

UNITED STATES PATENT OFFICE

1,945,067

PROCESS FOR THE PHOTOCHEMICAL OXIDATION OF ORGANIC AND INORGANIC COMPOUNDS

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No Drawing. Application September 6, 1930,
Serial No. 480,194, and in Austria October 19,
1929

8 Claims. (Cl. 260—108)

This invention relates to a process for the photochemical oxidation of organic and inorganic compounds.

It is a fact which has been known in practice and in science for a long time that light initiates or accelerates chemical reactions. In particular Ciamician and his pupils have investigated and described a large number of such photochemical processes very exhaustively. Many other research workers have been engaged on similar investigations (full list of publications will be found in Houben-Well's "Methoden der Organischen Chemie", vol. II). Light has more particularly two striking effects: A condensing action and an oxidizing action or an action accelerating processes of oxidation, and the latter kind of photochemical process is also of outstanding technical importance. M. Weger (Berichte 36, 309) was the first to observe that alkylated aromatic hydrocarbons for example could be converted into carboxylic acids by light in the presence of oxygen. This reaction was developed later by Ciamician (Berichte 45, 38) as a basis for systematic research. Thus he found that when toluene was exposed to light, benzoic acid was produced, and on p-xylene being exposed to light, p-tolnic acid was produced. After experiments had been carried out which at first had produced negative results, (Berichte 46, 421) it was found possible to photo-oxidize naphthalene to phthalic acid by modifying the reaction conditions. Benrath and Mayer (Berichte 45, 2707) were the first to discover that such reactions could be accelerated by the presence of additional substances. These authors stated that phenanthraquinone accelerates the oxidation of toluene, whilst being oxidized itself at the same time to diphenic acid.

A substance which is more suitable from the technical point of view for the acceleration of the oxidation of such aromatic hydrocarbons has been found by A. Eckert (Berichte 58, 313) in anthraquinone. The advantage of the anthraquinone consists in that it remains unchanged during the reaction, that is to say it acts as a true catalyst. Moreover, other oxidation processes can also be accelerated with this reaction accelerator. In the Eckert process however, in addition to the oxidation, condensation processes also take place so that for example, when starting from alkylated aromatic hydrocarbons, the oxi-

dation product obtained is not pure. Thus, when oxidizing toluene with free access of air and in the presence of 5% anthraquinone, there will be formed after a certain time of exposure to light: 33% benzoic acid, 10% iso- and hydro- benzoic acid, 0.1% dibenzyl and 0.2% benzaldehyde. 55

The object of the process in the present invention is to carry out the oxidation of organic and inorganic substances by irradiation in the presence of oxygen and with the use of anthraquinone or substitution products thereof as catalyst, in such a manner as to increase the speed of the reaction and to cause same to take place without any substantial formation of intermediate products and condensation products, in a given direction, in order thus to enable the process to be used industrially and economically even in the relatively unfavourable conditions as regards light of Central Europe. 60

This end is achieved according to the invention by causing the catalysis which has been started by means of anthraquinone or substitution products thereof, to continue with the co-operation of catalysts of a different kind. 65

It has been found for instance that alkaline agents as soda lye, potash lye, milk of lime and the like affect the photochemical oxidation of organic substances—using a substance of the type of anthraquinone as transfer catalyst—more particularly when the irradiation takes place in an atmosphere of pure oxygen, in such a manner that practically the whole of the oxygen consumed is utilized only for the formation of one single product of oxidation, and at the same time the speed of reaction is increased many times. At the present time it is impossible to state with certainty whether this accelerating and regulation action of alkaline agents is due to the fact that the anthrahydroquinone formed in the primary stage, dissolves in the alkali and in consequence the reduction phase of the catalyst can take in a better manner, so that the active oxygen generated by the re-oxidation is formed in larger quantities in the secondary stage and is available for the oxidation, or whether other processes intervene. 70

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processes intervene. The first assumption seems to be supported by the observation that the alkaline solution is coloured an intense red by the dissolved anthrahydroquinone as long as any free alkali is present, and that the accelerating 80

and regulating action of the alkali ceases from the moment when the alkali is neutralized for example by the acids formed. At that moment the colour of the alkali layer changes from red to colourless.

6 A very similar accelerating and regulating action on the photochemical oxidation when using anthraquinone and the like as catalyst, is exercised by adsorption catalysts such as carbon
 10 suitable for adsorption purposes, in the form of grains or powder, or suitable inorganic gels, more particularly silica gel. A similar though less powerful action can be obtained with white or bleached fuller's earth, porous granular clay and
 15 the like. The efficiency of the adsorbents depends to a very great extent on the nature of same, on their special properties and on their method of manufacture.

Metallic salts and oxides may also be used as
 20 auxiliary or promoter catalysts for processes of this kind, the salts being both of the inorganic and organic type. Copper, bismuth, iron, vanadium and silver salts are more particularly suitable for the purpose. It must be pointed
 25 out that the action of many metal compounds on photochemical processes has been discovered by C. Neuberg. Thus the author in question has investigated the action of ferric sulphate in the insolatation of benzoic acid, and found that this
 30 acid was oxidized to salicylic acid (Biochem. Zeit. 27, 271 and 29, 290; Benrath J. pr. 2, 96).

The co-operation of alkaline auxiliary catalysts or of adsorbents is not sufficient in itself for ensuring in practice a homogeneous reaction, in the case of some photochemical oxidations using a catalyst of the anthraquinone type. In such cases it is advisable to utilize jointly auxiliary catalysts from several of the groups above referred to, more particularly to use metal salts or
 40 oxides in addition to alkaline agents or adsorbents.

Example I

30 litres of commercially pure toluene are introduced into a glass vessel of 60 litres capacity, whereupon 0.4% anthraquinone is added and 5 litres of lime water or weak milk of lime are introduced as a layer under the toluene. The vessel after the displacement or expulsion of the atmospheric nitrogen, is thereupon connected to an oxygen reservoir enabling the consumption of oxygen to be measured. When operating in this manner, it will be seen that the quantities of oxygen consumed will vary with the intensity of the irradiation. In exposing to sunlight or daylight, it will be found when measuring the intensity of the light by means of the Eder-Hecht "grey wedge" photometer that the quantity of oxygen consumed, reduced to 0° and 760 mm. pressure, will be proportional to the measured intensities of light, within the limits of practical error. The aqueous alkaline layer is coloured an intense brownish-red colour. After a given period of exposure to light, which depends of course on the size of the effective exposure surface as well as on the quantity and degree of concentration of the milk of lime employed, the red colour of the aqueous layer will suddenly change to colourless. If the quantity of oxygen consumed from the beginning of the experiment up to this moment be ascertained, and if the theoretical quantity of benzoic acid which should have been formed from the toluene and the oxygen consumed according to the equation of the reaction, be calculated, it will be found after

analyzing the aqueous layer, that practically all the oxygen has been consumed for the formation of benzoic acid. The aqueous layer represents a practically saturated solution of calcium benzoate which is nearly colourless and has a slightly aromatic smell. On the calcium benzoate solution being evaporated to a fraction of its volume and thereupon acidified with hydrochloric acid, perfectly white benzoic acid, absolutely free from chlorine and having the melting point of 122° C. will be precipitated. After a single recrystallization from water, it will comply with the most stringent requirements, for instance it can be used direct for the manufacture of sodium benzoate for food preserving purposes.

80 By irradiating toluene in two identical vessels under exactly the same conditions of exposure, using 5% anthraquinone as catalyst, first without and then with, the addition of milk of lime, it will be found that after a certain time, there will be formed with the known process (without auxiliary catalysts) 32 grs. benzoic acid and 15 grs. of other oxidation and condensation products, whereas when using the present process 420 grs. benzoic acid will be formed and only scarcely 95 perceptible quantities of other products of oxidation. Referred to the formation of benzoic acid, the speed of reaction of the present process is accordingly about 13 times that of the old process. The same effect is produced by soda lye, potash 100 lye or any other agent with an alkaline reaction.

If the lye be mixed with, for example 0.01% copper sulphate and 0.01% bismuth nitrate before the introduction of a layer of the same under the toluene, the speed of reaction will be increased by about 60%. The most advantageous combination of metals and the optimum concentration of the same depend on the nature of the body to be oxidized, on the concentration of the lye and on the depth of the layer of the 110 body to be oxidized.

Example II

30 litres of commercially pure toluene are introduced into a glass vessel of about 60 litres 120 capacity whereupon 0.4% anthraquinone and 1.5 kg. of granular carbon are added, and irradiation is carried out in an atmosphere of oxygen. The consumption of oxygen will also be found to be proportional to the quantity of light.

125 After the exposure to the same quantity of light as set forth in Example I, 380 gr. benzoic acid will be formed, that is to say the toluene contains 1.3% benzoic acid. If the irradiation be continued until the benzoic acid concentration 130 amounts to about 8%, then on the contents of the vessel being cooled, the benzoic acid will begin to crystallize out in white flakes, and if the contents of the vessel be drawn off and cooled, a thick paste of benzoic acid in toluene will be 135 produced. By separating off the benzoic acid in any manner from the mother-liquor, benzoic acid is obtained having a faintly perceptible brown tinge which, after having been kept for several days in the air, and especially when the air temperature amounts to 40-50° C. becomes practically inodorous and possesses a melting point of 122° C. A single recrystallization from water, is sufficient to obtain perfectly white, inodorous benzoic acid 140 absolutely free from chlorine.

145 Taking into account the amount of benzoic acid remaining in the mother-liquor and the quantity of benzoic acid absorbed by the carbon in accordance with the adsorption equilibrium, it can be calculated that, referred to the observed oxygen 150

consumption, 70% of the theoretical yield of benzoic acid will be obtained, whilst the remaining 30% of the oxygen has been consumed for the formation of other products of oxidation. The 8 yield depends of course to a very great extent on the properties of the carbon. By adding for example 0.04% of silver benzoate to the toluene or by impregnating the carbon with copper nitrate, it is easily possible to obtain a quantitative yield of benzoic acid.

10 A similar effect to that possessed by carbon can be brought about by the addition of white or bleached fuller's earth or of pieces of unglazed fire-clay for example in the form of "Raschig" 15 rings, the action of which can also be increased by suitable impregnation with metal salts or oxides.

Example III

20 A 50% solution of commercial paraffin oil (white refined) in benzene is prepared. 30 litres of this solution are mixed in a glass vessel with 0.4% anthraquinone and a layer of 5 litres of a 20% caustic soda solution is introduced under it. On irradiating this reaction mixture in an 25 oxygen atmosphere, fatty acids will be formed which dissolve in the lye as sodium salts.

If the operation be carried out without the 30 addition of metal salts, the oxygen consumption will be about 50% smaller than when oxidizing toluene under the same conditions. It is found that metal salts exercise an accelerating action 35 in this case also. Thus for example the addition of 0.1% uranium nitrate to the caustic soda solution accelerates the rate of reaction by about 40%, an addition of 0.05% vanadic acid and 0.1% iron sulphate accelerates the rate of reaction by 55%.

If the solution of fatty acids obtained be acidified, the fatty acids insoluble in water will be 40 precipitated in the form of a viscous oil and can be easily separated off. The nature of the fatty acids obtained depends to a great extent on the origin of the paraffin oil employed.

Example IV

45 If a 20% solution of lepidine (4-methyl-quinoline) in benzene be mixed with 1% anthraquinone and irradiated in an atmosphere of oxygen, a smooth oxidation to cinchoninic acid (quinoline-4 carboxylic acid takes place). On exposure to light, part of the cinchoninic acid formed will be separated in the form of crystals. The remainder can be isolated by shaking the benzene solution with caustic soda solution. The speed 55 of reaction is similar to that of the oxidation of toluene carried out under similar conditions.

The reaction proceeds in a different manner when the exposure takes place in the presence of 60 for example 0.5% anthraquinone and 0.1% iron cinchonate. In this case in addition to the oxidation, hydroxylation also takes place, 2 hydroxy-quinoline-4-carboxylic acid being formed in addition to a very small quantity of cinchoninic acid. Copper and silver salts for example 65 act in a similar manner to iron salts.

Example V

If a solution of chromic sulphate be mixed 70 with caustic soda solution in the manner described in the literature and left to stand until the chromium has separated out almost quantitatively in the form of a green precipitate and 0.5% anthraquinone- α -sulphonic acid, and 10% granular carbon be also added to the solution, 75 which is then irradiated in an oxygen atmos-

phere, a vigorous reaction takes place, chromic acid being formed which imparts to the solution a reddish yellow colour. The speed of reaction when working according to the present process with the addition of carbon is nearly ten times greater when compared with the processes described in the literature using atmospheric oxygen and without addition of carbon.

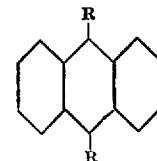
The oxidation of aqueous solutions of sulphur dioxide or hydrogen sulphide to sulphuric acid 80 can be accelerated in a similar manner for example by adding carbon or adsorbents having a similar action.

Example VI

90 If benzene be mixed with 0.5% anthraquinone and 0.05% ferric oxide and a layer of dilute hydrochloric acid be introduced under it; the reaction mixture being exposed to light in an atmosphere of oxygen, mono-chlorobenzene will be formed, the chlorine evolved by the hydrochloric acid exerting a chlorinating action on the benzene. The chlorobenzene can be separated from the benzene by fractional distillation. Better yields can be obtained by adding anthraquinone sulphonic acid to the hydrochloric acid used.

95 In the specification and claims, the following expressions are to be interpreted as follows:

100 *Anthraquinone type catalyst*.—Anthraquinone and its substitution products containing the ring system



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115 wherein R represents oxygen, hydrogen, carbon, nitrogen or combinations of said elements, such as, for example, naphthanthracenquinone, indanthren, pyranthron, flavanthren and also derivatives of anthraquinone, such as, for example, chlor-anthraquinone and anthraquinone α -sulphonic acid.

120 *Alkaline catalyst*.—An alkaline agent such as sodalye, potash lye, milk of lime and the like or one which will provide OH ions in solution.

125 *Adsorptive catalyst*.—An agent such as carbon in the form of powder or grains, suitable inorganic gels, such as silica gels, white or bleached fuller's earth, porous granular clay and the like.

130 *Metal compound catalyst*.—An agent, such as a metal salt or an oxide, for example, copper sulphate, copper nitrate, bismuth nitrate, silver benzoate, iron cinchonate, ferric oxide.

135 What I claim is:

1. The process of photochemical oxidation which comprises subjecting to irradiation the compound to be oxidized in the presence of oxygen and in conjunction with at least two different oxidizing catalysts, one of said catalysts being an anthraquinone type catalyst.

140 2. The process of photochemical oxidation, which comprises subjecting to irradiation the compound to be oxidized in the presence of oxygen and in conjunction with at least two different oxidizing catalysts, one of said catalysts being an anthraquinone type catalyst which starts the reaction and acts as a transfer catalyst, and at least another of said catalysts cooperating as a promoter catalyst.

145 3. The process according to claim 2, wherein the promoter catalyst is an alkaline catalyst.

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4. The process according to claim 2, wherein the promoter catalyst is an adsorptive catalyst.
5. The process according to claim 2, wherein the promoter catalyst is a metal compound catalyst.
6. The process according to claim 2, wherein an alkaline catalyst and a metal compound catalyst function as promoter catalysts.
7. The process according to claim 2, wherein an adsorptive catalyst and a metal compound catalyst function as promoter catalysts.
8. The process according to claim 2, wherein the promoter catalyst is an adsorptive catalyst 80 impregnated with a metal salt.

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