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HEXAFLUOROPHOSPHORIC ACID AND ORGANIC SULFUR COMPOUNDS

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This invention relates to novel adducts of organic sulfur-containing compounds and hexafluorophosphoric acid methods of preparing them, and the removal of sulfur compounds from hydrocarbons, particularly petroleum hydrocarbons. A more specific aspect of the invention is the separation of mixtures of organic sulfur-containing compounds.

It is well known that the presence of sulfur compounds is detrimental to various hydrocarbon fractions for a number of reasons, such as their corrosive action, disagreeable odor, etc. The removal of sulfur compounds from gasoline is particularly important, not only for the above reasons, but also because of the adverse effect that the sulfur compounds have on the susceptibility of gasoline to the addition of tetraethyl lead for improving anti-knock quality of the gasoline.

Various processes are known for the removal of detrimental sulfur compounds from petroleum hydrocarbons. The most important processes heretofore known include hydrodesulfurization, caustic treatment, and treatment with a mineral acid, such as sulfuric acid, hydrofluoric acid, or fluosulfonic acid. In the hydrodesulfurization process, a hydrocarbon fraction is contacted with hydrogen under conditions of elevated temperature and pressure in the presence of a hydrogenation catalyst. The organic sulfur compounds in the hydrocarbon fraction are hydrogenated to hydrogen sulfide which can then be removed by alkaline treatment, such as caustic treatment. However, this method of desulfurization is not only expensive but, in the case of cracked gasolines, the olefin content also becomes hydrogenated to a point where the anti-knock properties of the gasoline are seriously impaired. Caustic treatment of hydrocarbons is relatively expensive; furthermore, this treatment is suitable only for the removal of acidic sulfur compounds. It has recently been recognized that all types of sulfur compounds have deleterious effects on various product qualities. Therefore, caustic treatment is not altogether satisfactory. Treatment of hydrocarbon fractions with a mineral acid is often inadvisable since the acid will not only remove sulfur compounds, but also considerable quantities of hydrocarbons as well. Furthermore, such hydrocarbon constitutents as olefins and aromatics will react with a mineral acid. Treatment of cracked gasolines with mineral acids is particularly inadvisable because these stocks are degraded by loss of such anti-knock constituents as olefins and aromatics. It is obvious that a process for the removal of virtually all of the sulfur compounds from hydrocarbon fractions without substantial removal of hydrocarbons would be desirable.

The organic sulfur-containing compounds contained in various petroleum fractions include such compounds as mercaptans, including thiophenols and thiocresols; aliphatic, aromatic and cycloaliphatic sulfides and disulfides; cyclic sulfides such as polymethylene sulfides, thiophenes, penthiophenes, thionaphthenes, dibenzothiophenes, thianthrenes, and the like. It would be desirable not only to remove all of these sulfur compounds from petroleum fractions, but also to separate the various types of sulfur compounds from each other.

It is a principal object of this invention to provide novel adducts of organic sulfur-containing compounds and additaments therefor. A more specific object is to provide novel relatively oil-insoluble adducts of organic sulfur-containing compounds containing only carbon, hydrogen, and sulfur and a suitable additament. Another object is to provide a method of fractionating mixtures of organic sulfur-containing compounds. Still another object is to provide a method of removing organic sulfur compounds from hydrocarbons, particularly petroleum hydrocarbons. Other objects and advantages will become apparent from the following detailed description.

In accordance with the present invention, it has been found that hexafluorophosphoric acid forms adducts with organic sulfur-containing compounds, particularly organic sulfur-containing compounds containing only carbon, hydrogen and sulfur. More specifically, it has been found that hexafluorophosphoric acid forms adducts with hydrocarbyl sulfides, such as aliphatic, aromatic, cycloaliphatic, and cyclic sulfides. It has also been found that the formation of these adducts enables the separation of mixtures of organic sulfur compounds, as well as the removal of organic sulfur compounds from mixtures thereof with sulfur-free compounds particularly petroleum hydrocarbons and mixtures thereof.

The organic sulfur compounds which find most important application in the practice of the present invention are those which contain only carbon, hydrogen, and sulfur. These compounds can be represented by the structural formula: R—$(S)_n$—R' where R represents a hydrocarbon radical, R' represents a hydrocarbon radical or hydrogen (R and R' can be a single divalent group or radical forming a heterocyclic compound with $(S)_n$) and n represents an integer from 1 to 6, inclusive, preferably 1 to 3, inclusive. The various types of sulfur compounds which are represented by the above structural formula and are suitable for the practice of the invention are: alkyl mercaptans, such as methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl mercaptans; alkenyl mercaptans, such as propenyl and butenyl mercaptans, 2,3-butadiene-1-thiol, 3-methyl-2-butene-1-thiol, pentenyl mercaptans; cycloalkyl and cycloalkenyl mercaptans, such as cyclopentyl, cyclopentylmethyl, cyclohexyl, methylcyclohexyl, cyclohexylpropyl, cycloheptyl, and cyclopentenyl mercaptans, 2-decahydronaphthalenethiol; aryl mercaptans or thiophenols, such as thiophenol, methylthiophenols, phenylmethyl mercaptans, ethylthiophenols, phenylpropyl mercaptans, indanthiols, naphthalenethiols, naphthylmethyl mercaptans, methylnaphthalenethiols, acenaphthenethiols, phenylcyclohexylmethyl mercaptans; alkyl sulfides (including polysulfides), such as dimethyl sulfides, methyl propyl sulfides, methyl butyl sulfides, dipropyl sulfides, dibutyl sulfides, butyl octyl sulfides, butyl propyl sulfides, dioctyl sulfides, butyl amyl sulfides, diamyl sulfides, methyl decyl sulfides; alkenyl sulfides (including polysulfides), such as methyl allyl sulfides, divinyl sulfides, ethyl vinyl sulfides, diisopropenyl sulfides, dibutenyl sulfides; cycloalkyl and cycloalkenyl sulfides (including polysulfides), such as ethyl cyclopentyl sulfides, ethyl cyclohexyl sulfides, ethyl methylcyclohexyl sulfides, dicyclopentyl methyl sulfides, dicyclopentenyl methyl sulfides, and decahydronaphthyl ethyl sulfides; aromatic sulfides (including polysulfides), such as ethyl phenyl sulfides, ethyl methylphenyl sulfides, propyl phenyl sulfides, ethyl dimethylphenyl sulfides, butyl phenyl sulfides, hexyl phenyl sulfides, phenyl decyl sulfides, ethyl phenylethyl sulfides, methyl benzyl sulfides, benzyl octyl sulfides, benzyl ethyl sulfides, ethyl naphthyl sulfides, methyl naph-

thyl sulfides, diphenyl sulfides, dinaphthyl sulfides, phenyl benzyl sulfides; cyclic sulfides, such as thiacyclopropane, thiacyclobutane, thiacyclopentane, thiacyclohexanes, thiacyclooctanes, thiophenes, methylthiophenes, ethenylthiophenes, dimethylthiophenes, propylthiophenes, phenylthiophenes, dibenzothiophenes, thionaphthenes, thiopyrans, benzothiopyrans, dibenzothiopyrans, thianthrenes, and the like. Other suitable compounds containing only C, H, and S include the thioketones and thioaldehydes. It is preferred that the organic sulfur compound have not more than about 25 carbon atoms per molecule, and preferably not more than about 20 carbon atoms per molecule. The preferred compounds are the hydrocarbyl sulfides, including the polysulfides.

The essentially neutral, i. e. non-basic or non-nitrogenous, organic sulfur compounds are also preferred. If, however, basic organic sulfur compounds are employed, an additional amount of hexafluorophosphoric acid, equal to the base equivalent, should be used in the complex formation.

Although the above compounds are preferred, other organic sulfur compounds will also form adducts with HPF_6. Such compounds include the alkyl sulfites, such as di-methyl, di-ethyl, di-propyl, di-butyl, and di-amyl sulfites; the alkyl sulfates, such as di-methyl, di-ethyl, ethyl-isopropyl, ethyl-isobutyl, di-propyl, and di-butyl sulfates; sulfoxides; sulfones, and the like.

The adducts of the present invention are suitably formed by dissolving the organic sulfur-containing compound in a suitable sulfur-free solvent, for example, a liquid aliphatic, napthenic or aromatic hydrocarbon, such as pentane, cyclohexane, or toluene, cooling the solution to a suitable temperature, contacting the cooled solution with hexafluorophosphoric acid, and then separating the resulting precipitate which is an adduct of the sulfur compound and the acid. The process can be effected in any suitable manner wherein satisfactory contacting of the sulfur compound with the acid is obtained, and wherein provision is made for separating and recovering the desired precipitate. As hexafluorophosphoric acid is highly corrosive in a free state and dissociates very rapidly at room temperature into PF_5 and HF, it is preferred to utilize a solution of the acid in a suitable solvent, such as sulfur dioxide, thionyl fluoride, thionyl chloride, sulfuryl fluoride, sulfuryl chloride, carbon dioxide, carbonyl chloride, and carbonyl sulfide. The preparation of an anhydrous HPF_6-containing composition is described in detail in the copending application of Mulder et al., Serial No. 277,086, filed March 17, 1952, now U. S. Patent 2,718,456, such as by the interaction of HF and PF_5 in a suitable polar inorganic ionizing solvent for both the HF and PF_5, such as liquid SO_2 at −15° to +30° C. In another embodiment of the present invention, the hexafluorophosphoric acid can be formed in situ. For example, the hydrogen fluoride and phosphorus pentafluoride can be introduced as separate streams to the contacting zone containing the sulfur compound. The formation of the adducts is also preferably carried out in the substantial absence of water or water vapor. When a relatively high working temperature, such as room temperature, is used, it is sometimes desirable to effect the formation of the adducts under a pressure higher than atmospheric.

The following example will serve to illustrate the formation of the adducts of the present invention:

EXAMPLE I

About 10 grams of dipropyl sulfide was dissolved in pentane, and the solution was cooled with ice. While the cooled solution was being stirred, a solution of an excess of HPF_6 in sulfur dioxide was introduced into it. A solid precipitate was formed and most of the sulfur dioxide was allowed to evaporate. The precipitate was filtered off and then washed with pentane. The pentane was removed from the precipitate under vacuum without raising the temperature.

The above procedure was repeated with the following compounds: butyl octyl sulfide, benzyl octyl sulfide, phenyl decyl sulfide, benzothiophene, and dibenzothiophene. Where it proved difficult to dissolve the compound in pentane, toluene was used.

The resulting adducts were analyzed, and the pertinent data are given in Table I:

Table I

Sulfur Compound		Adduct (1 S comp.: 2 HPF_6)									
Name	Percent S	Percent S		Percent P		Percent F		Mol. ratio, HPF_6-S comp.		Solubility in—	
		theor.	exp.	theor.	exp.	theor.	exp.	calc. from percent S	calc. from percent F	alcohol	chloroform
Dipropyl sulphide	28.1	7.8	7.6	15.1	15.5	55.6	56.2	2.10:1	2.00:1	+	+
Butyloctyl sulphide	16.0	6.5	6.8	12.6	12.2	46.2	45.9	1.85:1	1.97:1	+	+
Benzyloctyl sulphide	13.5	6.1	6.7	11.7	11.5	43.2	42.4	1.74:1	1.92:1	+	+
Phenyldecyl sulphide	12.8	5.9	6.3	11.4	10.2	42.1	40.8	1.77:1	1.87:1	+	slightly soluble.
Benzothiophene	23.8	7.5	7.9	14.6	14.0	53.5	52.5	1.85:1	1.89:1	+	−
Dibenzothiophene sulphide	17.4	6.7	6.3	13.0	11.8	47.9	48.1	2.22:1	2.02:1	+	−

It will be noted from the data in Table I that the adducts are composed of sulfur compound and hexafluorophosphoric acid in the approximate mole ratio of 1 to 2, respectively.

The adducts can be decomposed to regenerate the sulfur compound and HPF_6 by heating or by treatment with a strong base, for example, an aqueous caustic solution. In cases where the heat necessary for regeneration may decompose the sulfur compound, it is advisable to use caustic treatment.

It has been ascertained that a critical temperature exists above which a given adduct will not form. Thus, by a judicious selection of operating temperatures, a mixture of two or more organic sulfur-containing compounds, all of which form adducts with HPF_6, can be separated. For example, the mixture is contacted with HPF_6, the treatment being carried out at intervals of decreasing temperatures; the adduct which forms at each temperature stage can then be removed from the remaining sulfur compounds. If desired, the treatment may be carried out at a temperature sufficiently low to precipitate all of the sulfur compounds in the mixture. The temperature of the resulting precipitate is then gradually raised so that the decomposition of the adducts is effected in stages, suitable separation of remaining adduct and regenerated components being effected at each desired stage. The regenerated sulfur compounds can be separated from the adducts which are not decomposed, if necessary, by the application of a solvent, such as pentane, benzene, toluene, sulfur dioxide, diethylether, etc., which will preferentially dissolve the regenerated sulfur compound. Thus, dipropyl sulfide, which forms a stable adduct with HPF_6 at room temperature, can be separated from a mixture thereof

with dibenzothiophene, which will not form an adduct with HPF_6 at a temperature above about 0° C.

It is also possible to separate mixtures of organic sulfur-containing compounds by contacting the mixture with HPF_6 at a temperature sufficiently low to precipitate all of the sulfur compounds in the mixture, and then treating the resulting precipitate with a solvent which is selective for adducts of certain types of sulfur compounds. For example, as shown by illustrative data in Table I, chloroform acts as a selective solvent for the adducts of the dialkyl sulfides, but does not dissolve the adducts of the heterocyclic sulfur compounds. Thus, adducts of dipropyl, butyl octyl, or benzyl octyl sulfides can be separated from adducts of benzothiophene or of dibenzothiophene, by solution of the former in chloroform.

In accordance with a preferred embodiment of the present invention, the formation of adducts of organic sulfur-containing compounds and HPF_6 is utilized in the desulfurization of hydrocarbons, particularly petroleum hydrocarbons. This embodiment of the invention is applicable to the treatment of normally gaseous hydrocarbons, such as ethane, propane, butane and/or the corresponding gaseous olefins, containing sulfur compounds, and is particularly applicable to the desulfurization of normally liquid hydrocarbon fractions, such as gasoline, kerosene, diesel oil, gas oil, fuel oil, etc.

Desulfurization of sulfur-containing hydrocarbon fractions can be effected by contacting the hydrocarbon charging stock in any suitable manner with HPF_6, or with reagents (PF_5 and HF) which will form HPF_6 in situ. The resulting adducts of the sulfur compounds and HPF_6 are then separated from the treated hydrocarbons. The HPF_6 is preferably applied in solution in a suitable solvent as described above. The hydrocarbon charging stock is preferably diluted with a light hydrocarbon, such as pentane, in order to facilitate separation of the resulting adducts from the hydrocarbon and to prevent contamination of the adducts with the hydrocarbon. The desulfurization may be either a batch or continuous type of operation.

Generally, the amount of HPF_6 applied will correspond to the composition of the adducts which are to be formed. Solid adducts are thereby formed. The solid adducts can be easily separated from the hydrocarbon in any suitable manner, for example, by filtration. If an excess amount of HPF_6 is employed, the resulting adducts will dissolve in the excess acid. Depending on the amount of acid employed, the resulting adducts will be partially or wholly dissolved in HPF_6. Thus, depending on the amount of acid employed, a liquid phase and a solid phase, two liquid phases, or two liquid phases and one solid phase are obtained. It is preferred to employ an amount of HPF_6 which will result in the formation of either one liquid phase and one solid phase, or of two liquid phases.

After separation of the treated hydrocarbon phase, from the phase containing the adducts of HPF_6 and the sulfur compounds, the adducts can be decomposed, as by heating, to regenerate HPF_6 which is then recycled to the contacting step.

Fractionation of the sulfur compounds contained in the petroleum hydrocarbon feed can be effected, as well as desulfurization of the feed, by a judicious selection of operating temperatures in the same manner as described above. For example, the desulfurization treatment can be carried out in stages at gradually decreasing temperatures; the adducts formed at each temperature stage are then removed from the mixture. According to another method, described above, the desulfurization can be effected at a temperature sufficiently low to form adducts of substantially all of the sulfur compounds in the mixture. The resulting precipitate, after separation from the desulfurized hydrocarbons, is then gradually heated to decompose the adducts in stages, and the sulfur compound regenerated at each temperature stage is then removed from the adducts which are not decomposed, if necessary, in the presence of a solvent which is selective for the regenerated sulfur compound. Separation of the adducts in the resulting precipitate can also be effected by treatment of the precipitate with a solvent which is selective for adducts of certain types of sulfur compounds in the manner described above.

Preferred embodiments of the application of the invention are illustrated by the following examples:

EXAMPLE II

One hundred parts by weight of a Mexican gas oil having a boiling range of from about 255° to about 355° C., and having a sulfur content of about 2.21% by weight in the form of organic sulfur compounds, was diluted with about 300 parts by weight of pentane. The mixture was continuously maintained at a temperature of about 0° C. During a period of about 10 minutes, a solution of about 25 parts by weight of HPF_6 in liquid SO_2 was added to the mixture with vigorous agitation. The SO_2 evaporated off almost immediately. A solid adduct of the organic sulfur compounds present in the oil was formed. In the complete absence of moisture from the air the solid adduct was filtered off through a filter of rust-proof steel. About 29.5 parts by weight of adduct were obtained.

The adduct was then decomposed by the addition of an excess quantity of aqueous caustic soda. Two layers were formed; the top layer consisted of about 12.7 parts by weight of sulfur compounds with a sulfur content of about 14.9% by weight.

The filtrate separated from the solid adduct, comprising desulfurized hydrocarbons, was washed with aqueous caustic solution. Any caustic remaining in the filtrate was removed therefrom by water-washing. The filtrate was dried and the pentane was distilled off; 84.1 parts by weight of a raffinate, having a sulfur content of about 0.23% by weight, was obtained.

EXAMPLE III

One hundred parts by weight of a West Texas gas oil having a boiling range of from about 280° to about 380° C., and having a sulfur content of about 1.39% by weight, was diluted with about 300 parts by weight of pentane. The mixture was contacted with a solution of about 20 parts by weight of HPF_6 in liquid SO_2 in the same manner as described in Example II. The resulting adduct was removed by filtration.

The adduct was then decomposed by the addition of an excess quantity of aqueous caustic soda. The top layer obtained consisted of about 9.0 parts by weight of sulfur compounds with a sulfur content of about 12.2% by weight.

The filtrate was washed with aqueous caustic and then water-washed. The washed filtrate was dried and the pentane was distilled off. About 88.4 parts by weight of a raffinate, having a sulfur content of about 0.28% by weight, was obtained.

By utilizing hexafluorophosphoric acid as the desulfurizing agent, loss of hydrocarbon material by reaction with or by extraction by the desulfurizing agent is substantially completely avoided.

We claim as our invention:

1. A process for desulfurizing a hydrocarbon material containing sulfur compounds which comprises contacting said hydrocarbon material in liquid phase, in the substantial absence of water and at a temperature no higher than ambient room temperature, with a solution of perfluorophosphoric acid (HPF_6) in liquid sulfur dioxide in proportions to form solid adduct of at least a portion of the sulfur compounds and perfluorophosphoric acid, whereby such a solid adduct is formed, separating the solid adduct of sulfur compound and perfluorophosphoric acid from the hydrocarbon material, and decomposing the adduct to separate the components thereof.

2. The process, according to claim 1, wherein the con-

tacting step is carried out at a temperature of not more than about 0° C.

3. The process, according to claim 1, wherein the hydrocarbon material is a normally liquid hydrocarbon fraction.

4. The process, according to claim 1, wherein the hydrocarbon material is a gas oil fraction.

5. A process according to claim 1, wherein the hydrocarbon material is a liquid petroleum hydrocarbon fraction.

6. A process in accordance with claim 4, wherein the gas oil is diluted with a light hydrocarbon.

7. A process for the separation of a mixture of at least two organic sulfur-containing compounds A and B, which comprises contacting the mixture in liquid phase, in the substantial absence of water, with a solution of hexafluorophosphoric acid (HPF_6) in liquid sulfur dioxide under condition of temperature, no higher than ambient room temperature, and proportions of perfluorophosphoric acid and sulfur compound to form solid adduct of perfluorophosphoric acid with essentially only sulfur compound A to the exclusion of sulfur compound B whereby such solid adduct is formed, and separating said solid adduct from the remainder of the mixture which is enriched in sulfur compound B.

8. A process according to claim 7, wherein the mixture is one of at least two hydrocarbyl sulfides.

9. A process for the separation of a mixture of a dialkyl sulfide and a heterocyclic sulfur compound which comprises contacting said mixture in liquid phase dissolved in a liquid hydrocarbon, in the substantial absence of water, with a solution of hexafluorophosphoric acid (HPF_6) in liquid sulfur dioxide, at a temperature not above about 0° C., and in proportions to form solid adducts of the dialkyl sulfide and of the heterocyclic sulfur compound with hexafluorophosphoric acid, whereby such solid adducts are formed, and separating the adduct of the dialkyl sulfide from the adduct of the heterocyclic sulfur compound by selectively dissolving the adduct of the dialkyl sulfide in chloroform without dissolving the adduct of the heterocyclic sulfur compound.

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