

UNITED STATES PATENT OFFICE

2,473,990

MANUFACTURE OF HALOGENATED
AROMATIC COMPOUNDSJohn L. Darragh, Berkeley, Calif., assignor to
California Research Corporation, San Fran-
cisco, Calif., a corporation of DelawareNo Drawing. Application October 22, 1945,
Serial No. 623,870

18 Claims. (Cl. 260—650)

1

This invention relates to a novel method of halogenating aromatic compounds and has particular application to the chlorination of a benzene nucleus.

Heretofore, aromatic hydrocarbons have been chlorinated by passing the chlorine and hydrocarbon over an iron catalyst. In the chlorination of benzene this has given a mixture of mono, di, and polychlorobenzene compounds. For example, in the prior art if sufficient chlorine is used to theoretically chlorinate 88 per cent of the benzene to monochlorobenzene, the actual product will consist of 32 per cent unreacted benzene, 52 per cent monochlorobenzene, and 16 per cent of polychlorinated products.

Since the demand for dichlorobenzene is limited, it has been the practice to use less than the theoretical amount of chlorine to favor the production of monochlorobenzene. This requires that the unreacted benzene be returned to the reaction chamber. Even under such precautions, large amounts of dichlorobenzene are formed.

Because of the limited demand for dichlorobenzene, a process is needed which has flexibility so that it can be made to favor the production of either monochlorobenzene or dichlorobenzene in accordance with the market demand. A process which would give better yields of monochlorobenzene and a higher benzene and chlorine utilization than can be obtained in the prior art would not only make it possible to lower the cost of monochlorobenzene but would also make it practical to lower the cost of all the chemicals derived from monochlorobenzene.

Numerous catalysts such as metallic iron, halides of iron, aluminum chloride, copper chloride, antimony trichloride, cerium chloride, stannic chloride, zinc chloride, phosphorus pentachloride, molybdenum chloride, bromine, iodine, sulfur dioxide, sulfuric acid and porous carbon have been employed for the chlorination of benzene. However, with each process too much dichlorobenzene is produced and the yields of monochlorobenzene are correspondingly low.

By practicing the present invention, the disadvantages of the prior processes are largely overcome.

It is an object of this invention to chlorinate aromatic compounds in a manner which will produce low yields of the dichlorinated derivative.

A further object of this invention is to afford a method whereby the aromatic compound can be chlorinated in a manner to give high yields of the monochloro derivative.

An additional object resides in providing flexi-

2

bility in the amount of dichloro derivative formed with high chlorine utilization.

A further object is to chlorinate a benzene nucleus using the theoretical amount of chlorine to give the monochlorinated derivative in good yields.

The invention contemplates a method whereby the amount of unchlorinated aromatic hydrocarbon is substantially decreased over that of the prior art.

It has been found that, with certain newly discovered chlorination catalysts, the distribution between monochlorination and polychlorination of a benzene nucleus can be shifted to the production of a mono-chloro product substantially to the exclusion of polychloro compounds. Further, it has been discovered that such a shift of distribution can be effected without the necessity of a large excess of the aromatic hydrocarbon being chlorinated.

Briefly stated, the invention comprises liquid phase chlorination of an aromatic compound of the benzene series in the presence of a catalytically active metal silicate containing lattice water and interlattice adsorbed water. (The terms "lattice water" and "interlattice water" are used here as defined in the U. S. Geological Survey Bulletin 928-C, pages 159-166 (1943). Such silicates are substantially free of hydrous water.) As hereinafter disclosed, the catalyst selected preferably is one capable of causing formation of the monochloro derivative substantially to the exclusion of polychloro compounds. However, the invention in its broader aspects embraces a catalytically active metal silicate containing lattice water and interlattice adsorbed water which increases utilization of chlorine in a nuclear chlorination reaction, with or without exclusion of polychloro compound formation.

More particularly, the invention involves liquid phase chlorination of the benzene nucleus of an aromatic compound in the presence of a catalytically active complex polyvalent metal silicate containing lattice water and interlattice adsorbed water, such as magnesium iron aluminum silicate, as a chlorination catalyst. A magnesium iron aluminum silicate catalyst containing lattice water and interlattice adsorbed water but substantially free of hydrous water and capable of causing nuclear monochlorination substantially to the exclusion of nuclear polychlorination is preferred.

Still more particularly the invention involves liquid phase chlorination of the benzene nucleus of an aromatic compound in the presence of an activated bentonite clay catalyst.

Examples of suitable chlorination catalysts embraced by the present invention comprise catalytically active silicates, containing lattice water and interlattice water, of the polyvalent metal complex silicate type, such as activated natural montmorillonite clays and synthetic aluminum silicates. Such silicate catalysts, embraced by this invention, are conveniently available under the trade names of Filtrol X-197, Filtrol X-202, Palm, Houdry, and Universal Oil Type B. The detailed analyses of such silicates are shown in Table I.

with chlorine in a ratio up to one part by weight of benzene to 1½ parts by weight of chlorine. Suitable temperatures of chlorination are 45° F. to 212° F.; from 50° F. to 120° F. is a preferred temperature range where the catalyst is an activated montmorillonite type clay, such as Filtrol X-197, Filtrol X-202, or Palm. The chlorination is effected by treatment of the aromatic compound in liquid phase with chlorine in the presence of one per cent of the catalyst. (Weight percentage based on the aromatic compound.) However, a smaller or larger amount of catalyst

TABLE I
Composition of clay catalysts
[Moisture free basis]

Constituent	Natural Clays			Synthetic	
	Filtrol X-197	Filtrol X-202	Palm	Houdry	Universal Oil Products Type B
SiO ₂	64.98	63.18	72.40	90-92	94
Al ₂ O ₃	14.57	15.07	16.15	10-8	2
ZrO ₂					4
Fe ₂ O ₃	2.25	2.20	2.20		
MgO.....	4.62	4.40	4.61		
CaO.....	1.84	0.30	1.16		
TiO ₂	0.89	0.57	trace		
H ₂ SO ₄	8.50	13.15	9.13		
Na ₂ O.....	trace	trace	1.68		
K ₂ O.....	trace	trace	1.41		
PbO.....	trace	trace	0.15		
MnO.....	0.04	0.02	0.02		
Cl.....	0.01	0.02	Nil		
CO ₂	0.05	0.05	Nil		
Total.....	97.75	98.96	99.91		
Moisture (loss in weight at 212° F. for 16 hours).....	7.00	6.40	7.80		
Loss on Ignition at 1300° F.....	18.10	18.30	17.80		

These natural clays are mined from the earth in many localities and treated with sulfuric acid to activate them. They are then employed by several industries as adsorbents. The Filtrol clays have been developed by the Filtrol Company of Los Angeles from the deposits near Chito, Arizona. The Palm clays are mined near Otay, California, and sold by the Standard Oil Company of California. The Houdry Synthetic and Universal Oil Type B silicates are available at the usual well known sources.

Clay catalysts which have been further activated by controlled dehydration are preferred. Such an activated catalyst may be prepared by removal of relatively free water of hydration normally present in commercial clays and retaining lattice water and interlattice water in the catalyst structure. A suitable process for removing only relatively free water of hydration comprises heating the clay catalyst at about 212° F. for six to sixteen hours or until the moisture content is reduced to a value in the range of from approximately 4% to 12% by weight depending on the moisture content of the clay before drying. Other methods of activation, such as treatment under vacuum at lower temperatures or a reduction of the moisture content by suitable dehydrating chemicals, are not precluded—for example, calcium chloride, or the like. In the activation of the clay catalysts, it is important to avoid heating to excessively high temperatures, such as would produce incipient fusion, calcination, removal of lattice water and interlattice water, or otherwise cause collapse of the porous structure of the catalyst.

In practicing the invention, nuclear chlorination of an aromatic compound of the benzene series may be effected, for example, by treatment

may be used. The catalyst may be used in the pellet form, but the granular form is preferred. It is preferred that the reaction be carried out in the absence of direct sunlight to prevent chlorination in the side chain.

The preparation of suitable catalysts is illustrated as follows:

A convenient quantity of the clay is taken from the shipping bag, placed in a casserole and heated in a drying oven at 212° F. for sixteen hours. This reduces the moisture content by about six per cent. It is then placed in a desiccator over a drying agent until needed. The synthetic aluminum silicates are prepared by the well known procedure of heating silica with the metallic oxide or carbonate.

The following are given as specific examples for carrying out the chlorination process according to the present invention.

The chlorinator consists of a glass tube eighteen inches long and one and one-half inches in diameter with a sintered glass plate in the bottom. To the bottom of the tube is connected a glass tube of 5 mm. bore for introducing the chlorine below the glass plate. The reaction tube is provided with a water jacket for cooling or heating the reaction mixture. The upper end of the reaction tube is fitted with an efficient reflux condenser and a caustic soda scrubber for adsorption of the by-product hydrochloric acid.

The reaction chamber is charged with the aromatic compound, the clay catalyst, and the chlorine. The temperature is quickly adjusted to the range of 60° F. to 70° F. and the reaction is allowed to proceed for four hours. At the end of this time, the ratio of the aromatic compound to catalysts and to the chlorine used together with the results obtained are shown in Table II.

TABLE II

Chlorination of aromatic compounds in the presence of activated clay and ferric chloride catalysts

Catalyst used	Chlorine used, percent of theory based on complete conversion to mono-chloro derivative	Catalyst used based on compound chlorinated, percent	Benzene, percent	Monochloro-benzene, percent	Dichloro-derivative, percent	Loss and resin, percent
BENZENE						
Filtrol X-202.....	75	1	26	69	3	2
Filtrol X-197.....	75	1	24	74	2	2
Palm.....	75	1	26	70	2	2
FeCl ₃	75	1	36	49	13	2
Filtrol X-202.....	85	1	17	77	4	2
Filtrol X-197.....	85	1	20	73	5	2
Palm.....	85	1	18	76	4	2
FeCl ₃	85	1	25	60	13	2
Filtrol X-202.....	100	1	8	81	9	2
Filtrol X-197.....	100	1	10	75	13	2
Palm.....	100	1	16	65	17	2
FeCl ₃	100	1	18	61	19	2
TOLUENE						
Filtrol X-202.....	92	1	8	90	12	2
FeCl ₃	95	1	16	70	12	2
XYLENE						
Filtrol X-202.....	80	1	28	60	10	2
FeCl ₃	80	1	34	48	16	2

An examination of the products produced with the new and prior art catalyst reveals that the new catalyst gives phenomenally low yields of the dichloroderivative. Furthermore, the new

the clay catalyst for chlorinating benzene together with the chlorination of benzene in the presence of ferric chloride are shown in Table IV.

TABLE IV

Chlorination of benzene for four hours with Filtrol X-202 catalyst containing different amounts of moisture and compared with chlorination with ferric chloride

Catalyst		Chlorine Present percent of theory based on monochloro-derivative	Reaction Temperature	Products Obtained				
Pretreatment	Moisture			Benzene	Chloro-benzene	Polychloro benzenes	Loss and Resin	Cl not reacting
	Percent		° F.	Percent	Percent	Percent	Percent	Percent
None.....	18	97	80	13	75	9	2	4.5
Dried at 212° F. for 18 hours.....	12	90	80	15	78	5	2	0.7
Calcined at 1,300° F. for 3 hrs. and dried over P ₂ O ₅	0.0	33	60-70	Benzene did not take appreciable chlorine				
FeCl ₃ —No pretreatment.....		85	60-70	25	60	12	2	
Do.....		95	60-70	22	58	18	2	

catalyst not only gives high yields of the monochloroderivative but chlorinates more of the original aromatic compound.

The data in Table III below show that synthetic aluminum silicates catalyze the reaction between benzene and chlorine and that 95% to 97% of the chlorine required to give the theoretical monoderivative reacts.

TABLE III

Aluminum silicates as catalysts for reacting chlorine with benzene

Catalyst used	Compound Chlorinated	Total Chlorine Added percent of theory to give monochlorobenzene	Percent of Chlorine Which Reacted
Houdry Synthetic.....	Benzene.....	100	95
Universal Oil Type B.....	do.....	100	97

The influence of moisture on the activity of

The data show that the dried catalyst inhibits formation of the dichlorobenzene and shifts the reaction to the formation of mono-chlorobenzene. The dried catalyst also promotes the highest utilization of benzene and chlorine. The data further bring out the fact that even the undried catalyst (not activated) promotes higher yields of mono-chlorobenzene and lower yields of dichlorobenzene than the prior art catalyst ferric chloride.

Although the invention has been illustrated by numerous specific examples, it will be apparent to those skilled in the art that various modifications may be made in carrying out the process while retaining the benefit of the discoveries herein disclosed. For instance, the specific examples relate to the chlorination of benzene, toluene, and xylene, but the invention embraces the nuclear chlorination of other aromatic compounds of the benzene series, such as nitro benzene, hydroxy benzene, benzene sulfonic acid, aniline, benzaldehyde, benzoic acid, phenylenediamine, nitro

7

aniline, hydroquinone, quinone and naphthalene. Furthermore, the invention embraces chlorination in the presence of the catalysts herein disclosed at temperatures other than those given for illustrative purposes and with other proportion of reacting ingredients.

What I claim is:

1. The method of chlorinating the benzene nucleus of an aromatic compound of the benzene series that comprises causing said aromatic compound to react in the liquid phase with chlorine in the presence of a magnesium-iron-alumino-silicate catalyst.

2. A process which comprises intimately contacting liquid benzene and gaseous chlorine in the presence of an activated montmorillonite clay at a temperature of from 45° F. to 212° F.

3. A process which comprises reacting an aromatic compound having a replaceable nuclear hydrogen atom in liquid phase at a temperature of from about 45° F. to about 212° F. with chlorine under nuclear chlorinating conditions and separating a nuclear chlorinated aromatic product, said chlorination reaction being catalyzed with a polyvalent metal silicate containing lattice water and interlattice water and substantially free from hydrous water only.

4. A process as defined in claim 3, in which said polyvalent metal silicate is an activated magnesium-iron-alumino-silicate catalyst.

5. A process as defined in claim 3, in which said polyvalent metal silicate is an activated montmorillonite clay catalyst.

6. A process as defined in claim 3, in which said polyvalent metal silicate is an active bentonite clay catalyst.

7. A process which comprises reacting an aromatic compound having a replaceable nuclear hydrogen atom in liquid phase at a temperature of from about 45° F. to about 212° F. with chlorine under nuclear chlorinating conditions and separating a nuclear chlorinated aromatic product, said chlorination reaction being catalyzed with a polyvalent metal silicate containing lattice water and interlattice water, activated by removal of hydrous water only.

8. A method as defined in claim 7, in which said polyvalent metal silicate is an activated magnesium-iron-alumino-silicate catalyst.

9. A method as defined in claim 7, in which said polyvalent metal silicate is an activated montmorillonite clay catalyst.

8

10. A method as defined in claim 7, in which said polyvalent metal silicate is an active bentonite clay catalyst.

11. A process which comprises chlorinating a hydrocarbon of the benzene series by reacting said hydrocarbon with chlorine under nuclear chlorinating conditions to form hydrogen chloride and chlorinated hydrocarbon, said chlorination being catalyzed at a temperature below about 212° F. with a polyvalent metal silicate, activated by removal of hydrous water only, and recovering the chlorinated hydrocarbon.

12. A process as defined in claim 11, in which said polyvalent metal silicate is an activated magnesium-iron-alumino-silicate catalyst.

13. A process as defined in claim 11, in which said polyvalent metal silicate is an activated montmorillonite clay catalyst.

14. A process as defined in claim 11, in which said polyvalent metal silicate is an active bentonite clay catalyst.

15. A process which comprises chlorinating benzene by reacting from about 25 to 125 parts of chlorine per hundred parts of benzene to form hydrogen chloride and chlorinated hydrocarbon, said reaction being catalyzed at a temperature of from 50° F. to 125° F. with a polyvalent metal silicate, activated by removal of hydrous water and containing lattice water and interlattice water.

16. A process as defined in claim 15, in which said polyvalent metal silicate is an activated magnesium-iron-alumino-silicate catalyst.

17. A process as defined in claim 15, in which said polyvalent metal silicate is an activated montmorillonite clay catalyst.

18. A process as defined in claim 15, in which said polyvalent metal silicate is an active bentonite clay catalyst.

JOHN L. DARRAGH.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,935,648	Mares	Nov. 21, 1933

FOREIGN PATENTS

Number	Country	Date
715,009	France	Nov. 24, 1931