United States Patent

Davis

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[54] FRACTIONATION OF C_{13} BICYCLIC AROMATIC HYDROCARBONS DI OR TRIANHYDRIDE COMPLEX FORMATION

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[52] **U.S. Cl.** ..... **260/674 N**

[51] **Int. Cl.** **C07c 7/00**

[58] **Field of Search** ..... 260/674 N

[56] **References Cited**

UNITED STATES PATENTS

2,941,017	6/1960	Veatch et al	260/674
2,885,453	5/1959	Fishel	260/674
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[57] **ABSTRACT**

Mixtures of C_{13} bicyclic aromatic hydrocarbons containing trimethylnaphthalenes are difficult to fractionate by conventional techniques such as distillation or crystallization. However, by contacting such mixtures with the dianhydride of 1,2,4,5-benzenetetracarboxylic acid, the dianhydride of 1,2,3,4-benezenetetracarboxylic acid or the trianhydride of 1,2,3,4,5,6-benzenehexacarboxylic acid, a solid complex of certain hydrocarbons and the polyanhydride is formed. Separation of the solid complex and its subsequent decomposition results in a complexate that is substantially richer in those trimethylnaphthalenes which are preferentially complexed. These trimethylnaphthalenes can be demethylated to dimethylnaphthalenes which have utility in the production of dyes.

8 Claims, No Drawings

FRACTIONATION OF C_{13} BICYCLIC AROMATIC HYDROCARBONS DI OR TRIANHYDRIDE COMPLEX FORMATION

CROSS REFERENCES TO RELATED APPLICATIONS

The present application is copending with the following listed applications filed of even date herewith, all applications being of common ownership.

Ser. No.	Inventor(s)	Title
33,980	R. I. Davis K. A. Scott	"Fractionation of Eutectic Mixture of Dimethyl naphthalenes by Dianhydride Complexation"
33,949	R. I. Davis	"Fractionation of C_{13} Bicyclic Aromatic Hydrocarbons by Tetrahalophthalic Anhydride Complex Formation"
33,951	K. A. Scott	"Fractionation of C_{12} Bicyclic Aromatic Hydrocarbons by 2-Cloro, 4-Nitrobenzoic Acid Complex Formation"
33,981	R. I. Davis TF K. A. Scott	"Fractionation of C_{12} Bicyclic Aromatic Hydro carbons by Di or Trian hydride Complex Formation"

BACKGROUND OF THE INVENTION

This invention relates generally to a process for fractionating difficult-to-separate C_{13} bicyclic aromatic hydrocarbons and, in particular, the isomers of trimethyl-naphthalene. More specifically, it relates to a process for fractionating isomers of trimethylnaphthalene by the initial contacting of the isomers with a di or trianhydride defined hereinafter.

One of the methyl groups attached to the trimethyl-naphthalene can be removed and the resulting dimethyl-naphthalenes oxidized to naphthalenecarboxylic acids which are used in the production of dyes and pigments. A more detailed discussion of the utility of these dimethyl-naphthalenes appears in "Naphthalenecarboxylic Acids" by K. A. Scott in Kirk Othmer, Encyclopedia Of Chemical Technology, 2nd Edition, Vol. 13.

For convenience, trimethylnaphthalene or trimethyl-naphthalenes herein will be referred to as TMN with specific TMN isomers being indicated by reference to the location of the methyl groups. For example, 1,3,7-trimethylnaphthalene will be referred to as 1,3,7-TMN.

TMN are found in coal tar, lignite tar, crude oil, shale oil and in petroleum gas oil produced by catalytic cracking. In these hydrocarbon mixtures, TMN are usually present in rather dilute concentration. However, by known processes such as distillation, crystallization and solvent extraction, TMN can be recovered in concentrated form from the previously mentioned sources. In demethylating these TMN to dimethylnaphthalenes, it is usually preferable that each isomer be demethylated by itself since generally each isomer requires slightly different reaction conditions for optimum demethylation.

Most, if not all, of the isomers of TMN usually are present in these hydrocarbon mixtures. These TMN isomers, as well as certain other C_{13} alkylnaphthalenes, such as 2-methyl-3-ethyl-naphthalene, have boiling points which are extremely close to each other. This closeness in boiling points makes it extremely difficult to distill apart the individual isomers or distill some isomers from other C_{13} alkylnaphthalenes. These boiling points are as follows:

C_{13} Alkylnaphthalenes	Boiling Points, ° F.*
2-methyl-3-ethylnaphthalene	531
1,2,3-TMN	541
1,2,4-TMN	540
1,2,5-TMN	536
1,2,6-TMN	536
1,2,7-TMN	532
1,2,8-TMN	545
1,3,5-TMN	536
1,3,6-TMN	536
1,3,7-TMN	536
1,3,8-TMN	545
1,4,5-TMN	545
1,4,6-TMN	532
1,6,7-TMN	536
2,3,6-TMN	531

*API project 44, Table 23-2-(33.5211)

Since 1,2,5-TMN, 1,2,6-TMN, 1,3,5-TMN, 1,3,6-TMN, 1,3,7-TMN and 1,6,7-TMN have the same boiling points, these isomers cannot be separated by distillation.

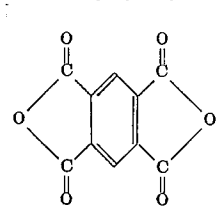
Summarizing, the separation of TMN isomers from each other by known methods is difficult if not practically impossible. There is a need for another purification and/or separation method or a method which facilitates existing procedures.

SUMMARY OF THE INVENTION

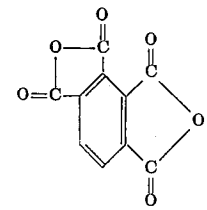
This invention relates to a method for the fractionation of TMN by selected complexation with the dianhydride of 1,2,4,5-benzenetetracarboxylic acid, the dianhydride of 1,2,3,4-benzenetetracarboxylic acid or the trianhydride of 1,2,3,4,5,6-benzenehexacarboxylic acid. A C_{13} bicyclic aromatic hydrocarbon mixture containing TMN is contacted with one of the aforementioned solid polyanhydrides. The resulting solid TMN-polyanhydride complex is separated from the mixture. The solid complex is decomposed and subsequently released TMN have a composition substantially different from the original hydrocarbon mixture.

DESCRIPTION

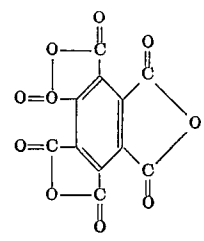
The complexing agent used in this invention is the dianhydride of 1,2,4,5-benzenetetracarboxylic acid, also known as pyromellitic dianhydride, the dianhydride of 1,2,3,4-benzenetetracarboxylic acid or the trianhydride of 1,2,3,4,5,6-benzenehexacarboxylic acid. These three polyanhydrides for convenience are referred to herein as PMDA (I), DA (II) and TA (III), respectively. The structures representing these three polyanhydrides are as follows:



(I)



(II)



(III)

It is believed that the complexes formed herein are π complexes, i.e., that they are causes by combination between the π electrons of the two rings involved. The polyanhydride apparently accepts a share in the π electrons of the compound which is complexed with it. Steric factors appear to have a strong effect, since according to the theory of π complex formation, the two rings must be close together and parallel in order for the complex to form. These complexes are distinct from the acid-base type as exemplified by complexes of $HF{\cdot}BF_3$ and xylenes and also from clathrate complexes of, for example, the urea-paraffin type.

Complexing occurs over a relatively wide temperature range with the rate of complex formation increasing with temperature. The lower temperature limits are dictated by practical considerations regarding the rate of complex formation. The upper temperature limits of the process are governed by the thermal stability of the given complex. Thus it is apparent that the optimum temperature for the operation of the present process depends upon both the rate of complex formation and the stability factor. In general, the temperatures employed will be below the melting point of polyanhydride. These polyanhydride melting points are: PMDA, 540°–546° F.; DA, 382°–386° F.; TA, greater than 590° F. Preferably, the temperatures employed will fall in the range from a temperature at which the TMN are liquid to the melting point of the polyanhydride. The more preferred temperature range for the complexing step is between 100° and 300° F. However, an inert solvent, as defined hereinafter, with a freezing point lower than the C_{13} bicyclic aromatic hydrocarbons can be used thereby permitting complexing to take place at lower temperatures.

The feed to this process can include, in addition to at least two TMN isomers, other compounds that do not alter or destroy the structure of the complex. In general, appreciable quantities of undesirable compounds that will react with a polyanhydride are to be avoided. Compounds such as C_4 to C_{20} alkanes, alkenes, cycloalkanes, cycloalkenes or mixtures thereof were found to be relatively inert and had no appreciable effect upon the complex formation. Other inert compounds include CCl_4 and ethers.

Since this process is for fractionating TMN, hydrocarbons boiling outside the boiling range of C_{13} bicyclic aromatic hydrocarbons and which form complexes with polyanhydrides should not be present in appreciable quantities in the feed. For example, dimethylnaphthalenes are known to form a complex with polyanhydrides (See Cross References to Related Applications). This problem can be avoided by treating only C_{13} bicyclic aromatic hydrocarbons containing TMN. Preferably, the C_{13} bicyclic aromatic hydrocarbons are C_{13} alkylnaphthalenes and ideally they are only TMN.

The amount of PMDA, DA or TA employed in the complexing step can vary over a wide range depending on the fractionation desired. The amount of polyanhydride used is related to the amount of TMN present. If an extremely large ratio of polyanhydride to TMN is used and sufficient time is allowed, all the TMN would complex and no TMN fractionation could be obtained. On the other hand, the amount of polyanhydride used can be greater than the amount necessary to ultimately form a complex containing all the TMN in the mixture being treated if the length of time allowed for complexing is relatively short. Preferably, the amount of polyanhydride contacting the hydro-carbon mixture would be in the range of 0.01 to 3.0 moles of polyanhydride per mole of TMN. A more preferred narrower range would be from 0.10 to 1.5 moles of polyanhydride per mole of TMN. Contacting of the C_{13} bicyclic aromatic hydrocarbons with polyanhydride can be performed in one contacting stage or a plurality of distinct contacting stages.

The TMN can be easily separated from the complex by heating the latter under vacuum and recovering the TMN as a distillate. By employing such a preferred operation, the polyanhydride is regenerated and can be reused for further complexing. Recovery of the complexed TMN can also be done by elution of the complex with an inert sol-vent such as C_4 to C_{20} alkanes, alkenes, cycloalkanes or cycloalkenes or mixtures thereof or destruction of the polyanhydride by such agents as water or aqueous base.

Thus in this invention, a C_{13} bicyclic aromatic hydrocarbon mixture containing TMN is contacted in a liquid phase with solid PMDA, DA or TA. The amount of polyanhydride used is sufficient to complex with at least one of the TMN, preferably being 0.01 to 3.0 moles of polyanhydride per mole of TMN. The temperature of contacting is less than the melting point of the polyanhydride. The resulting mixture of said aromatic hydrocarbons and polyanhydride can be maintained at ambient temperature, e.g., 50° to 100° F., until the desired complexing occurs. Alternatively, the resulting mixture, after contacting at the initial temperature, can be elevated to a higher temperature, the latter being less than the melting point of polyanhydride, to reduce the time required to reach the desired complexation. The solid TMN-polyanhydride complex can be separated from the resulting admixture at a suitable elevated temperature although it is preferred to reduce the temperature to, e.g., 0° to 100° F., prior to removing the complex.

Suitable agitation of the C_{13} bicyclic aromatic hydrocarbons containing TMN can occur during or after the addition of the polyanhydride and/or heating and/or cooling steps.

The solid TMN-polyanhydride can be decomposed in several ways. For example, after the solid TMN-polyanhydride complex has been separated, the complex can be heated under vacuum and the TMN removed as distillate. Preferably, the complex should be washed to remove liquid from the surface of the solids. This liquid will have a composition equal to the uncomplexed material and its presence reduces the effectiveness of separation. Another way to decompose the complex is to use a suitable inert solvent such as C_4 to C_{20} alkanes, alkenes, cycloalkanes, cycloalkenes or mixtures thereof, in sufficient quantity, and add it to the solid complex as a result of which the complex will decompose. The C_4 to C_{20} solvent should have a boiling point such that it can easily be separated from the TMN by distillation. The solid polyanhydride is removed and the remaining TMN-solvent mixture is fractionated.

An alternative procedure comprises adding a suitable inert solvent and then raising the temperature of the resulting complex-solvent combination. In this latter technique, the use of elevated temperature reduces the necessary amount of solvent. Upon decomposition of the complex, the polyanhydride is removed from the hot inert solvent.

Still another way to decompose the complex is to contact the TMN-polyanhydride complex with a compound which will react with the polyanhydride, thereby releasing the TMN. Among such materials are water, aqueous sodium hydroxide, aqueous calcium hydroxide, etc. The advantage of using aqueous sodium hydroxide, etc., is that the formation of a salt which dissolves in the water enhances the separation of the complexate from the water. When the polyanhydride is not reacted with any compound to release the DMN, it can be used to contact untreated C_{13} bicyclic aromatic hydrocarbons and/or the noncomplexate from the first contacting step. This procedure can be repeated as often as necessary to achieve the desired concentration of TMN.

The noncomplexate remaining, after one or more solid TMN-polyanhydride complexes have been removed, can be contacted with fresh recycled polyanhydride for further processing according to this invention.

The following example illustrates this invention:

EXAMPLE

The PMDA used was a white powder having a purity of 98⁺percent. Its melting point was 540° to 546° F., particle size was 95/percent less than 10 microns and boiling point was 745° to 752° F. The composition of the hydrocarbon liquid treated is shown in the following Table and is referred to as feed.

The feed was treated in the following manner. One mole of PMDA per 5 moles of TMN present in the feed was added to the liquid at room temperature. The resulting mixture was slowly heated to 270° F. and then cooled to 65° to 75° F. and held at that temperature for about 30 minutes. The solid complex was filtered out and subsequently washed and vacuum dried. Afterwards, the complex was vacuum distilled. The distillate or complexate had a different composition than the original hydrocarbon liquid, such composition being shown along with the composition of the noncomplexate in the fol-

lowing Table. Also, shown in the Table is the weight or mole ratio of a specific TMN in the complexate to the same TMN in the noncomplexate. If this ratio equals one, no change in concentration occurred; if this ratio is greater than one, complexation of the specific TMN was preferential; and if less than one, complexation of the specific TMN was not preferential.

TABLE

Formation of TMN–PMDA Complexes

Compounds	Feed	Weight Percent Complexate	Weight Percent Noncomplexate	Ratio of Compound in Complexate to Noncomplexate
Lower Boiling Compounds	0.7	trace	2.0	—
1,3,7-TMN	1.2	1.3	1.1	1.2
1,3,6-TMN	48.9	43.9	49.2	0.89
1,4,6-TMN	20.6	18.0	20.8	0.87
1,3,5-TMN	17.6	28.4	15.0	1.9
2,3,6-TMN	2.3	2.1	2.3	0.91
1,2,7-TMN	1.3	1.1	1.9	0.78
2,3,5-TMN	1.1	1.1	1.0	1.1
Others	6.3	4.1	6.7	—
TOTAL	100.0	100.0	100.0	—

When other polyanhydrides, i.e., DA and TA, are used with a hydrocarbon mixture such as the feed in the aforementioned Table, selective complexing will occur. Other C_{13} bicyclic aromatic hydrocarbon mixtures containing TMN will fractionate in an analogous manner using one of the following: PMDA, DA and TA.

The invention claimed is:

1. A method of fractionating a mixture of C_{13} bicyclic aromatic hydrocarbons containing trimethylnaphthalenes comprising:

a. contacting said mixture in liquid phase with a solid complexing polyanhydride selected from the following group: the dianhydride of 1,2,4,5-benzenetetracarboxylic acid, the dianhydride of 1,2,3,4-benzenetetracarboxylic acid and the trianhydride of 1,2,3,4,5,6-benzenehexacarboxylic acid, at a temperature below the melting point of the polyanhydride to complex preferentially with at least one of the trimethylnaphthalenes and form a solid complex containing less than the total amount of trimethylnaphthalenes in said mixture;

b. separating the solid complex from the resulting admixture;

c. and decomposing the solid complex to recover the resulting complexate having a proportion of trimethylnaphthalenes different from that in the starting hydrocarbon mixture.

2. A method according to claim 1 wherein the mixture of hydrocarbons is contacted with the polyanhydride at 50° to 100° F., after which the temperature of said resulting admixture is increased to within the range of 100° to 300° F., after which the solid complex is separated at 0° to 100° F.

3. A method according to claim 1 wherein the temperature at which the polyanhydride is contacted with said mixture is in the range of 100° to 300° F. and the solid complex is separated at 0° to 100° F.

4. A method according to claim 1 wherein the mixture of hydrocarbons consists essentially of a mixture of C_{13} alkylnaphthalenes containing trimethylnaphthalenes.

5. A method according to claim 1 wherein the mixture of hydrocarbons consists essentially of a mixture of trimethylnaphthalenes.

6. A method according to claim 1 wherein the amount of polyanhydride contacting the mixture is in the range from 0.01 to 3.0 moles per mole of trimethylnaphthalenes.

7. A method according to claim 1 wherein the mixture of said hydrocarbons consists essentially of a mixture of C_{13} alkylnaphthalenes containing trimethylnaphthalenes, the contacting polyanhydride is selected from the following group: dianhydride of 1,2,4,5-benzenetetracarboxylic acid and dianhydride of 1,2,3,4-benzenetetracarboxylic acid, the amount of dianhydride contacting the C_{13} alkylnaphthalenes is in the range from 0.1 to 1.5 moles per mole of trimethylnaphthalenes, the temperature at which the dianhydride is contacted with said alkylnaphthalenes is in the range of 100° to 300° F. and the solid complex is separated at 0° to 100° F.

8. A method of fractionating a mixture of trimethylnaphthalenes comprising:

a. contacting said mixture in liquid phase with a solid complexing polyanhydride selected from the following group: the dianhydride of 1,2,4,5,-benzenetetracarboxylic acid, the dianhydride of 1,2,3,4-benzenetetracarboxylic acid and the trianhydride of 1,2,3,4,5,6-benzenehexacarboxylic acid, at a temperature below the melting point of the polyanhydride to complex preferentially with at least one of the trimethylnaphthalenes and form a solid complex containing less than the total amount of trimethylnaphthalenes in said mixture;

b. separating the solid complex from the resulting admixture;

c. and decomposing the solid complex to recover the resulting complexate having a proportion of trimethylnaphthalenes different from that in the starting trimethylnaphthalene mixture.

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