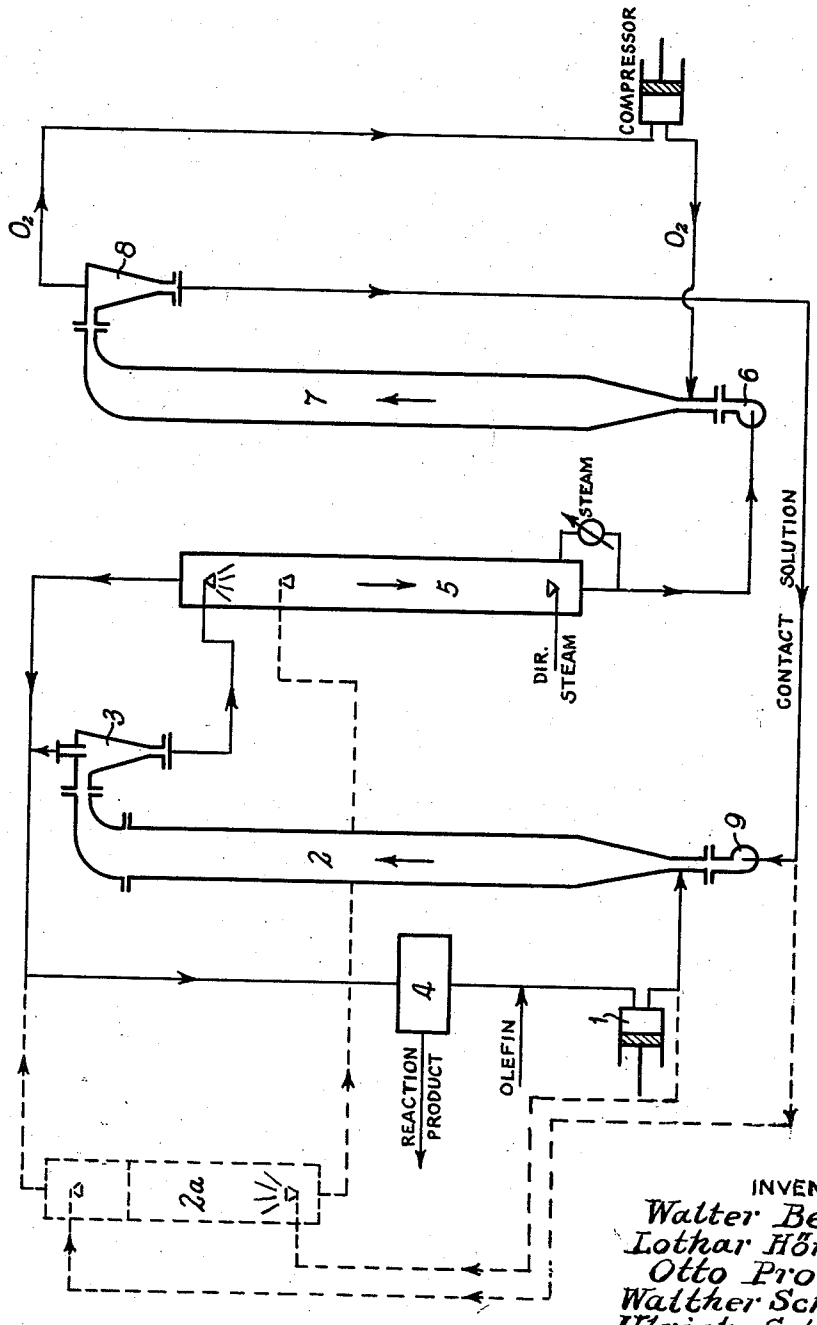
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PROCESS FOR OXIDIZING OLEFINS TO ALDEHYDES AND KETONES

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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. These processes, however, do not produce acetaldehyde or acetic acid 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.

Still further, it has been described 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. It has also been described to reduce palladous chloride by means of isobutylene under the same conditions. It is, however, known that carbon dioxide is not evolved either in this latter reduction or in those reductions which are carried out in the presence of ethylene or propylene as a reducing agent.

In application Ser. No. 747,116, filed July 8, 1958, in which four of the present inventors are co-inventors, a process is 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 the aforesaid application 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.

According to the aforecited invention there may be used as redox systems, for example, those that contain compounds of metals which under the reaction conditions employed may appear in various oxidation stages, for example compounds of copper, mercury, cerium, thallium, tin, lead, titanium, vanadium, antimony, chromium, molybdenum, uranium, manganese, iron, cobalt, nickel, or osmium, and also inorganic redox systems other than specified above, such as sulfite/sulfate, arsenite/arsenate or iodide/iodine 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 aforesaid invention, for example, compounds of palladium, iridium, ruthenium, rhodium or platinum. Compounds of this series of metals are capable of forming addition compounds or complex compounds with ethylene. 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. The use of air is, however, confined to certain limits, if the unreacted gases are circulated, inasmuch as nitrogen concentrates as ballast material. Instead of ethylene there may also be used a gas mixture containing ethylene and, for example saturated hydrocarbons. The reaction may also be carried out in the presence of a noble metal.

The reaction may be supported or carried out by addition of an active oxidizer, such as ozone, peroxidic compounds, especially hydrogen peroxide or sodium peroxide, potassium peroxide, potassium persulfate, ammonium persulfate, alkali percarbonate, alkali perborate, peracetic acid, diacetyl peroxide, benzoyl peroxide, toluyl peroxide, oxygen compounds of nitrogen, such as nitrogen dioxide and nitrogen pentoxide or mixtures of nitrogen oxides containing the same, nitryl halides such as nitryl chloride, free halogen such as chlorine, bromine, or bromotrichloride, halogen-oxygen compounds such as chlorine dioxide, hypochlorous acid, chloric acid, perchloric acid, bromic acid, iodic acid, periodic acid, or compounds of the higher valence stages of metals, such as manganese, cerium, chromium, selenium, lead, vanadium, silver, molybdenum, cobalt, or osmium, for instance potassium permanganate, sodium bichromate, lead tetraacetate, vanadium pentoxide, silver difluoride, selenium dioxide, cerium-(IV) sulfate, osmium tetroxide. The addition of an active oxidizer facilitates the re-formation of the higher oxidation stage of the active catalyst component which is necessary for carrying out the reaction. These oxidizing agents may also be produced during the reaction. If desired, an oxidizing catalyst may be added. 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 hydrosulfate, a halogen or a halogen-oxygen compound, for example those mentioned above, 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 aforesaid process is carried out in solution at relatively low temperatures. Preferably a pure aqueous solution is used, but the reaction may likewise be carried out in aqueous solutions in which the water is diluted with a hydrophilic solvent such as acetic acid, ethylene glycol, propylene glycol, glycerol, dioxane or mixtures thereof.

The aforesaid process can be carried out with special advantage at temperatures within 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 provided that the temperature used is above 100° C. 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. and 120° C. It is furthermore of importance to carry out the process in an acid to neutral medium. The preferred pH-values are within 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).

It is likewise described in the aforesaid application that difficulties which may appear in working in the liquid phase can be overcome by modifying the ratio of olefin to oxygen. Such difficulties may reside in the precipitation of cuprous chloride or other compounds formed which cause cloggings and undesired disturbances in operation. In view of the fact that these precipitated salts are no longer available for the reaction, the yield decreases more or less rapidly. The moment at which the olefin to oxygen ratio must be modified, can be readily determined by continuously measuring the pH.

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, for example hydrohalic acid or organic compounds splitting off hydrohalic acid under the reaction conditions, or acid salts. It is especially advantageous to adjust the reaction medium to a certain pH at the onset of the reaction, for example by means of hydrochloric acid, and to regulate the olefin-oxygen ratio during the reaction. The pH may of course also be modified during reaction by addition of an acid.

The pH is measured by using a device of known type. The pH may be measured continuously with electrodes arranged in the reactor, or discontinuously by measuring the pH of samples withdrawn in certain intervals of time. In a special technical variant of this method the pH-measuring device has 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.

Sometimes the presence of a salt, such as sodium chloride or potassium chloride may prove advantageous. For example, by the presence of these salts—like that of hydrochloric acid itself or of other alkali metal or alkaline earth metal halides such as LiCl, $CaCl_2$, or other salts such as $FeCl_3$, $ZnCl_2$ or $CuCl_2$—the solubility of CuCl, which may be formed in the course of the reaction and which is only very sparingly soluble in water (0.11% at 80° C.) is improved.

The aforesaid process can be carried out at atmospheric pressure, under a raised pressure and under reduced pressure, that is, under 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.

The reaction may be supported by increasing the ethylene and/or oxygen concentration in the reaction space. This can be achieved, 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, mono- or polyhydric alcohols, acylic 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 to acetic acid.

It is described in the aforesaid invention that under the conditions specified above under which ethylene yields acetaldehyde, propylene yields preponderantly acetone and propionaldehyde. α and β-butylene yield preponderantly methylethyl ketone, 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 reactions 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.

For stoichiometric reasons the molar ratio of olefin bound to oxygen must be 2:1 in the complete oxidation of 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 especially that consisting of olefin in excess or other inert gases, such as nitrogen; oxygen and ethylene are restored as they are consumed.

The aforesaid process may be carried out for example by contacting the olefin and oxygen or air simultaneously with the catalytic substances.

Now we have found that it is often very advantageous to contact the olefin and the oxidizing agent separately with the liquid catalyst used. This mode operating has the advantage that the composition of the gas mixture need not be controlled carefully and that even in recirculating ethylene air may be used as oxidizing medium without disadvantages being involved. This variant may be be performed by contacting olefin and oxidizing agent in periodic alternation with the circulating catalyst liquid in a vessel; in a continuous operation there may be used to this end a reciprocally reversible double apparatus, or olefin and oxidizing agent are contacted with the circulating catalyst liquid in several reaction vessels. In this variant, pure olefin may be replaced by a mixture of oxygen and olefin, the oxygen content of which is outside the range of explosivity, i.e. for example, between 1% and 10%, preferably between 3% and 10% of oxygen, calculated upon the amount of olefin used. For example, the explosive limit of an ethylene-oxygen gas mixture is at atmospheric pressure at 20.1% of oxygen. In this modified variant the reaction is preferably carried out in such a manner that the oxygen is almost or completely consumed in the reaction vessel and the catalyst is then regenerated in the regeneration vessel. In this vessel the contact medium is contacted in a further separated stage with the oxidizing medium in an amount sufficient to bring about regeneration, for example oxygen or air. Regeneration is brought about under known conditions, for example at 50–150° C. and may be carried out under pressures and at temper-

atures being different from those of the first stage in which the catalyst is contacted with the olefin.

Depending on the conditions applied in this case the olefin dissolved in the catalyst medium is also oxidized and the dissolved reaction product is removed by stripping. In order to produce a good stripping effect, regeneration may also be brought about using mixtures of oxygen or air with steam.

Contacting olefin and oxidation agent separately with the contact medium involves the advantage that the process can always be carried out under atmospheric pressure and, more especially under superatmospheric pressure, with gas mixtures which are outside the inflammability limit and absolutely harmless.

As compared with the variant to contact pure olefin and oxidation agent with the contact medium, the use of a mixture of olefin with a small amount of oxidizing agent in one stage and of additional oxidizing agent in the second stage offers the further advantage that an occasional separation of undesired solid products is avoided at the place where an olefin-oxygen mixture enters into the reactor, which contains oxygen in an amount smaller than corresponds to the stoichiometric composition as regards the conversion to the carbonyl compound, and the composition of which gas mixture is outside the inflammability limit. A separation of solid substances would cause reduction of the catalytically active substance in the contact liquid and accordingly a reduction of the contact activity; on the other hand, such separation would involve cloggings in conduits, cocks or nozzles. Such separation of solid substances does not appear if the olefin in admixture with a minor amount of oxygen or air is contacted in the first stage with the contact solution, and if the contact solution is regenerated in a second stage by addition of a further amount of oxidizing agent. If the olefin and the oxidizing agent, or an olefin containing a small amount of oxygen and the oxidizing medium, for example oxygen, are contacted separately in the manner described above with the catalyst, it may be advantageous to free the olefin-treated contact solution before it is being contacted in a second phase with the oxidizing gases, from residual unreacted olefin and residual reaction product, for example by stronger heating or stripping with an inert gas, such as nitrogen or steam. By connecting the head of the reaction tower of one phase with the lower liquid inlet of the regeneration tower and vice versa, it is possible to produce a closed liquid cycle, so that pumps can be dispensed with. The ascending gas currents circulate the liquid vigorously; this circulation can be measured by flow meters or another suitable device.

If it is feared that the mixture comprising residual oxygen or residual air and aldehyde, for example acetaldehyde, could rise slightly above the lower explosive limit, the head of the regeneration tower may readily be provided with a safety device of known type to prevent explosion, such as bursting disks, a breakdown security device (gravel pots) or the like. The danger of explosion is however extremely low in view of the acetaldehyde-air-mixture being saturated with water vapor and in view of the relatively low content of oxygen, which is smaller than the oxygen content of the air.

The present process may, e.g. be carried out in an apparatus shown in the appended drawing. A current of olefins is introduced through a compressor 1 into reactor 2 or 2*a* in direct or counter current to the catalyst liquid, and the gas is finely distributed in the catalyst solution by means of a suitable device, for example a frit, a mixing nozzle, an oscillatory sieve, a vibrator, a rapid agitator or the like.

The olefin is converted in this solution to a carbonyl-containing reaction product leaving the reactor together with unreacted olefin, if desired via a cyclone 3. The reaction product is separated in a separating device 4 from olefin in excess, which latter substance is then recirculated together with a fresh amount of olefin into the reactor via compressor 1. The reaction liquid is then conducted to a stripper 5, where it is treated with steam to be directly or indirectly freed from olefin and residues of reaction product. The gases obtained by stripping are conducted, if desired, to separating device 4. The stripped reaction solution is then introduced into regenerator 7 by means of a pump 6 or a static incline, and is intimately contacted in generator 7 with oxygen or gases containing oxygen. The regenerator may be designed so that the contact liquid flows in a countercurrent to the oxygen-containing gases, which leave the regenerator through cyclone 8, and may be returned into the cycle by means of a compressor. The contact liquid is then communicated in the regenerated state to reactor 2 or 2*a* by means of pump 9. All partial operations may be carried out individually or together at a raised pressure, at a reduced pressure, or at atmospheric pressure.

The various embodiments of the process of this invention have the mutual advantage, that explosive gas mixtures are not liable to occur even when operating under a raised pressure, and that each gas current can be circulated separately and replenished by fresh gas to the necessary extent. It is also possible to use air as oxidizing agent in view of the fact that a concentration of nitrogen has here no detrimental effect.

The process of this invention may be carried out with catalysts and under the conditions broadly described in application Ser. No. 747,116 and referred to above.

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 contain inert gas and may be free from oxygen, but may likewise contain oxygen, is reintroduced, suitably into the lower part of the reactor, and an amount of olefin corresponding to that consumed during the reaction is introduced into the reactor through one or more inlets which may be arranged one above the other or to the recirculated gas. Alternatively, the residual gas is admixed with an amount of ethylene corresponding to that consumed and the resulting gas mixture which may be free from oxygen content or in which the ratio of olefin and oxygen is, for example, 95 to 99 percent or 90 to 95 percent of olefin (for example ethylene) to 5 to 1 percent or 10 to 5 percent, resp. of oxygen, is introduced into the reactor. In this variant of the invention the oxidizing agent, i.e. preferably oxygen, if desired in admixture with inert gases, such as air, is suitably introduced separately for sake of security, especially when no diluting gas is present.

As is stated in the aforesaid application it may be advantageous to add a dispersant, for example an alkylphenyl sulfonate or a product obtained by the reaction of ethylene oxide, propylene oxide, or butylene oxide with phenols or aliphatic alcohols, and/or a protective colloid, such as proteins or gum arabic to the liquid catalyst. Finely dispersed solid substances may also be added, if desired. The activity of these substances resides in the fact that free noble metal which has intermediately formed and is reconverted into active compounds by the reactants used in the instant process, cannot aggregate to form large particles. The catalyst is therefore especially finely distributed, and the degree of distribution is stable. As solid pulverulent substances there may be used, for example, charcoal powder or kieselguhr. It is also possible to use a combination comprising dispersant, protective colloid and finely distributed solid substance.

As is also described in the above cited application 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 con-

taining 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.

As stated above the escaping reaction gases may be re-used or recirculated. Furthermore 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 catalysts used in the present reaction may become depleted of halogen in the course of time, a fact which possibly causes a reduction in the rate of conversion. The loss of halogen may be counteracted by addition of halogen or hydrohalic acid or organic substances splitting off halogen or hydrohalic acid under the reaction conditions as already stated.

Such depletion of halogen is to be attributed substantially to the formation of volatile halogenated by-products, for example methyl chloride or ethyl chloride, which together with the carbonyl compounds produced entrain the halogen from the catalyst more or less rapidly. It has been ascertained that a certain amount of carboxylic acid corresponding to the olefin, is produced during the reaction, for example acetic acid; such acid concentrates in the liquid and increases the solubility of the reaction products. This favors the formation of halogen-containing volatile by-products and promotes the depletion of halogen. In addition thereto, the carboxylic acids which have concentrated, especially acetic acid, react with the copper ions, which is unfavorable because the copper salts formed, such as copper acetate, are relatively inert towards the olefin oxidation. In many cases it is therefore necessary to counteract such accumulation of carboxylic acids in the reaction space and to take care that these acids appear in as low a concentration as possible. This may be done by suitable continuous or discontinuous measures, for example by distillation, extraction or precipitation. A preferred variant in operating under atmospheric pressure consists for example in that the carboxylic acids formed are allowed to distil over together with the evaporating water; the water consumed is then replaced by a corresponding amount of fresh water. The amount of carboxylic acid removed in this manner is dependent on the surface of the reactor, the temperature used and the amount of gas flowing through, and may be modified by varying these factors. According to another variant the entire contact solution is worked up, carboxylic acid contained in the catalyst is removed, and the contact solution is recirculated into the apparatus.

In order to avoid operative disturbances part of the contact liquid may be withdrawn periodically or continuously and freed from carboxylic acid, partially or substantially, for example by distillation, and the liquid obtained may be added again to the contact medium.

It is also stated in the above cited application that the reaction of the present invention is favourably influenced by irradiation with rays rich in energy, preferably ultraviolet light, especially in the case where oxygen is used as oxidizing medium and such embodiment may likewise be applied in the present process. 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.

In practice it is advantageous to use a mercury quartz lamp as source of radiation arranged in the catalyst so that the light energy is fairly substantially utilized. If the reaction is carried out with an apparatus into which oxygen or an oxygen-containing gas is introduced separately from the olefin or olefin-containing gas or even an olefin-oxygen mixture, it is preferred to arrange the source of radiation in the vicinity of the oxygen inlet, so that that part which is rich in oxygen is especially well radiated. The oxygen is thereby activated as long as it has a high partial pressure. In the present process it is advantageous to arrange the source of radiation at the lower end of the regeneration vessel, immediately above the oxygen inlet. Activation may also be brought about by adding a compound of a radio-active element to the catalyst solution.

It is known that at a constant volume of the reaction liquid and in the case where the reaction does not run completely in one direction, the rate of conversion is the better the higher and narrower the design of the reactor. It is also evident that such reaction proceeds the better, the finer the gaseous components are distributed in the liquid. The catalyst solutions suitable for use in the process of this invention have sometimes the property of foaming after some time. On the one hand this favors the reaction in view of the fact that the gases are finely distributed in the catalyst liquid; sometimes foam-forming agents are intentionally added to the liquid. On the other hand, foaming means that the reaction space available is only insufficiently used, since only part of the contact solution is in the reactor.

The process of this invention may be carried out for example in vertically arranged tubes provided with frits or oscillatory agitators. The process may also be carried out in usual reaction towers, for example wash towers, suitably filled with filling material. 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.

The conversion and the space/time/yield depend substantially on the fine distribution of the gas, the time of stay in the apparatus, and the composition of the catalyst liquid, the temperature and the pressure used. The optimum time of stay can readily be determined by a simple test.

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 material, since there is the risk 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.

Condensates which separate from the reacted gas, especially aqueous condensates, may also be recirculated to again participate in the reaction, for example as such or after separation of higher and/or lower boiling reaction products.

It is not necessary that the catalysts used are made of fine chemicals; they may rather be produced from suitable metals of commercial purity. Metals such as copper and iron may be readily dissolved even by not-oxidizing acids, such as hydrochloric acid and acetic acid, if desired by addition of an oxidizing agent if copper is used, or by passing through during the dissolving process a gaseous oxidizing medium such as oxygen or air enriched with oxygen. The contaiminations contained in commercially pure metals do not affect the reaction if the solutions obtained are used as catalysts for the olefin

oxidation. More especially, the catalytic activity remains practically unaffected by small amounts of foreign metals which may appear in copper or iron of commercial purity. The anion forming agents contained in metals, such as sulfur, phosphorous, carbon, silicon, etc. are converted upon being dissolved to either hydrogen compounds, for example H_2S, which escape together with the reaction gases, or oxidized to acids of a higher valence stage, for example H_2SO_4, which do not affect the reaction, or converted partially into insoluble compounds, for example CuS, which appear only in minor amounts and, if necessary, can readily be separated from the catalyst, for example by filtration, before the catalyst is used.

The solutions so obtained are then admixed with the noble metal compound which is added in substance or in the dissolved state, if desired diluted with water, and the concentration of hydrogen ions is adjusted to the degree desired; the solutions so prepared may then directly be used as a catalyst for the olefin oxidation in the liquid phase.

Solvents suitable for dissolving the metals are chiefly hydrochloric acid and acetic acid in view of the fact that the presence of these acids proves especially advantageous in oxidizing olefins to aldehydes, ketones and acids. Acids other than those indicated above may, however, also be used, for example nitric acid. In this case, it is preferred to remove the acid in excess in order to adjust the solution to the pH desired and to use the solution so treated as a catalyst. If desired the salt of the metals may also partially be converted into the corresponding chlorides and/or acetates.

Palladium chloride or other noble metal chlorides need not be used, since there may also be employed the metals themselves, e.g. metallic palladium, suitably in a finely divided and finely distributed state, which reacts, for example, with copper chloride, and is converted to palladium chloride or a compound other than palladium chloride.

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

Although the catalysts have generally a good activity even after a prolonged time of reaction, especially when anions are added during the reaction, it may be advantageous to regenerate the catalyst from time to time. Some variants for such regeneration are described hereinafter.

It may be that the activity of the catalyst, especially when the catalyst is used for a very long period of time, is more or less reduced by the formation of a minor amount of by-products, or by foreign substances which may have been introduced. The by-products formed consist partially of organic compounds which are water-soluble at least to a certain degree, such as acetic acid, oxalic acid, higher aldehydes or ketones, or chlorinated organic compounds. These by-products may entrain precipitations, for example of heavy metal oxalates. Foreign substances possibly introduced into the catalyst may derive from, for example, contaminations of the gases, or the corrosion of parts of the apparatus, for example iron parts or the lining of the reactor.

The catalyst may be freed from these contaminations and regenerated in a simple manner by precipitating the cupric chloride as cuprous chloride and the noble metal compound as elementary metal. Precipitation is preferably carried out with the exclusion of substantial amounts of oxygen by the action of carbon monoxide, hydrogen, or one or more olefins, for example ethylene, propylene, or the butylenes, or of any other olefins or a mixture of several of these precipitating agents. The mixture of cuprous chloride and noble metal is advantageously washed, mixed with water and an acid, suitably hydrogen chloride if desired in the form of hydrochloric acid, and may then be reused in the reaction in this state, or more suitably after oxidation with oxygen or an oxygen-containing gas, such as air. If a particular oxidation is dispensed with and olefin and oxidation agent are allowed to act simultaneously upon the catalyst to be reused, oxidation is brought about in the following reaction by the oxidizing agent, especially by the oxygen contained in the reaction gas. After the regenerated but not yet oxidized catalyst has been reintroduced into the reactor, the amount of oxygen contained in the reaction gas may temporarily be increased, if desired. If in reducing the catalyst oxygen is not completely excluded, it is only necessary to use a somewhat larger amount of reducing agent.

This mode of execution is especially interesting if in addition to the noble metal the catalyst contains substantial amounts of copper salts, since these two rather expensive components of the catalyst—CuCl and noble metal—precipitate, while all other impurities or additions, for example iron salts, remain in the solution and are thus separated from the catalytically active substance.

The noble metal precipitates quantitatively and so does CuCl, except for a minor amount thereof which is soluble in water. In reusing the catalyst it is therefore advisable to add the corresponding amount of fresh $CuCl_2$ and/or CuCl+HCl. If the catalyst contains further additions, such as iron salts, it is also suitable to replenish these frequently cheap substances.

The simplest manner allowing CO and/or olefins and/or hydrogen to act upon the catalyst is to introduce these substances into the catalyst solution. In most cases this may be done under normal conditions, but it may be advantageous to use a higher temperature and/or a raised pressure. More severe conditions are opportune especially when hydrogen is used, which is the weakest reducing agent among the substances mentioned above. In using olefins as reducing agents the oxidizing activity of the catalyst may be used for a further formation of aldehydes, ketones and acids.

It is furthermore advisable prior to allowing the above gases to act upon the catalyst to entirely or partially neutralize or buffer the acid to a relatively low pH which is preferably in the range between 2 and 4. At too strong an acidity the reaction proceeds too slowly or is incomplete after the usual time of reduction. In addition thereto CuCl is remarkably soluble in concentrated hydrochloric acid, which may involve losses of copper. It should be noted that a further amount of hydrochloric acid is formed during the reduction of the copper or noble metal chloride, and this amount of acid must possibly also be neutralized or buffered. Reduction at a pH higher than 4 is often regarded to be disadvantageous since hydroxides are likewise precipitated, though a regeneration by precipitating the hydroxides or basic salts of the metals used is likewise possible.

Neutralization or buffering may be made in the usual manner with alkaline reacting substances, such as sodium hydroxide solution, sodium carbonate, sodium acetate, chalk, lime and similar compounds. The said reducing gases may be circulated for reasons of economy, and if carbon monoxide is used, may also be subjected to a CO_2 wash. If a larger amount of catalyst is used, it is advantageous in order to avoid operating disturbances to regenerate always a small amount of catalyst and subsequently to add the regenerated portion to the major quanity of said catalyst.

A possibility to recover palladium metal consists in subjecting the catalyst in known manner and in a strong acid medium to the action of acetylene. A palladium-acetylene compound precipitates which can be readily separated and freed from cations and anions by means of

a water wash. The palladium-acetylene compound so obtained may be then converted in the air or in the presence of ammonium nitrate to palladium oxide which in turn is capable of being converted directly to the chloride by means of hydrochloric acid. In this variant it is especially advantageous that acetylene can act on the palladium compound in the presence of hydrogen.

A further type of regeneration which is likewise already described in co-pending application Ser. No. 747,116 is important for those catalysts in which a liquid is present, that is to say which are used in the purely liquid phase or contain solid substances as described above, such as active carbon.

More especially such regeneration is important for those catalysts which contain iron- and/or copper compounds and compounds of noble metals of group VIII of the periodic table, and the activity of which has been reduced by precipitation of insoluble compounds, for example in the form of oxalates and/or iron oxide hydrate. These precipitations may be discharged continuously or periodically and taken up, if desired following a thermal treatment, in a mineral acid, preferably hydrohalic acids, such as hydrochloric acid, and may be then reintroduced into the reaction zone. This enables the initial activity of the catalyst to be restored so that undisturbed operation is possible during a long period of time.

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

Example 1

In an apparatus shown in the accompanying drawing and illustrated hereinbefore a gas current of an olefin, e.g. ethylene, containing about 7% of oxygen is contacted in reactor 2 or 2*a* with a liquid catalyst. The catalyst used contains 1 kg. of $CuCl_2.2H_2O$, 10 grams of $PdCl_2$ and 45 cc. of concentrated hydrochloric acid in 10 liters of water. The reaction temperature is about 90° C. and atmospheric pressure is applied. In separating device 4 the reaction product is freed from unreacted oxygen and olefin, which are reintroduced into the cycle via compressor 1 together with a fresh amount of olefin and oxygen in a concentration that corresponds to the conditions set forth above.

Example 2

A reaction tube (1 meter long; capacity 500 cc.) is charged with a catalyst solution containing, per liter of water, 1.5 grams of $PdCl_2$, 100 grams of $CuCl_2.2H_2O$ and 2 cc. of 10 N-hydrochloric acid, and ethylene is passed through at a rate of 30 liters per hour. A regeneration tube (1 meter long; capacity: 1000 cc.) is charged with the same solution and 100 liters of air are passed through per hour. Both gases are finely distributed by means of frits. By connecting the headpiece of the reaction tower with the lower liquid inlet of the regeneration tower and vice versa, a closed liquid cycle is produced, so that pumps can be dispensed with. The ascending gas currents circulate the liquid vigorously; in the instant example the circulation rate is above 100 liters per hour; it may be throttled as desired, for example, to 80 liters per hour. The rate of circulation may be measured, for example, by means of a flow meter. The towers are heated to a temperature of about 80–85° C. From the escaping gas currents which are charged with acetaldehyde vapor, acetaldehyde may be isolated in known manner, for example by conducting the gases separately through wash towers. The ethylene may be reintroduced to participatae again in the process, if desired after branching off a small amount of gas. Under these conditions, the conversion is after a certain induction period between 30 and 40% of the ethylene introduced into the reactor. Solid separations do not occur even after a prolonged time of reaction.

Example 3

A catalyst containing, per liter of water, 4 grams of palladium chloride and 100 grams of ferric chloride is used in a two-stage apparatus as described in Example 2 at a working temperature of 85° C. to 90° C. The reaction tower is charged, per liter of catalyst liquid, with 30 liters/hour of ethylene which is introduced by means of a glass frit. The regeneration tower is gassed with 100 liters of air per hour and liter of catalyst liquid, which flows from the head of the reaction tower into the regeneration tower and is freed between the two towers from acetaldehyde by stripping. The gas leaving the zone of regeneration is used as stripping gas. The currents of gas leaving the reaction tower and the regeneration tower are separately washed with water to separate the acetaldehyde.

We claim:

1. A continuous 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 first stage with a liquid catalyst of water, a salt of a noble metal selected from the group consisting of palladium, iridium, ruthenium, rhodium, and platinum, and as a redox system, a salt of a metal showing several valence states under the reaction conditions applied, contacting said liquid catalyst with oxygen in a separate second stage in the absence of substantial amounts of olefin, and circulating said liquid catalyst between said first and second stages.

2. A process as in claim 1 wherein a compound yielding anions of a strong inorganic acid under the reaction conditions is supplied to the liquid catalyst.

3. A process as in claim 1 wherein at least one of the reactants is admixed with an inert diluent.

4. A process as in claim 1 wherein a soluble neutral salt of a strong inorganic acid is additionally present in the liquid catalyst.

5. A process as in claim 1 wherein said olefinic hydrocarbon, oxygen and liquid catalyst are contacted in said first stage at a pressure from about atmospheric pressure to 50 atmospheres gauge and at a temperature between 50° and 160° C.

6. A continuous 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 in a first stage with a liquid catalyst of water, a salt of a noble metal selected from the group consisting of palladium, iridium, ruthenium, rhodium, and platinum, and as a redox system, a salt of a metal showing several valence states under the reaction conditions applied, contacting said liquid catalyst with oxygen in a separate second stage in the absence of substantial amounts of olefin, and circulating said liquid catalyst between said first and second stages.

7. A process as in claim 6 wherein a compound yielding anions of a strong inorganic acid under the reaction conditions is supplied to the liquid catalyst.

8. A process as in claim 6 wherein at least one of the reactants is admixed with an inert diluent.

9. A process as in claim 6 wherein a soluble neutral salt of a strong inorganic acid is additionally present in the liquid catalyst.

10. A process as in claim 6 wherein said olefinic hydrocarbon and liquid catalyst are contacted in said first stage at a pressure from about atmospheric pressure to 50 atmospheres gauge and at a temperature between 50° and 160° C.

11. A process as in claim 6 wherein gaseous compounds from said first stage are recycled to said first stage.

12. A continuous 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 (1) contacting said olefinic hydrocarbon and oxygen with a catalytic aqueous solution containing halogen ions selected from the group consisting of chlorine and bromine ions, a salt of palladium and a salt of a multivalent metal selected from the group consisting of iron and copper, (2) separating the carbonyl compound from the catalytic aqueous solution, (3) contacting the latter with oxygen to regenerate said catalytic aqueous solution and (4) recycling said regenerated catalytic aqueous solution to step (1) of the process.

References Cited in the file of this patent

UNITED STATES PATENTS

1,999,620	Van Peski et al.	Apr. 30, 1935
2,523,686	Engel	Sept. 26, 1950
2,614,125	Detling	Oct. 14, 1952
2,690,457	Hackmann	Sept. 28, 1954

FOREIGN PATENTS

891,209	France	Nov. 29, 1943
713,791	Germany	Nov. 14, 1941
767,409	Great Britain	Feb. 6, 1957

OTHER REFERENCES

Phillips: Amer. Chem. Jour., volume 16, pages 255–77 (pages 261 and 265–72 relied upon) (1894).

Chatt: Chem. Abstracts, volume 48, page 5067 (1954).