As brick-lining there may be used, for example, ceramic material, carbon bricks impregnated with hardenable artificial resins and similar known materials.

The following examples illustrate the invention but they are not intended to limit it thereto:

Example 1

20 liters of ethylene and 10 liters of oxygen are passed per hour by means of two frits at a temperature of 80° C. through a catalyst containing, per liter of water, 1 gram of PdCl_2 , 20 grams of trichloroacetic acid and 100 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. The conversion to acetaldehyde, calculated upon the ethylene used, is about 40% after 3 days.

The rate of conversion may be kept at this degree, for example by addition of hydrochloric acid, distilling off acetic acid or the like. Precipitations are not observed even after a prolonged period of time. Acetaldehyde is washed out and the residual gas is again used in the reaction.

Example 2

The catalyst used was the copper salt of trichloroacetic acid admixed with 1 gm. PdCl_2 , 90 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 1 liter of water. The procedure is the same as that described in Example 1. The conversion from ethylene to acetaldehyde is at 45% after one day; this rate of conversion can be maintained even during a long period of reaction without precipitations occurring, provided that the procedure is the same as described in Example 1.

Example 3

A catalyst containing the iron salt of trichloroacetic acid is prepared as follows: 8 grams of FeCl_3 are dissolved in water, ammonia is added, $\text{Fe}(\text{OH})_3$ is filtered off, washed out and then dissolved with a solution containing, per liter of water, 24 grams of trichloroacetic acid, 2 grams of PdCl_2 and 100 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$. 20 liters of ethylene and 5 liters of oxygen are then passed through the catalyst solution at 80°C . About 25% of the ethylene used are converted to acetaldehyde. The rate of conversion can be kept at that level for a long period of time without precipitations occurring if the process is carried out as described in Example 1.

Example 4

20 grams of trichloroacetic acid are dissolved in 245 cc. of 0.5 N-sodium hydroxide solution, and 2 grams of PdCl_2 , 100 grams of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 755 cc. of water are added. 20 liters of ethylene and 10 liters of oxygen are then passed per hour through the solution at 80°C . The rate of conversion is at 45% provided that the procedure is the same as described in Example 1.

Example 5

The catalyst used is the same as that described in Example 4. Under otherwise identical conditions a mixture of 20 liters of ethylene and 5 liters of oxygen, which is outside the limit of inflammability, is passed through the catalyst solution. The conversion is 25% without precipitations occurring.

I claim:

1. A process for the conversion of an olefinic hydrocarbon to a carbonyl compound selected from the group consisting of aldehydes and ketones by oxidation of an olefinic carbon atom of said olefinic hydrocarbon to a

carbonyl group, which process consists essentially of contacting said olefinic hydrocarbon and oxygen, in a neutral to acid medium with water and a catalyst of (a) a salt of a noble metal selected from the group consisting of palladium, iridium, ruthenium, rhodium, and platinum, and (b) as a redox system, copper chloride, said contacting taking place in the presence of a compound selected from the group consisting of trichloroacetic acid, dibromoacetic acid, salts of these acids, and mixtures of the aforementioned compounds.

2. A process as in claim 1 wherein said compound selected from the group consisting of trichloroacetic acid, dibromoacetic acid, salts of these acids, and mixtures of the aforementioned compounds is present in an amount of from 1 to 50 percent by weight, calculated as free acid and referred to the amount of copper present and calculated as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

3. A process as in claim 1 wherein said compound selected from the group consisting of trichloroacetic acid, dibromoacetic acid, salts of these acids, and mixtures of the aforementioned compounds is present in an amount of from 20 to 25 percent by weight, calculated as free acid and referred to the amount of copper present and calculated as $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

4. A process as in claim 1 wherein said salt of a noble metal is a salt of palladium and in which the ratio of palladium to copper present in said catalyst is between 25:1 and 500:1.

5. A process as in claim 1 wherein said contacting takes place in the presence of trichloroacetic acid.

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