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TREATMENT OF HYDROCARBONS

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This invention relates more particularly to a process for the manufacture of derivatives of aromatic hydrocarbons, particularly those formed by replacing ring hydrogen atoms with aliphatic hydrocarbon radicals.

The value of the various aromatic hydrocarbons as bases for the manufacture of chemical derivatives is well known. They serve as a starting point for the manufacture of a large number of dyestuffs, explosives, disinfectants, solvents, fuels, etc. By successively replacing the ring hydrogen atoms with methyl and other aliphatic residues, the homologs of benzol are produced.

In the production of aromatics by the destructive distillation of coal or other hydrocarbon mixtures such as those constituting the various fractions of petroleum, there are normally produced in the mono-nuclear series preponderating yields of benzol and its closely related homologs such as toluol and the xylols, these latter being the mono and di methyl derivatives of benzol respectively. There is practically no production of homologs containing aliphatic residues of higher molecular weight such as, for example, ethyl benzol, propyl benzol, etc. While the present process may be employed to produce any alkyl derivative of benzol including the methyl derivatives, it is particularly applicable to the production of the higher alkyl derivatives.

To briefly review the alkylation art with the object of distinguishing it from the process of the present invention, it may be stated that the oldest method consists in using olefins to treat aromatics in the presence of sulfuric acid. In these reactions there is evidence to show that there is first an ester formation between the olefins and the acid and sulfonic acid formation in the case of the aromatics, these primarily formed materials then interacting to form alkyl derivatives and at least partially regenerating the sulfuric acid according to the following general equations.

$$(1)\quad \underset{\text{Ethylene}}{C_2H_4}+H_2SO_4=\underset{\text{Ethyl sulfuric acid}}{C_2H_5HSO_4}$$

$$(2)\quad \underset{\text{Benzol}}{C_6H_6}+H_2SO_4=\underset{\text{Benzol sulfonic acid}}{C_6H_5SO_3H}+H_2O$$

$$(3)\quad C_6H_5SO_3H+C_2H_5HSO_4+H_2O=\underset{\text{Ethyl benzol}}{C_6H_5-C_2H_5}+2H_2SO_4$$

By substituting other olefins or mixtures of olefins for the ethylene shown in the equation it is possible to more or less efficiently produce a large number of alkylated derivatives of benzol. The efficiency of reactions of the above character is limited to a considerable extent by the tendency of the sulfuric acid to polymerize the olefins rather than add them to the aromatic nucleus and also that it has a definite tendency to oxidize all the hydrocarbons involved and produce undesirable by-products, these being sometimes of a heavy tarry character.

It is also known in the art to employ metal halides such as for example, aluminum chloride and its more or less equivalent materials to effect reactions of the above general character. These types of catalysts tend to foster polymerizing reactions among olefins to a great extent and also tend to form sludges consisting of compounds formed by the direct addition of olefins and the chlorides which are difficult to decompose for the regeneration of the catalyst. There is also a considerable tendency to carbonization if elevated temperatures are employed and the reactions are difficult to control in the sense that if, for example, a mono alkyl derivative is desired there are concurrently formed di and tri and even higher derivatives corresponding to a certain equilibrium.

In one specific embodiment the present invention comprises the manufacture of alkyl derivatives of aromatic hydrocarbons by treatment with paraffin hydrocarbons in the presence of phosphoric acid at elevated temperatures of from about 700° F. to about 900° F.

The alkyl derivatives thus formed may be used for increasing the antiknock value of gasoline motor fuels by blending, as well as for the preparation of pure alkylated products.

In the operation of the process, an aromatic and a paraffin are heated in the presence of approximately 10% by weight of a phosphoric acid, orthophosphoric acid (H_3PO_4) of about 90% concentration being generally utilizable. When the paraffin employed is liquid such as, for example, hexane, the mixture of hydrocarbons in the proportions necessary for producing best yields of the desired alkylated product is maintained in agitation with the acid in exteriorly heated rotating bombs or the hydrocarbons and acid may be pumped through tubular heating elements to allow continuous operation, reliance being placed upon the turbulence produced in the heating coil to assure effective contact.

If an aromatic is to be alkylated with a normally gaseous paraffin such as, for example, butane or lower, the gas may be pumped under pressure into a bomb containing the aromatic and the phosphoric acid, whereupon the bomb is heated and shaken until the alkylation reactions are completed.

As before in the case of liquid paraffins, reactions may be brought about between normally gaseous paraffins and liquid aromatics in continuous tubular heating elements by injecting the gaseous paraffin into the continuously flowing stream of aromatic hydrocarbon and phosphoric acid. This and other methods of contacting, such as, for example, atomizing a liquid aromatic and phosphoric acid in proper proportions into an atmosphere of the gaseous paraffin hydrocarbon, will suggest themselves to those familiar with these types of industrial operations. Arrangements may be made to pass mixtures of the vapors of aromatics and paraffins upwardly counterflow to descending streams of liquid phosphoric acid in towers filled with relatively inert fragmentary material such as crushed silica in order to insure effective contact.

The temperature and pressure conditions under which alkylation reactions occur will vary with each combination of aromatic and paraffin which may be employed and with the amount of phosphoric acid used. In the case of lower boiling normally liquid paraffins typified by hexane, when these are used to alkylate the lower boiling aromatics such as benzol, toluol and the xylols, temperatures in the neighborhood of 800 to 900° F. are commonly suitable. In the case of batch operation in pressure vessels the pressure may rise as high as 100 atmospheres at the operating temperature, and owing to the formation of some fixed gases as a result of side reactions there will ordinarily be some residual gas pressure when the bomb is cooled to atmospheric temperature.

The type of reactions which occur in the present process is sharply differentiated from those which employ olefins to alkylate aromatics and produce their higher homologs. In the present instance the paraffins undergo decomposition in the presence of phosphoric acid to form active radicals which then unite with the aromatics to form the desired alkyl derivatives. In the absence of other groups of hydrocarbons the simpler aromatics are unaffected by phosphoric acid under the preferred conditions of operation. In a sense the reactions involved may be looked upon as coming under the definition of condensation reactions since there is elimination of some hydrogen and the formation of lower boiling paraffins, as will be shown in later examples.

The process thus utilizes normally unreactive paraffins to combine with and alkylate aromatics. Its practical utility appears in that various paraffins and mixtures of paraffins may be employed instead of the more reactive olefins. For example, instead of utilizing the olefins in cracked hydrocarbon gas mixtures for alkylation of aromatics, (the olefins normally constituting only minor percentages of the total gas mixture) naturally occurring paraffin gases may be employed or straight run gasoline fractions containing little or no olefins. In the case of cracked gases the olefins may be removed by absorption in acids or in more generally known alkylation reactions and the residual gases then employed to alkylate further amounts of aromatics in the presence of the phosphoric acid catalyst by methods already indicated.

The mechanism of the reactions leading to the formation of alkylated aromatics according to the present process is apparently similar to that obtaining when aromatics are alkylated with olefins after the paraffins have been partially dehydrogenated and the residues rendered reactive in the presence of the phosphoric acid. To illustrate the probable reactions which take place in the case of a single paraffin and a single aromatic, the following equations are given for comparison with those previously shown in connection with the alkylation of aromatics with olefins in the presence of sulfuric acid.

$$(1)\quad \underset{\text{Ethane}}{C_2H_6}+\text{heat}\left(\begin{matrix}H_3PO_4\\ \text{Catalyst}\end{matrix}\right)\rightleftarrows \underset{\text{Ethylene}}{C_2H_4}+H_2$$

$$(2)\quad C_2H_4+H_3PO_4\rightleftarrows \underset{\text{Mono-ethyl phosphate}}{C_2H_5H_2PO_4}$$

$$(3)\quad \underset{\text{Toluene}}{C_7H_8}+H_3PO_4\rightleftarrows C_7H_7H_2PO_3+H_2O$$

$$(4)\quad C_7H_7H_2PO_3+H_2O+C_2H_5H_2PO_4\rightleftarrows \underset{\text{Methyl ethyl benzol}}{C_7H_7C_2H_5}+2H_3PO_4$$

The above reactions are suggestive of the steps which occur and which result in the formation of the alkylated products though it is not intended to infer that they offer a complete explanation of the observed facts.

The following example will serve to illustrate the nature of the reactions involved and the results obtainable by the use of the process although the scope of the invention is not limited by the specific data given.

Benzene and hexane were heated in a rotary pressure vessel at 832° F. (450° C.) for 20 hours in the presence of 89% phosphoric acid. Three runs were made. The results are tabulated as follows:

Run No.	Benzene chgd.	Hexane chgd.	Phosphoric acid	Hrs. on run	Maximum press. @ 450° C.	Final press. @ 25° C.	Liquid recovery
	Pts. by wt.	*Pts. by wt.*	*Pts. by wt.*		*(Atm.)*	*(Atm.)*	*Pts. by wt.*
1	51	50.0	10.3	20	125	17	79
2	50	51.5	10.5	20	103	8.5	79
3	50	53.0	10.5	20	128	17.5	81

The liquid composite was submitted to a fractional distillation.

	Boiling point		Percent	Bromine number	I. R. @ 30° C.
	°C.	°F.			
1	57–67	135–152	12	8	1.4204
2	67–71	152–160	18.0	7	1.4242
3	71–81	160–178	20.5	3	1.4394
4	81–83	178–181	9.0	2	1.4578
5	83–91	181–196	8.0	2	1.4650
6	91–101	196–214	6.0	3	1.4793
7	101–115	214–239	4.0	3	1.4850
8	115–150	239–302	3.5	5	1.4843
9	150–160	302–320	4.5	4	1.4862
10	160–170	320–338	6.0	4	1.4881
11	170–190	338–374	3.5	4	1.4920
12	190–220	374–428	2.0	7	1.4998
13	220–245	428–473	1.5	9	1.5249
14	Bottoms.	----------	1.5	----------	----------

Fraction 10 was treated with a 15% fuming sulfuric acid; everything was soluble in the acid which indicates that only alkylaromatic hydrocarbons are present; the olefinic hydrocarbons are absent as the bromine number of the fraction is only 4. This contained 10% of saturated hydrocarbons, the remainder being aromatics.

The per cent of aromatic hydrocarbons boiling above 239° F. (115° C.) is 42 parts by weight, which means that 28% by weight of higher aromatics was formed, based on the weight of benzene charged; some of the benzene being recovered. This raises the amount of alkylated benzene to above 35%.

It will be seen that practically all of the materials formed boil within the range of commercial gasoline specifications. Tests showed that the composite liquid was of unusually high anti-knock value of the order of that shown by iso-octane used as a standard of reference in rating motor fuels by the engine test.

The novel and useful character of the invention is evident from the preceding specification and single instance of numerical data introduced but neither is to be considered as imposing undue limitations upon its generally broad scope.

We claim as our invention:

1. A process for the alkylation of aromatic hydrocarbons to produce more valuable products therefrom, which comprises subjecting a mixture comprising said aromatic hydrocarbons and paraffinic hydrocarbons to the action of an acid of phosphorus at an alkylating temperature between approximately 700° F. and 900° F. whereby the paraffinic hydrocarbons undergo decomposition, the products of which decomposition combine with said aromatic hydrocarbon to alkylate same, and recovering the alkyl derivatives thus formed.

2. A process for the alkylation of aromatic hydrocarbons to produce more valuable products therefrom, which comprises subjecting a mixture comprising said aromatic hydrocarbons and paraffinic hydrocarbons to the action of a phosphoric acid catalyst at an alkylating temperature between approximately 700° F. and 900° F. whereby the paraffinic hydrocarbons undergo decomposition, the products of which decomposition combine with said aromatic hydrocarbon to alkylate same, and recovering the alkyl derivatives thus formed.

3. A process such as claimed in claim 1 characterized in that the process is carried out at a pressure between atmospheric and approximately 100 atmospheres.

4. A process such as claimed in claim 1 wherein the paraffinic hydrocarbons are gaseous.

5. A process for the alkylation of aromatic hydrocarbons which comprises subjecting the aromatic in the presence of a paraffinic hydrocarbon to the action of a phosphoric acid at a temperature between approximately 700° F. and 900° F. and under superatmospheric pressure, and recovering the alkyl derivative thus formed.

6. A process for the alkylation of aromatic hydrocarbons of the benzene series which comprises subjecting the aromatic in the presence of a paraffinic hydrocarbon to the action of a phosphoric acid at a temperature between approximately 700° F. and 900° F.

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