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(54) Title: FUNCTIONALIZED COPOLYMERS OF TERMINALLY FUNCTIONALIZED PERFLUORO (ALKYL VINYL ETHER) REACTOR WALL FOR PHOTOCHEMICAL REACTIONS, PROCESS FOR INCREASING FLUORINE CONTENT IN HYDROCARBONS AND HALOHYDROCARBONS AND OLEFIN PRODUCTION

(57) Abstract: A photochemical reaction apparatus including a reactor and a light source situated so that light from the light source is directed through a portion of the reactor wall is disclosed. The apparatus is characterized by the portion of the reaction wall comprising a functionalized copolymer of a terminally functionalized perfluoro (alkyl vinyl ether). Also described is a photochemical reaction process using said reactor. The functional group of the copolymer of the apparatus and the process is selected from $-SO_2F$, $-SO_2Cl$, $-SO_2H$, $-CO_2R$ (where R is H or C1-C3 alkyl), $-PO_3H_2$, and salts thereof. A process for increasing the fluorine content of at least one compound selected from hydrocarbons and halohydrocarbons, comprising: (a) photochlorinating said at least one compound, and (b) reacting the halogenated hydrocarbon in (a) with HF. A process for producing an olefinic compound, comprising: (a) photochlorinating at least one compound selected from hydrocarbons and halohydrocarbons containing at least two carbon atoms and at least two hydrogen atoms to produce a halogenated hydrocarbon containing a hydrogen substituent and a chlorine substituent on adjacent carbon atoms; and (b) subjecting the halogenated hydrocarbon produced in (a) to dehydrohalogenation.

TITLE

FUNCTIONALIZED COPOLYMERS OF TERMINALLY FUNCTIONALIZED PERFLUORO
(ALKYL VINYL ETHER) REACTOR WALL FOR PHOTOCHEMICAL REACTIONS,
PROCESS FOR INCREASING FLUORINE CONTENT IN HYDROCAEBONS AND
HALOHYDROCARBONS AND OLEFIN PRODUCTION

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FIELD OF THE INVENTION

This invention relates to the field of photochemical reactions, and
particularly to materials suitable for use in photochemical reaction
10 apparatus.

BACKGROUND OF THE INVENTION

Photochemical reactions use light as a source of energy to
promote chemical processes. Ultraviolet (UV) and visible light are widely
15 used in chemical synthesis both in laboratories and in commercial
manufacturing. Well known photochemical reactions include
photodimerization, photopolymerization, photohalogenation,
photoisomerization and photodegradation. For example,
cyclobutanetetracarboxylic dianhydride can be synthesized by
20 photodimerization of maleic anhydride in a glass reactor using a mercury
UV lamp (P. Boule et al., Tetrahedron Letters, Volume 11, pages 865 to
868, (1976)). Most of the vitamin D production in the United States is
based on UV photolysis in a quartz vessel using light between 275 and
300 nm.

25 In photochlorination, chlorine (Cl₂) reacts with a saturated or
unsaturated starting material, in the presence of a ultraviolet light source.
This process is widely used to form carbon-chlorine bonds under mild
conditions (e.g., room temperature) compared to the elevated
temperatures normally required for thermal chlorination (R. Roberts et al.,
30 Applications of Photochemistry, TECHNOMIC Publishing Co., Inc. 1984.).
For example, E. Tschiukow-Roux, et al. (J. Phys. Chem., Volume 88,
pages 1408 to 1414 (1984)) report photochlorination of chloroethane and
Walling et al. (J. Amer. Chem. Soc., Volume 79, pages 4181 to 4187
(1957)) report photochlorination of certain substituted toluenes. U.S.
35 Patent No. 5,190,626 describes the use of photochlorination in removing
unsaturated compounds such as vinylidene chloride from CCl₂FCH₃
product. Chlorine-containing compounds such as CCl₂FCH₃ may be
readily converted to olefinic compounds (e.g., CCIF=CH₂) by

dehydrohalogenation or to fluorine-containing compounds (e.g., CF_3CH_3) by fluorination using hydrogen fluoride (HF).

Typically in photochlorinations, light from a suitable source (e.g., an incandescent bulb or a UV lamp) is directed through a reactor wall to

5 interact with the reactants therein. The portion of the reactor wall through which the light passes must have a suitable transmittance to allow light of a wavelength required for the photochlorination to enter the reactor. Typically, quartz or borosilicate glass like Pyrex™ glass have been employed as transparent materials. Quartz is expensive, but has a low

10 cut-off wavelength at about 160 nm; Pyrex™ glass is less expensive, but has a relatively high cut-off wavelength at about 275 nm. Due to their reactivity, quartz and Pyrex are not appropriate materials of construction for chemical reactions involving base or HF. There is a need for additional materials which can be used for this purpose in photochemical

15 reactions (e.g., photochlorinations).

SUMMARY OF THE INVENTION

This invention provides an apparatus for photochemical reactions comprising a reactor and a light source situated so that light from the light

20 source is directed through a portion of the reactor wall. In accordance with this invention, the apparatus is characterized by said portion of the reaction wall comprising a functionalized copolymer of a terminally functionalized perfluoro(alkyl vinyl ether) wherein the functional group of the copolymer is selected from the group consisting of $-\text{SO}_2\text{F}$, $-\text{SO}_2\text{Cl}$, $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{R}$ (where R is H or $\text{C}_1\text{-C}_3$ alkyl), $-\text{PO}_3\text{H}_2$, and salts thereof.

This invention also provides a photochemical reaction process wherein light from a light source is directed through a reactor wall to interact with reactants in said reactor. In accordance with this invention, the process is characterized by the light directed through the reactor wall

30 being directed through a functionalized copolymer of a terminally functionalized perfluoro(alkyl vinyl ether) wherein the functional group of the copolymer is selected from the group consisting of $-\text{SO}_2\text{F}$, $-\text{SO}_2\text{Cl}$, $-\text{SO}_3\text{H}$, $-\text{CO}_2\text{R}$ (where R is H or $\text{C}_1\text{-C}_3$ alkyl), $-\text{PO}_3\text{H}_2$, and salts thereof.

35 DETAILED DESCRIPTION

In accordance with this invention, copolymers of terminally functionalized perfluoro(alkyl vinyl ethers) (such as Nafion®) are used as photochlorination reactor materials through which light is able to pass for

the purpose of interacting with the reactants, thereby promoting the photochemical reaction. Suitable functionalized copolymers include copolymers of at least one perfluorinated alkylene monomer with a terminally functionalized perfluoro(alkyl vinyl ether). Of note are

5 copolymers of tetrafluoroethylene with a terminally functionalized perfluoro(alkyl vinyl ether).

Suitable terminally functionalized perfluoro(alkyl vinyl ether) monomers include $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$,

10 $\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, and

15 $\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$.

Suitable functionalized copolymers include copolymers of $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$ with perfluorinated alkylene monomers. Nafion® thermoplastic resins are melt-processable perfluorinated copolymers of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonyl fluoride. The $-\text{SO}_2\text{F}$ end groups of a copolymer of a terminally functionalized perfluoro(alkyl vinyl ether) can be converted through hydrolysis to $-\text{SO}_2\text{OH}$ end groups. The $-\text{SO}_2\text{OH}$ end groups can be further treated with base to form salts. Suitable salt-forming cations include lithium, sodium, potassium, and ammonium. The acid, salt, and acid fluoride forms of these copolymers can be used in this invention as light transparent containers for photochemical reactions. Of note are copolymers having equivalent weights between 800 to 1500. Of particular note are copolymers having equivalent weights between 900 to 1200 (e.g., copolymers having an equivalent weight between 950 to 1100).

20 Equivalent weight is the ratio of the molecular weight of the copolymer to hydrogen in the acid form of the copolymer.

The portion of the reactor wall fabricated from such polymeric materials may be limited to a fraction of the reactor wall (e.g., a window of the polymeric material positioned in a reactor principally fabricated from another material) or may constitute all or essentially all of the reactor wall (e.g., a tube reactor fabricated from the polymeric material).

A suitable photochlorination apparatus includes a reactor in which light having a suitable wavelength (e.g., from about 250 nm to about 400 nm) can irradiate the reaction components for a time sufficient to convert at least a portion of the starting materials to one or more compounds having a higher chlorine content. The reactor may be, for example, a tubular reactor fabricated from functionalized perfluoro(alkyl vinyl ether) copolymer (e.g., either a coil or extended tube), or tank fabricated from

functionalized perfluoro(alkyl vinyl ether) copolymer, or a tube or tank fabricated from an opaque material which has a window fabricated from functionalized perfluoro(alkyl vinyl ether) copolymer. Typically, the thickness of the functionalized perfluoro(alkyl vinyl ether) copolymer is 5 sufficient to permit transmittance of the light of sufficient intensity to promote the reaction (e.g., 0.02 mm to 1 mm). Where additional structural reinforcement is desired while maintaining the chemical resistance offered by the functionalized perfluoro(alkyl vinyl ether) copolymer, a layer of reinforcing material fabricated from a highly transmitting material (e.g., 10 quartz) or a mesh of transmitting or opaque material may be used outside of the functionalized perfluoro(alkyl vinyl ether) copolymer layer.

The apparatus also includes a light source. The light source may be any one of a number of arc or filament lamps known in the art. The light source is situated such that light having the desired wavelength may 15 be introduced into the reaction zone (e.g., a reactor wall or window fabricated from a functionalized perfluoro(alkyl vinyl ether) copolymer and suitably transparent to light having a wavelength of from about 250 nm to about 400 nm).

Ordinarily the apparatus also includes a chlorine (Cl_2) source and a 20 source of the material to be chlorinated. The chlorine source may be, for example, a cylinder containing chlorine gas or liquid, or equipment that produces chlorine (e.g., an electrochemical cell) that is connected to the reactor. The source of the material to be chlorinated may be, for example, a cylinder or pump fed from a tank containing the material, or a chemical 25 process that produces the material to be chlorinated.

Of note are processes in accordance with this invention for increasing the chlorine content of at least one compound selected from hydrocarbons and halohydrocarbons; processes in accordance with this invention for increasing the fluorine content of at least one compound 30 selected from hydrocarbons and halohydrocarbons; and processes in accordance with this invention for producing at least one olefinic compound from a hydrocarbon or halohydrocarbon containing at least two carbon atoms and at least two hydrogen atoms. As described more fully below, all of these processes involve reaction with chlorine in the presence 35 of light.

Increasing Chlorine Content

Included in this invention is a process for increasing the chlorine content of a halogenated hydrocarbon compound or a hydrocarbon

compound by reacting said compound with chlorine (Cl₂) in the presence of light.

Halogenated hydrocarbon compounds suitable as starting materials for the chlorination process of this invention may be saturated or

5 unsaturated. Saturated halogenated hydrocarbon compounds suitable for the chlorination processes of this invention include those of the general formula C_nH_aBr_bCl_cF_d, wherein n is an integer from 1 to 4, a is an integer from 1 to 9, b is an integer from 0 to 4, c is an integer from 0 to 9, d is an integer from 0 to 9, the sum of b, c and d is at least 1 and the sum of a, b, 10 c, and d is equal to 2n + 2. Saturated hydrocarbon compounds suitable for chlorination are those which have the formula C_qH_r where q is an integer from 1 to 4 and r is 2q + 2. Unsaturated halogenated hydrocarbon compounds suitable for the chlorination processes of this invention include those of the general formula C_pH_eBr_fCl_gF_h, wherein p is an integer from 2 to 4, e is an integer from 0 to 7, f is an integer from 0 to 2, g is an integer from 0 to 8, h is an integer from 0 to 8, the sum of f, g and h is at least 1 and the sum of e, f, g, and h is equal to 2p. Unsaturated hydrocarbon compounds suitable for chlorination are those which have the formula C_iH_j where i is an integer from 2 to 4 and j is 2i. The chlorine content of 15 saturated compounds of the formula C_nH_aBr_bCl_cF_d and C_qH_r and/or unsaturated compounds of the formula C_pH_eBr_fCl_gF_h and C_iH_j may be increased by reacting said compounds with Cl₂ in the vapor phase in the presence of light. Such a process is referred to herein as a photochlorination reaction.

20 The photochlorination of the present invention may be carried out in either the liquid or the vapor phase. For vapor phase photochlorination, initial contact of the starting materials with Cl₂ may be a continuous process in which one or more starting materials are vaporized (optionally in the presence of an inert carrier gas, such as nitrogen, argon, or helium)

25 and contacted with chlorine vapor in a reaction zone. A suitable photochlorination reaction zone is one in which light having a wavelength of from about 250 nm to about 400 nm can irradiate the reaction components for a time sufficient to convert at least a portion of the starting materials to one or more compounds having a higher chlorine content.

30 The source of light may be any one of a number of arc or filament lamps known in the art. Light having the desired wavelength may be introduced into the reaction zone by a number of means. For example, the light may enter the reaction zone through a lamp well or window fabricated from a

functionalized perfluoro(alkyl vinyl ether) copolymer suitably transparent to light having a wavelength of from about 250 nm to about 400 nm. Likewise, the walls of the reaction zone may be fabricated from such a material so that at least a portion of the light used for the photochlorination 5 can be transmitted through the walls.

Alternatively, the process of the invention may be carried out in the liquid phase by feeding Cl₂ to a reactor containing the starting materials. Suitable liquid phase reactors include vessels fabricated from a functionalized perfluoro(alkyl vinyl ether) copolymer in which an external 10 lamp is directed toward the reactor and metal, glass-lined metal or fluoropolymer-lined metal reactors having one or more wells or windows fabricated from a functionalized perfluoro(alkyl vinyl ether) copolymer for introducing light having a suitable wavelength. Preferably the reactor is provided with a condenser or other means of keeping the starting 15 materials in the liquid state while permitting the hydrogen chloride (HCl) released during the chlorination to escape the reactor.

In some embodiments it may be advantageous to conduct the photochlorination in the presence of a solvent capable dissolving one or more of the starting materials and/or chlorination products. Preferred 20 solvents include those that do not have easily replaceable hydrogen substituents. Examples of solvents suitable for step (a) include carbon tetrachloride, 1,1-dichlorotetrafluoroethane, 1,2-dichlorotetrafluoroethane, 1,1,2-trichlorotrifluoroethane, benzene, chlorobenzene, dichlorobenzene, fluorobenzene, and difluorobenzene.

Suitable temperatures for the photochlorination of the starting 25 materials of the formula are typically within the range of from about -20°C to about 60°C. Preferred temperatures are typically within the range of from about 0°C to about 40°C. In the liquid phase embodiment, it is convenient to control the reaction temperature so that starting material is 30 primarily in the liquid phase; that is, at a temperature that is below the boiling point of the starting material(s) and product(s).

The pressure in a liquid phase process is not critical so long as the liquid phase is maintained. Unless controlled by means of a suitable 35 pressure-regulating device, the pressure of the system increases as hydrogen chloride is formed by replacement of hydrogen substituents in the starting material by chlorine substituents. In a continuous or semi-batch process it is possible to set the pressure of the reactor in such a way that the HCl produced in the reaction is vented from the reactor (optionally

through a packed column or condenser). Typical reactor pressures are from about 14.7 psig (101.3 kPa) to about 50 psig (344.6 kPa).

The amount of chlorine (Cl₂) fed to the reactor is based on whether the starting material(s) to be chlorinated is(are) saturated or unsaturated, 5 and the number of hydrogens in C_nH_aBr_bCl_cF_d, C_qH_r, C_pH_eBr_fCl_gF_h, and C_iH_j that are to be replaced by chlorine. One mole of Cl₂ is required to saturate a carbon-carbon double bond and a mole of Cl₂ is required for every hydrogen to be replaced by chlorine. A slight excess of chlorine over the stoichiometric amount may be necessary for practical reasons, 10 but large excesses of chlorine will result in complete chlorination of the products. The ratio of Cl₂ to halogenated carbon compound is typically from about 1:1 to about 10:1.

Specific examples of photochlorination reactions of saturated halogenated hydrocarbon compounds of the general formula 15 C_nH_aBr_bCl_cF_d and saturated hydrocarbon compounds of the general formula C_qH_r which may be carried out in accordance with this invention include the conversion of C₂H₆ to a mixture containing CH₂ClCCl₃, the conversion of CH₂ClCF₃ to a mixture containing CHCl₂CF₃, the conversion of CCl₃CH₂CH₂Cl, CCl₃CH₂CHCl₂, CCl₃CHClCH₂Cl or 20 CHCl₂CCl₂CH₂Cl to a mixture containing CCl₃CCl₂CCl₃, the conversion of CH₂FCF₃ to a mixture containing CHClFCF₃ and CCl₂FCF₃, the conversion of CH₃CHF₂ to CCl₃CClF₂, the conversion of CF₃CHFCHF₂ to a mixture containing CF₃CClFCHF₂ and CF₃CHFCClF₂, and the conversion of CF₃CH₂CHF₂ to CF₃CH₂CClF₂.

25 Specific examples of photochlorination reactions of unsaturated halogenated hydrocarbon compounds of the general formula C_pH_eBr_fCl_gF_h and unsaturated hydrocarbon compounds of the general formula C_iH_j which may be carried out in accordance with this invention include the conversion of C₂H₄ to a mixture containing CH₂ClCH₂Cl, the conversion of C₂Cl₄ to a mixture containing CCl₃CCl₃, the conversion of 30 C₃H₆ a mixture containing CCl₃CCl₂CCl₃, and the conversion of CF₃CCl=CCl₂ to a mixture containing CF₃CCl₂CCl₃.

Of note is a photochlorination process for producing a mixture containing 2-chloro-1,1,1-trifluoroethane (i.e., CH₂ClCF₃ or HCFC-133a) 35 by reaction of CH₃CF₃ with Cl₂ in the vapor phase in the presence of light in accordance with this invention. Also of note is a catalytic process for producing a mixture containing 1,2,2-trichloro-1,1,3,3,3-pentafluoropropane (i.e., CCIF₂CCl₂CF₃ or CFC-215aa) or 1,2-dichloro-

1,1,1,3,3,3-hexafluoropropane (i.e., $\text{CClF}_2\text{CClFCF}_3$ or CFC-216ba) by the chlorination of a corresponding hexahalopropene of the formula $\text{C}_3\text{Cl}_{6-x}\text{F}_x$, wherein x equals 5 or 6.

5 Contact times of from 0.1 to 60 seconds are typical; and contact times of from 1 to 30 seconds are often preferred.

Mixtures of saturated hydrocarbon compounds and saturated halogenated hydrocarbon compounds and mixtures of unsaturated hydrocarbon compounds and unsaturated halogenated hydrocarbon compounds as well as mixtures comprising both saturated and 10 unsaturated compounds may be chlorinated in accordance with the present invention. Specific examples of mixtures of saturated and unsaturated hydrocarbons and halogenated hydrocarbons that may be used include a mixture of $\text{CCl}_2=\text{CCl}_2$ and $\text{CCl}_2=\text{CClCCl}_3$, a mixture of $\text{CHCl}_2\text{CCl}_2\text{CH}_2\text{Cl}$ and $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CH}_2\text{CCl}_3$ and 15 $\text{CCl}_3\text{CHClCH}_2\text{Cl}$, a mixture of $\text{CHCl}_2\text{CHClCCl}_3$, $\text{CCl}_3\text{CH}_2\text{CCl}_3$, and $\text{CCl}_3\text{CCl}_2\text{CH}_2\text{Cl}$, a mixture of $\text{CHF}_2\text{CH}_2\text{CF}_3$ and $\text{CHCl}=\text{CHCF}_3$, and a mixture of $\text{CH}_2=\text{CH}_2$ and $\text{CH}_2=\text{CHCH}_3$.

Increasing the Fluorine Content

Included in this invention is a process for a halogenated 20 hydrocarbon compound or a hydrocarbon compound by reacting said compound with chlorine (Cl_2) in the presence of light as described above; and then reacting the halogenated hydrocarbon produced with hydrogen fluoride. Fluorination reactions are well known in the art. They can be conducted both in either the vapor phase or liquid phase using a variety of 25 fluorination catalysts. See for example, Milos Hudlicky, Chemistry of Organic Fluorine Compounds 2nd (Revised Edition), pages 91 to 135 and references cited therein (Ellis Harwood-Prentice Hall Publishers, 1992). Of note are vapor phase fluorinations in the presence of a fluorination catalyst. Preferred fluorination catalysts include chromium catalysts (e.g., 30 Cr_2O_3 by itself or with other metals such as magnesium halides or zinc halides on Cr_2O_3); chromium(III) halides supported on carbon; mixtures of chromium and magnesium (including elemental metals, metal oxides, metal halides, and/or other metal salts) optionally on graphite; and mixtures of chromium and cobalt (including elemental metals, metal 35 oxides, metal halides, and/or other metal salts) optionally on graphite, alumina, or aluminum halides such as aluminum fluoride.

Fluorination catalysts comprising chromium are well known in the art (see e.g., U. S. Patent No. 5,036,036). Chromium supported on

alumina can be prepared as described in U. S. Patent No. 3,541,834. Chromium supported on carbon can be prepared as described in U. S. Patent No. 3,632,834. Fluorination catalysts comprising chromium and magnesium may be prepared as described in Canadian Patent No. 2,025,145. Other metals and magnesium optionally on graphite can be prepared in a similar manner to the latter patent.

5 Preferred chromium fluorination catalysts comprise trivalent chromium. Of note is Cr_2O_3 prepared by pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, Cr_2O_3 having a surface area greater than about 200 m^2/g , and Cr_2O_3 prepared by 10 pyrolysis of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ or having a surface area greater than about 200 m^2/g some of which are commercially available.

15 Halogenated hydrocarbon compounds suitable for the fluorination of this invention include saturated compounds of the general formula $\text{C}_m\text{H}_w\text{Br}_x\text{Cl}_y\text{F}_z$, wherein m is an integer from 1 to 4, w is an integer from 0 to 9, x is an integer from 0 to 4, y is an integer from 1 to 10, z is an integer from 0 to 9, and the sum of w, x, y, and z is equal to $2n + 2$.

15 Examples of saturated compounds of the formula $\text{C}_m\text{H}_w\text{Br}_x\text{Cl}_y\text{F}_z$ which may be reacted with HF in the presence of a catalyst include 20 CH_2Cl_2 , CHCl_3 , CCl_4 , C_2Cl_6 , C_2BrCl_5 , $\text{C}_2\text{Cl}_5\text{F}$, $\text{C}_2\text{Cl}_4\text{F}_2$, $\text{C}_2\text{Cl}_3\text{F}_3$, $\text{C}_2\text{Cl}_2\text{F}_4$, C_2ClF_5 , C_2HCl_5 , $\text{C}_2\text{HCl}_4\text{F}$, $\text{C}_2\text{HCl}_3\text{F}_2$, $\text{C}_2\text{HCl}_2\text{F}_3$, C_2HClF_4 , C_2HBrF_4 , $\text{C}_2\text{H}_2\text{Cl}_4$, $\text{C}_2\text{H}_2\text{Cl}_3\text{F}$, $\text{C}_2\text{H}_2\text{Cl}_2\text{F}_2$, $\text{C}_2\text{H}_2\text{ClF}_3$, $\text{C}_2\text{H}_3\text{Cl}_3$, $\text{C}_2\text{H}_3\text{Cl}_2\text{F}$, $\text{C}_2\text{H}_3\text{ClF}_2$, $\text{C}_2\text{H}_4\text{Cl}_2$, $\text{C}_2\text{H}_4\text{ClF}$, $\text{C}_3\text{Cl}_6\text{F}_2$, $\text{C}_3\text{Cl}_5\text{F}_3$, $\text{C}_3\text{Cl}_4\text{F}_4$, $\text{C}_3\text{Cl}_3\text{F}_5$, C_3HCl_7 , $\text{C}_3\text{HCl}_6\text{F}$, $\text{C}_3\text{HCl}_5\text{F}_2$, $\text{C}_3\text{HCl}_4\text{F}_3$, $\text{C}_3\text{HCl}_3\text{F}_4$, $\text{C}_3\text{HCl}_2\text{F}_5$, $\text{C}_3\text{H}_2\text{Cl}_6$, $\text{C}_3\text{H}_2\text{BrCl}_5$, $\text{C}_3\text{H}_2\text{Cl}_5\text{F}$, $\text{C}_3\text{H}_2\text{Cl}_4\text{F}_2$, $\text{C}_3\text{H}_2\text{Cl}_3\text{F}_3$, $\text{C}_3\text{H}_2\text{Cl}_2\text{F}_4$, $\text{C}_3\text{H}_2\text{ClF}_5$, $\text{C}_3\text{H}_3\text{Cl}_5$, $\text{C}_3\text{H}_3\text{Cl}_4\text{F}$, $\text{C}_3\text{H}_3\text{Cl}_3\text{F}_2$, $\text{C}_3\text{H}_3\text{Cl}_2\text{F}_3$, $\text{C}_3\text{H}_3\text{ClF}_4$, $\text{C}_3\text{H}_4\text{Cl}_4$, $\text{C}_4\text{Cl}_4\text{Cl}_4$, $\text{C}_4\text{Cl}_4\text{Cl}_6$, $\text{C}_4\text{H}_5\text{Cl}_5$ and $\text{C}_4\text{H}_5\text{Cl}_4\text{F}$.

15 Of note is a process for producing 1,1,1,2,2-pentafluoroethane (i.e., CHF_2CF_3 or HFC-125) by the photochlorination of 1,1,1,2-tetrafluoroethane (i.e., CH_2FCF_3 or HFC-134a) to produce 2-chloro-30 1,1,1,2-tetrafluoroethane (i.e., CHClFCF_3 or HCFC-124); and the fluorination of the HCFC-124 to produce HFC-125. HFC-125 may also be produced by the photochlorination of 1,1,2,2-tetrafluoroethane (i.e., CHF_2CHF_2 or HFC-134) to produce 2-chloro-1,1,2,2-tetrafluoroethane (i.e., CCI_2CHF_2 or HCFC-124a); and fluorination of the HCFC-124a to 35 produce HFC-125. Also of note is a process for producing 1,1,1,3,3,3-hexafluoropropane ($\text{CF}_3\text{CH}_2\text{CF}_3$ or HFC-236fa) by the photochlorination of 1,1,1,3,3-pentafluoropropane ($\text{CF}_3\text{CH}_2\text{CHF}_2$ or HFC-245fa) to produce 3-chloro-1,1,1,3,3-pentafluoropropane (i.e., $\text{CF}_3\text{CH}_2\text{CClF}_2$ or

HCFC-235fa); and fluorination of the HCFC-235fa to produce HFC-236fa. Further discussion of producing HFC-236fa by fluorination is provided in U.S. Patent Application No. 60/638277 (Docket No. FL-1105) which was filed December 22, 2004, and is incorporated herein by reference.

5 In one embodiment of the invention, the photochlorination and further fluorination can be conducted in situ and the fluorinated product(s) recovered. In a second embodiment, the effluent from the photochlorination step may be fed to a second reactor for fluorination. The photochlorination product mixture can be fed to a fluorination reactor with 10 or without prior separation of the products from the photochlorination reactor. Of note are processes where the photochlorination product mixture is directly fed to a fluorination reactor without prior separation of the products from the photochlorination reactor. In a third embodiment, HF can be fed together with chlorine and the other photochlorination 15 starting materials to the photochlorination reactor and the effluent from the photochlorination reactor can be directed to a fluorination zone optionally containing a fluorination catalyst; and additional HF, if desired, can be fed to the fluorination zone.

Producing Olefins

20 Included in this invention is a process for producing an olefin from a halogenated hydrocarbon compound or a hydrocarbon compound by reacting said compound with chlorine (Cl₂) in the presence of light as described above; and then subjecting the halogenated hydrocarbon produced by the photochlorination to 25 dehydrohalogenation. Dehydrohalogenation reactions are well known in the art. They can be conducted both in either the vapor phase or liquid phase using a variety of catalysts. See for example, Milos Hudlicky, Chemistry of Organic Fluorine Compounds 2nd (Revised Edition), pages 489 to 495 and references cited therein (Ellis Harwood-Prentice Hall Publishers, 1992). Of note are vapor phase dehydrohalogenations in 30 the presence of a catalyst. Suitable catalysts for dehydrohalogenation include carbon, metals (including elemental metals, metal oxides, metal halides, and/or other metal salts); alumina; fluorided alumina; aluminum fluoride; aluminum chlorofluoride; metals supported on alumina; metals supported on aluminum fluoride or chlorofluoride; magnesium fluoride supported on aluminum fluoride; metals supported on fluorided alumina; alumina supported on carbon; aluminum fluoride or chlorofluoride supported on carbon; fluorided alumina supported on carbon; metals 35 supported on carbon; fluorided alumina supported on carbon; metals

supported on carbon; and mixtures of metals, aluminum fluoride or chlorofluoride, and graphite. Suitable metals for use on catalysts (optionally on alumina, aluminum fluoride, aluminum chlorofluoride, fluorided alumina, or carbon) include chromium, iron, and lanthanum.

5 Preferably when used on a support, the total metal content of the catalyst will be from about 0.1 to 20 percent by weight; typically from about 0.1 to 10 percent by weight. Preferred catalysts for dehydrohalogenation include carbon, alumina, and fluorided alumina.

Halogenated hydrocarbon compounds suitable for the dehydrohalogenation of this invention include saturated compounds of the general formula $C_mH_wBr_xCl_yF_z$, wherein m is an integer from 2 to 4, w is an integer from 1 to 9, x is an integer from 0 to 4, y is an integer from 1 to 9, z is an integer from 0 to 8, and the sum of w, x, y, and z is equal to $2n + 2$. The compound photochlorinated to produce the compound subjected to dehydrohalogenation (e.g., a saturated compound of the formula $C_nH_aBr_bCl_cF_d$ or a saturated compound of the formula C_qH_r as described above) should contain at least two carbon atoms and two hydrogen atoms (e.g., for said compounds of the formulas $C_nH_aBr_bCl_cF_d$ and C_qH_r w, n, a and q should be at least 2).

10 15 20 25 30 35 Of note are processes where the compound photochlorinated is a halogenated hydrocarbon that contains fluorine

Of note is a process for producing 1,1-difluoroethylene (i.e., $CF_2=CH_2$ or vinylidene fluoride) by the photochlorination of 1,1-difluoroethane (i.e., CHF_2CH_3 or HFC-152a) to produce 1-chloro-1,1-difluoroethane (i.e., $CClF_2CH_3$ or HCFC-142b); and the dehydrohalogenation of the HCFC-142b to produce 1,1-difluoroethylene. Also of note is a process for producing tetrafluoroethylene (i.e., $CF_2=CF_2$) by the photochlorination of 1,1,2,2-tetrafluoroethane (i.e., CHF_2CHF_2 or HFC-134) to produce 2-chloro-1,1,2,2-tetrafluoroethane (i.e., $CClF_2CHF_2$ or HCFC-124a); and the dehydrohalogenation of the HCFC-124a to produce tetrafluoroethylene. Also of note is a process for producing hexafluoropropylene ($CF_3CF=CF_2$) by the photochlorination of 1,2-dihydrohexafluoropropene (i.e., $CF_3CHFCHF_2$ or HFC-236ea) to produce 1-chloro-1,1,2,3,3,3-hexafluoropropene (i.e., $CF_3CHFCClF_2$ or HCFC-226ea); and dehydrohalogenation of the HCFC-226ea to produce hexafluoropropylene.

EXAMPLES

General Procedure for Chlorination and Product Analysis

Photochlorination was carried out using a 110 volt/275 watt sunlamp placed (unless otherwise specified) at a distance of 0.5 inches (1.3 cm) from the 5 outside of the first turn of the inlet end of a coil of fluoropolymer tubing material through which the materials to be chlorinated were passed. The fluoropolymer tubing used in the examples below was an 18 inch (45.7 cm) long Nafion® tube (0.065 inch (0.17 cm) OD X 0.055 inch (0.14 cm) ID) which was coiled to a diameter of 3 inches (7.6 cm) and contained suitable feed and exit ports. The 10 organic feed material and chlorine were fed to the tubing using standard flow-measuring devices. The gas mixture inside was exposed to light generated by the sunlamp. The experiments were conducted at ambient temperature (about 23°C) and under about atmospheric pressure. Organic feed material entering the tubing and the product after photochlorination were analyzed on-line using a 15 GC/MS. The results are reported in mole%. CFC-114 is $\text{CClF}_2\text{CClF}_2$. CFC-114a is $\text{CF}_3\text{CCl}_2\text{F}$. CFC-216ba is $\text{CF}_3\text{CClFCClF}_2$. HCFC-226ba is $\text{CF}_3\text{CClFCHF}_2$. 1.0 sccm (standard cubic centimeter per minute) is equal to about $1.7(10)^{-8}$ cubic meters per second.

20

Example 1

Photochlorination of HFC-134a

Feed gases consisting of HFC-134a at a flow rate of 5.0 sccm and chlorine gas at a flow rate of 2.5 sccm were introduced into the Nafion® tubing. After 25 exposure to light for one hour, the product was analyzed and found to contain 75.7 mole % of HFC-134a, 19.8 mole % of HCFC-124, 3.7 mole % of CFC-114a and 0.8 mole % of other unidentified compounds. The molar yield of CFC-114a compared to the total amount of CFC-114a and HCFC-124 was 15.7 %.

30

Example 2

Photochlorination of HFC-134

Feed gases consisted of HFC-134 at a flow rate of 5.0 sccm and chlorine gas at a flow rate of 2.5 sccm. After exposure to light for one hour, the product 35 was analyzed and found to contain 71.2 mole % of HFC-134, 27.4 mole % of HCFC-124a, 1.1 mole % of CFC-114 and 0.3 mole % of other unidentified compounds.

Example 3

Photochlorination of HFC-236ea

Feed gases consisted of HFC-236ea at a flow rate of 5.0 sccm and chlorine gas at a flow rate of 2.5 sccm. After exposure to light for one hour, the 5 product was analyzed and found to contain 61.1 mole % of HFC-236ea, 5.6 mole % of HCFC-226ba, 32.3 mole % of HCFC-226ea, 0.7 mole % of CFC-216ba and 0.3 mole % of other unidentified compounds.

Example 4

10 Photochlorination of HFC-236ea

Feed gases consisted of HFC-236ea at a flow rate of 5.0 sccm and chlorine gas at a flow rate of 7.5 sccm. After exposure to light for one hour, the 15 product was analyzed and found to contain 60.3 mole % of HFC-236ea, 5.7 mole % of HCFC-226ba, 33.0 mole % of HCFC-226ea, 0.7 mole % of CFC-216ba and 0.3 mole % of other unidentified compounds.

Example 5

Photochlorination of HFC-245fa

HFC-245fa was analyzed prior to chlorination and found to have a purity of 20 99.8 %. Feed gases consisted of HFC-245fa at a flow rate of 3.5 sccm and chlorine gas at a flow rate of 3.5 sccm. After exposure to light for one hour, the product was analyzed and found to contain 67.1 mole % of HFC-245fa, 31.7 mole % of HCFC-235fa, and 1.2 mole % of other unidentified compounds.

CLAIMS

What is claimed is:

1. A photochemical reaction apparatus comprising a reactor and a light source situated so that light from the light source is directed through a portion of the reactor wall, characterized by:
5 said portion of the reaction wall comprising a functionalized copolymer of a terminally functionalized perfluoro(alkyl vinyl ether); wherein the functional group of the copolymer is selected from the group consisting of -SO₂F, -SO₂Cl, -SO₃H, -CO₂R, -PO₃H₂, and salts thereof, wherein R is H or C₁-C₃ alkyl.
10
2. The photochemical reaction apparatus of Claim 1 wherein the functionalized copolymer is a copolymer of at least one perfluorinated alkylene monomer with a terminally functionalized perfluoro(alkyl vinyl ether).
15
3. The photochemical reaction apparatus of Claim 2 wherein the functionalized copolymer is a copolymer of tetrafluoroethylene with a terminally functionalized perfluoro(alkyl vinyl ether).
20
4. The photochemical reaction apparatus of Claim 3 wherein the functionalized copolymer is a copolymer of tetrafluoroethylene with a perfluoro(alkyl vinyl ether) monomer selected from the group consisting of FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, CH₃OC(O)CF₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, and
25 CH₃OC(O)CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, or is an acid or salt form thereof.
30
5. The photochemical reaction apparatus of Claim 4 wherein the functionalized copolymer is a copolymer of tetrafluoroethylene with FSO₂CF₂CF₂OCF(CF₃)CF₂OCF=CF₂, or is an acid or salt form thereof.
35
6. A photochemical process wherein light from a light source is directed through a reactor wall to interact with reactants in said reactor, characterized by:
 the light directed through the reactor wall being directed through a functionalized copolymer of a terminally functionalized perfluoro(alkyl vinyl ether) wherein the functional group of the copolymer is selected from the group consisting of -SO₂F, -SO₂Cl, -SO₃H, -CO₂R, -PO₃H₂, and salts thereof, wherein R is H or C₁-C₃ alkyl.

7. The photochemical process of Claim 6 wherein the functionalized copolymer is a copolymer of at least one perfluorinated alkylene monomer with a terminally functionalized perfluoro(alkyl vinyl ether).

5 8. The photochemical process of Claim 7 wherein the functionalized copolymer is a copolymer of tetrafluoroethylene with a terminally functionalized perfluoro(alkyl vinyl ether).

10 9. The photochemical process of Claim 8 wherein the functionalized copolymer is a copolymer of tetrafluoroethylene with a perfluoro(alkyl vinyl ether) monomer selected from the group consisting of $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, $\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, and $\text{CH}_3\text{OC}(\text{O})\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, or is an acid or salt form thereof.

15 10. The photochemical process of Claim 9 wherein the functionalized copolymer is a copolymer of tetrafluoroethylene with $\text{FSO}_2\text{CF}_2\text{CF}_2\text{OCF}(\text{CF}_3)\text{CF}_2\text{OCF}=\text{CF}_2$, or is an acid or salt form thereof.

20 11. The photochemical process of Claim 6 wherein the chlorine content of at least one compound selected from hydrocarbons and halohydrocarbons is increased by reaction with chlorine in the presence of light.

25 12. A process for increasing the fluorine content of at least one compound selected from hydrocarbons and halohydrocarbons, comprising:

- (a) photochlorinating said at least one compound in accordance with the process of Claim 11; and
- (b) reacting the halogenated hydrocarbon produced by the photochlorination in (a) with HF.

30 13. The process of Claim 12 wherein in (a) $\text{CF}_3\text{CH}_2\text{CHF}_2$ is photochlorinated to $\text{CF}_3\text{CH}_2\text{CClF}_2$; and in (b) $\text{CF}_3\text{CH}_2\text{CClF}_2$ is reacted with HF to produce $\text{CF}_3\text{CH}_2\text{CF}_3$.

35 14. The process of Claim 12 wherein in (a) $\text{CF}_3\text{CH}_2\text{F}$ is photochlorinated to CF_3CHClF ; and in (b) CF_3CHClF is reacted with HF to produce CF_3CHF_2 .

15. The process of Claim 12 wherein in (a) CHF_2CHF_2 is photochlorinated to $\text{CHF}_2\text{CClF}_2$; and in (b) $\text{CHF}_2\text{CClF}_2$ is reacted with HF to produce CF_3CHF_2 .

16. A process for producing an olefinic compound, comprising:

(a) photochlorinating at least one compound selected from hydrocarbons and halohydrocarbons containing at least two carbon atoms and at least two hydrogen atoms in accordance with the process of Claim 11 to produce a halogenated hydrocarbon containing a hydrogen substituent and a chlorine substituent on adjacent carbon atoms; and

(b) subjecting the halogenated hydrocarbon produced by the photochlorination in (a) to dehydrohalogenation.

10

17. The process of Claim 16 wherein in (a) a compound containing fluorine is photochlorinated.

15

18. The process of Claim 17 wherein in (a) CH_3CHF_2 is photochlorinated to produce CH_3CClF_2 ; and wherein in (b) CH_3CClF_2 is dehydrohalogenated to produce $\text{CF}_2=\text{CH}_2$.

20

19. The process of Claim 17 wherein in (a) CHF_2CHF_2 is photochlorinated to produce $\text{CHF}_2\text{CClF}_2$; and wherein in (b) $\text{CHF}_2\text{CClF}_2$ is dehydrohalogenated to produce $\text{CF}_2=\text{CF}_2$.

25

20. The process of Claim 17 wherein in (a) $\text{CF}_3\text{CHFCHF}_2$ is photochlorinated to produce $\text{CF}_3\text{CHFCClF}_2$; and wherein in (b) $\text{CF}_3\text{CHFCClF}_2$ is dehydrohalogenated to produce $\text{CF}_3\text{CF}=\text{CF}_2$.

INTERNATIONAL SEARCH REPORT

Int'l application No

PCT/JS2005/046265

A. CLASSIFICATION OF SUBJECT MATTER

B01J19/00 B01J19/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

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X	US 4 855 112 A (ADCOCK ET AL) 8 August 1989 (1989-08-08) column 1, line 5 - line 10; claims 1-10 column 7, line 12 - line 58; figures 1,6 column 8, line 57 - column 9, line 6 -----	1-20
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 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

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- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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& document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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