

A STUDY OF THE EXCHANGE OF AROMATIC HYDROGEN
ATOMS UNDER FRIEDEL-CRAFTS CONDITIONS
USING TRITIUM TRACER TECHNIQUES

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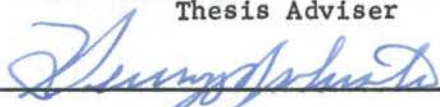
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INTRODUCTION

The general purpose of this work was to obtain more information about the mechanism of the ethylation of ethylbenzene with ethylene in the presence of aluminum bromide. More specifically the aim was to determine the source of the third hydrogen atom on the beta carbon of the ethyl group which was introduced.

If one could effect a Friedel-Crafts ethylation in the presence of ethylbenzene labeled with tritium in the para position, determine the activities of the diethylbenzenes produced and find the proportion of p-diethylbenzene among its isomers, one could calculate the specific activity of the p-diethylbenzene produced. Comparison of the specific activity of the p-diethylbenzene with the specific activity of the original ethylbenzene labeled with tritium in the para position might help to elucidate the mechanism of the Friedel-Crafts reaction.

During the necessary control experiments it was found that the above method is impractical since the tritium exchanges with hydrogen atoms under Friedel-Crafts conditions. Emphasis was then placed on determining the rate of these exchanges using various acceptors and various labeled molecules.

The systems studied were p-t-ethylbenzene as the donor with benzene as the acceptor, t-benzene as the donor with chlorobenzene as the acceptor, and tritium chloride as the donor with benzene as the acceptor. To obtain valid kinetic data on this reaction (24), it is essential

that a homogeneous system be used. Such a system has already been devised by Brown and co-workers (15); the solvent was 1,2,4-trichlorobenzene.

HISTORICAL

Kenner, Polanyi, and Szego (16) first observed the exchange of aromatic hydrogen atoms under Friedel-Crafts conditions. They studied the exchange between deuterium chloride and hydrogen atoms of the benzene ring. These workers reported only a slow exchange in the absence of a catalyst; however, in the presence of aluminum chloride, exchange occurred at a much more rapid rate. The conclusion was that the exchange involved the nucleophilic attack of the deuterium on the aromatic nucleus.

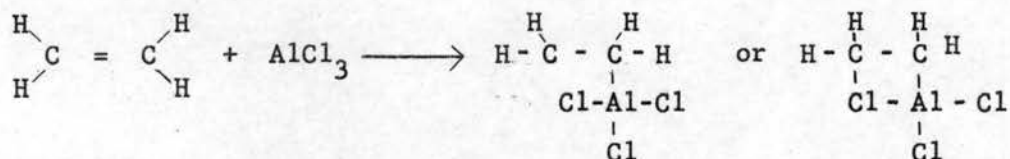
Comyns, Howard, and Willard failed to obtain an exchange between toluene and hydrogen chloride enriched with deuterium chloride in the absence of a catalyst; however, in the presence of high concentrations of stannic chloride exchange occurred at a measurable rate at 25° (8).

Olsson and Melander (21) studied the rate of exchange of ortho-, meta-, para- and alpha-tritium-labeled-toluene in concentrated sulfuric acid. They found that hydrogen atoms in the ortho and para positions exchange readily at elevated temperatures. The hydrogen atoms in the meta position exchanged slowly and essentially no exchange was observed with the hydrogen atoms in the alpha position even under drastic conditions.

The catalytic action of aluminum chloride and bromide was discovered by Charles Friedel and James Crafts (11, 12) in their well-known alkylation experiments. Balsohm (1) discovered that benzene could be alkylated

with ethylene in the presence of aluminum chloride, and believed as a result of his investigations that traces of hydrogen chloride were essential in order to supplement the catalytic activity of the Lewis acid, aluminum chloride.

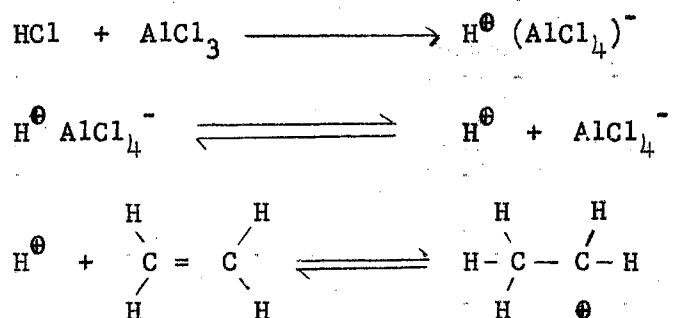
The reaction is of considerable industrial importance; however, published results of industrial research concerning the theoretical aspects of the reaction have been very sparse. Because of the lack of published research on the reaction, there are very few kinetic data available upon which to base a mechanism study. It has been necessary then in many cases to develop a mechanism study by means other than kinetic data. Hunter and Yohe (13) proposed a mechanism by which the Lewis acid is added directly to the ethylene:



These workers did not mention the necessity of the presence of hydrogen chloride as a catalyst. Price and Ciskowski (22) presented a similar mechanism using a boron trifluoride catalyst; however, few experimental data were presented to support the mechanism. Price and Meister (23) in 1939 presented stereochemical evidence of the isomerization of cis-stilbene to trans-stilbene in the presence of aluminum chloride or boron trifluoride.

Ipatieff, Pines, and Schmerling (25), with little evidence to support their conclusions, suggested a mechanism which proceeded through the addition of the hypothetical chloroaluminic acid, $\text{H}(\text{AlCl}_4)$, to the ethylene double bond. A mechanism such as this emphasizes the role of hydrogen chloride in the reaction.

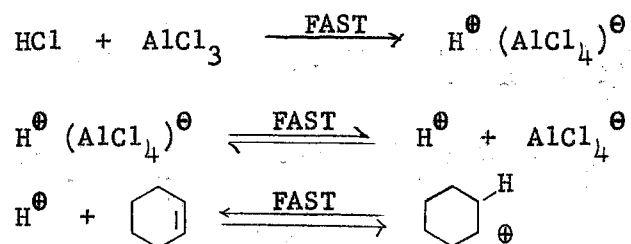
Thomas (24) supported the mechanism of Ipatieff, Pines, and Schmerling and went a bit further in postulating the formation of a carbonium ion in the course of the reaction:

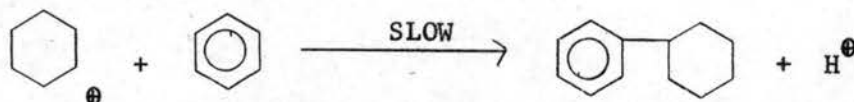


The last step in this mechanism is the electrophilic attack of the carbonium ion on the aromatic nucleus.

Ulich, Keutmann, and Gerhaas (25) presented kinetic studies in support of a reaction proceeding through the addition of hydrogen chloride to ethylene. The alkyl halide thus formed was subsequently ionized, forming a carbonium ion.

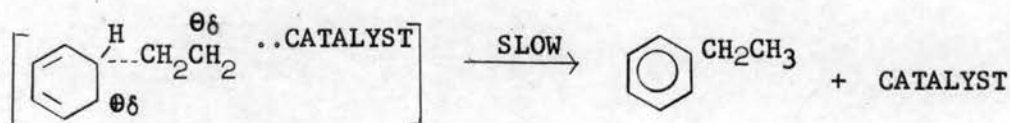
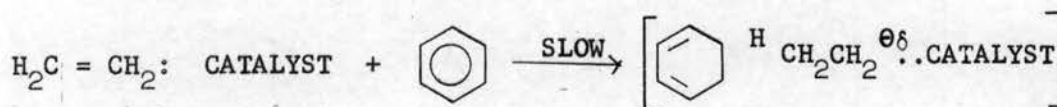
Lebedev (17, 18) obtained kinetic data for the alkylation of benzene with cyclohexene in the presence of various mixtures of aluminum chloride and hydrogen chloride. On finding the rate to be independent of the olefin concentration and dependent upon the hydrogen chloride concentration, Lebedev concluded that the reaction must involve the formation and subsequent ionization of chlorocyclohexane. Lebedev failed, however, to recognize other possible interpretations of his data such as the following:





Marks, Almond, and Reid (19) made an extensive kinetic study of the polyethylation of benzene with ethylene in the presence of aluminum chloride, but these investigators did not propose a reaction mechanism. Francis and Reid (10) made a comprehensive literature and experimental study of the monoethylation reaction, but again a mechanism was not proposed.

In the doctoral dissertation of C. F. Feldman (9) the following mechanism is proposed as a result of kinetic data using ethylene- C^{14} :



Brown and Brady (2) as a result of solubility studies of hydrogen chloride and hydrogen chloride-aluminum chloride mixtures in a variety of aromatic compounds concluded that Friedel-Crafts reactions using alkyl halides proceeded through the formation of both pi and sigma complexes. If one considers the aromatic nucleus as a planar ring structure with a high electron concentration immediately above and below the ring, one can picture a weak attraction between this electron cloud and an electrophilic group as involving a free movement around the electron cloud. This condition is termed a pi complex. As the attraction increases between the electron cloud and the electrophilic group, the

the electrophilic group is able to penetrate and distort the electron cloud with the formation of a covalent bond with a definite carbon atom of the benzene ring. This structure is termed a sigma complex. Brown and Brady concluded that the formation of the sigma complex is the rate-determining step in Friedel-Crafts alkylations using alkyl halides.

Jungk, Smoot, and Brown (15) found that homogeneous Friedel-Crafts reactions were possible when using alkyl halides if the alkylations were carried out in a sufficiently basic solvent such as 1,2,4-trichlorobenzene provided the aluminum bromide catalyst concentration did not exceed 0.3 molar.

EXPERIMENTAL

The use of high-vacuum techniques is essential in attacking a problem of this nature. The basic design of the vacuum frame hood and the high vacuum lines used may be found in the doctoral thesis of C. F. Feldman (9). All analyses were performed on an Applied Physics Corporation Model 30 Vibrating Reed Electrometer at the Radioisotopes and Radiations Laboratory. Samples were prepared for analysis by the method of Wilzbach, Kaplan, and Brown (26).

SEPARATION OF REACTION PRODUCTS

The first step in attacking the problem was to devise a method for separating the reaction products in a pure state in order to obtain their specific activity. Since all the organic components involved are reasonably volatile, fractional distillation was used throughout the study for separations. The following procedure was used in each case.

Thirty-ml. samples were withdrawn from the reaction solution at appropriate intervals and added to 75 ml. of distilled water. This mixture was immediately shaken vigorously to deactivate the aluminum bromide catalyst. The hydrocarbon layer was washed with more distilled water in a separatory funnel until the wash water gave no precipitate with silver nitrate. The samples were dried over Linde Molecular sieves No. 5A and calcium hydride. The samples were then distilled through a wire-packed fractionating column. The column was 10 in. high and 0.5 in.

Figure I

Apparatus For Purifying
1,2,4 - Trichlorobenzene

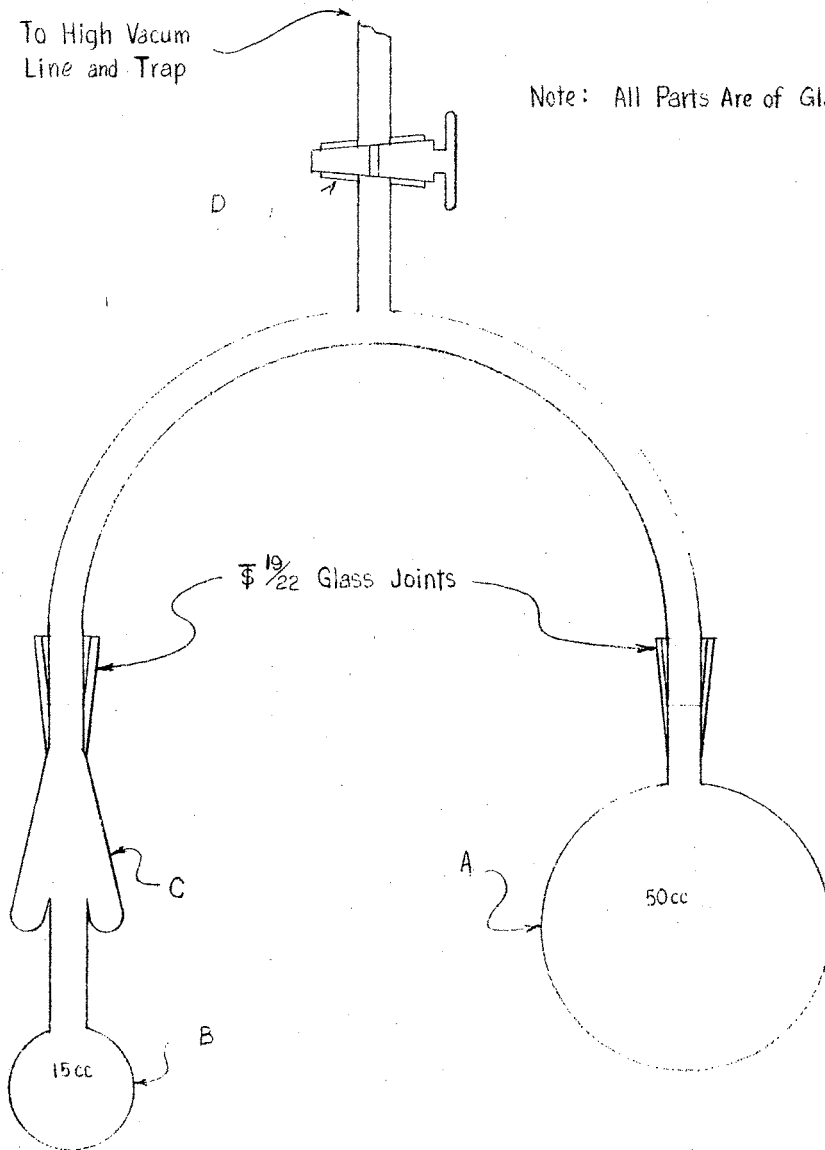
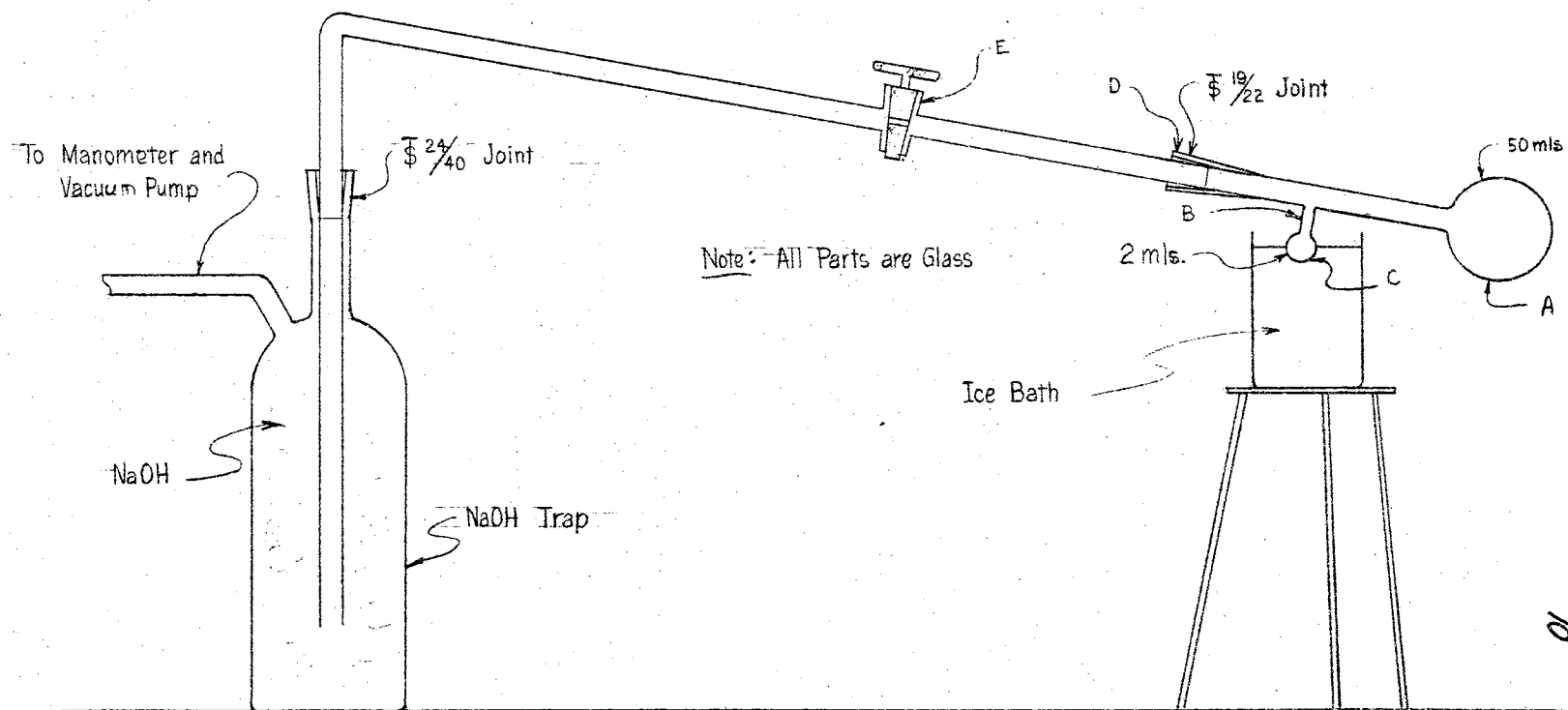


Figure II
*Apparatus For Preparation
Of Anhydrous Aluminum Bromide*



in diameter and possessed a hold-up of 0.5 ml. A center cut of each compound was taken in each case.

The 1,2,4-trichlorobenzene was further purified using the apparatus in Figure I. The center cut from the 1,2,4-trichlorobenzene distillation was placed in flask A and connected to the apparatus. A dry-ice-acetone bath was placed around A and the apparatus was evacuated to 1 micron pressure. The dry-ice-acetone bath was transferred to D and the 1,2,4-trichlorobenzene distilled over. The bath was then removed, ice was packed around C, and stopcock D was opened. When sufficient 1,2,4-trichlorobenzene had collected at C, the system was opened to the atmosphere and the distillate was removed from C with a bent pipette. No further purification was necessary on the remaining components.

PREPARATION OF REAGENTS

Preparation of Aluminum Bromide.

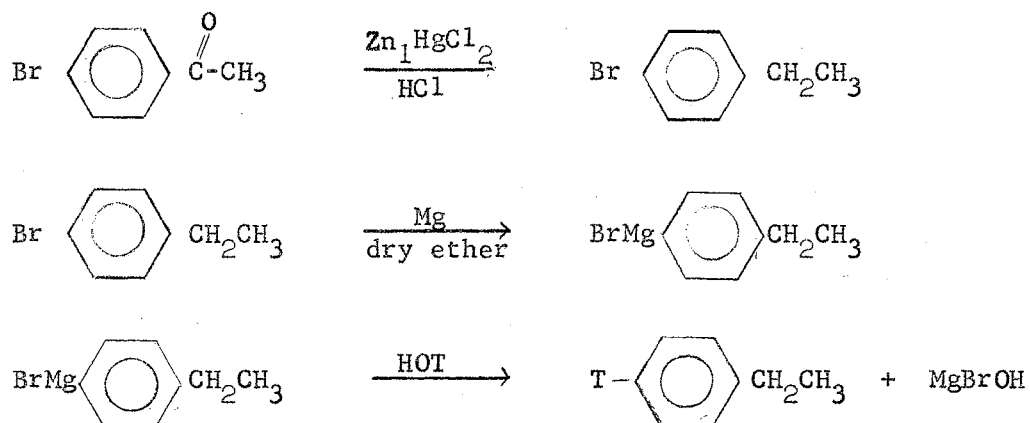
Aluminum bromide was prepared by a modification of the method employed by McAlister (20). The system was modified as shown in Figure II. Approximately 15 g. of technical grade aluminum bromide was placed at A and the entire section, previously tared to constant weight, was attached at D as shown. Stopcock E was opened and the system pumped down to 1 mm. of mercury pressure. A microburner adjusted to a small flame was placed directly under the aluminum bromide. Another microburner similarly adjusted was moved constantly between bulb C and the aluminum bromide. A creamy white solid collected at C as described by McAlister. When bulb C was approximately half-full, the burners were removed and bulb C was sealed off with a glass-blowing torch. The

system was then brought to atmospheric pressure. The remainder of section A along with the detached bulb was cleaned, dried, brought to constant weight, and the difference in weight recorded. Thus, weighed amounts of pure anhydrous aluminum bromide were prepared.

Care must be taken in this preparation that the section between bulb C and the larger tube is heated constantly during distillation since solid aluminum bromide may block the tube. If the flames are too hot, the collected aluminum bromide possesses a brownish-red color similar to that of free bromine. Despite these difficulties this appears to be a convenient method of preparing this reagent in a pure state.

Synthesis of p-t-Ethylbenzene.

This reagent was prepared by the Clemmenson reduction of p-bromoacetophenone followed by hydrolysis of the derived Grignard reagent with tritiated water according to the following equations:



In the Clemmenson reduction, a 1-liter round-bottom flask containing 10 g. of mercuric chloride, 100 g. of granular zinc, 100 ml. of water, 75 ml. of concentrated hydrochloric acid, and 30 g. of p-bromoacetophenone was fitted with a reflux condenser and placed in an electric

heating mantle. The mixture was refluxed for 20 hrs. with the addition of 75 ml. of concentrated hydrochloric acid every three hours. Upon completion of the reaction a dense oily green liquid was present; this material was separated and dried over anhydrous calcium sulfate and distilled in a 9-in. distilling column. Fifteen ml. of a green oily liquid were collected at 189-190°. The distillate was heated with a 10% solution of sodium bisulfite and dried over anhydrous calcium sulfate again.

Preparation of the Grignard reagent was effected in a 300-ml. three-neck round-bottom flask containing 3 g. of magnesium metal and 100 ml. of dry ether to which was fitted a drying tube, a reflux condenser and a 50-ml. dropping funnel which contained 15 ml. of *p*-bromoethylbenzene dissolved in 50 ml. of dry ether. As the *p*-bromoethylbenzene was added dropwise and the mixture stirred, a vigorous reaction occurred, yielding a brown precipitate and a green solution.

Hydrolysis of the Grignard reagent was effected in the same apparatus. To the dropping funnel was added 2 ml. of water-t (250 μ c./ml.) dissolved in 50 ml. of dry ether. Dropwise addition of this solution resulted in a vigorous reaction which partially dissolved the brown precipitate. Fifty ml. of 18% hydrochloric acid was then added in the same manner; the brown precipitate and the excess magnesium disappeared.

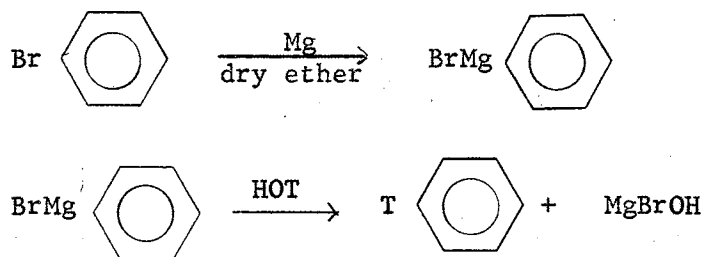
The ether layer was separated and dried over anhydrous calcium sulfate and distilled in the wire-packed column described previously. Following the ether fraction 5 ml. of a fraction boiling at 134-136° was collected having a refractive index of 1.4990. Ethylbenzene is reported to have a boiling point of 136.15° at 760 mm. mercury pressure and a refractive index of 1.4983 at 14.5° in the Handbook of Chemistry and Physics, forty-second edition. This material was stored over Linde

molecular sieves No. 5A and calcium hydride.

Assay of this liquid showed a specific radioactivity of $62.2\mu\text{c./mmole}$. Ninety ml. of Eastman reagent-grade ethylbenzene was then added. Assay of the diluted material gave a specific radioactivity of $5.57\mu\text{c./mmole}$.

Preparation of Benzene-t.

Preparation of benzene-t was effected by hydrolysis of the corresponding Grignard reagent with tritiated water as indicated below:



The Grignard reagent was prepared with the equipment described previously. Thus 12.8 g. of bromobenzene dissolved in 30 ml. of dry ether was added dropwise to the flask containing 3 g. of magnesium in 150 ml. of dry ether. A reddish-brown precipitate formed which was suspended due to the vigorous stirring.

Dropwise addition of 1 ml. ($250\mu\text{c./g.}$) of water-t dissolved in 50 ml. of dry ether, followed by 50 ml. of 18% hydrochloric acid effected the hydrolysis. Separation and drying of the ether layer followed by distillation yielded 6.4 ml. of benzene having a boiling point of $78-79^\circ$ and a refractive index of 1.4993. Benzene has a boiling point of 80.01° at 760 mm. mercury pressure and a refractive index of 1.5011 at 20° , as reported in the Handbook of Chemistry and Physics, forty-second edition. Assay of this material showed a specific activity of

79.03 μ c./mmole. Dilution with benzene obtained as described below yielded a liquid having an activity of 8.21 μ c./mmole. This reagent was stored over Linde molecular sieves No. 2A and calcium hydride until use.

Preparation of Benzene.

Eastman C. P.-grade benzene was washed with concentrated sulfuric acid until the red-colored thiophene was absent. The benzene was then washed five times with water, dried over Linde molecular sieves and calcium hydride and distilled through the wire-packed column previously described. The collected benzene boiled at 78-79° and showed a refractive index of 1.4990. This liquid was stored over the usual drying agent until use.

Preparation of Chlorobenzene.

Eastman reagent-grade chlorobenzene (refractive index, 1.5241) was used without further purification. Chlorobenzene is reported to have a refractive index of 1.5248 at 25° in the Handbook of Chemistry and Physics, forty-second edition. This material was stored over the usual drying agent until use.

Preparation of 1,2,4-Trichlorobenzene.

Eastman technical-grade 1,2,4-trichlorobenzene was twice distilled through the wire-packed column. The fraction boiling between 212-213° was collected and showed a refractive index of 1.5690. 1,2,4-Trichlorobenzene has a boiling point of 213° at 760 mm. mercury pressure and a refractive index of 1.5671 at 25° as reported in the Handbook of

Chemistry and Physics, forty-second edition. This compound was dried and stored in the same manner as the benzene was.

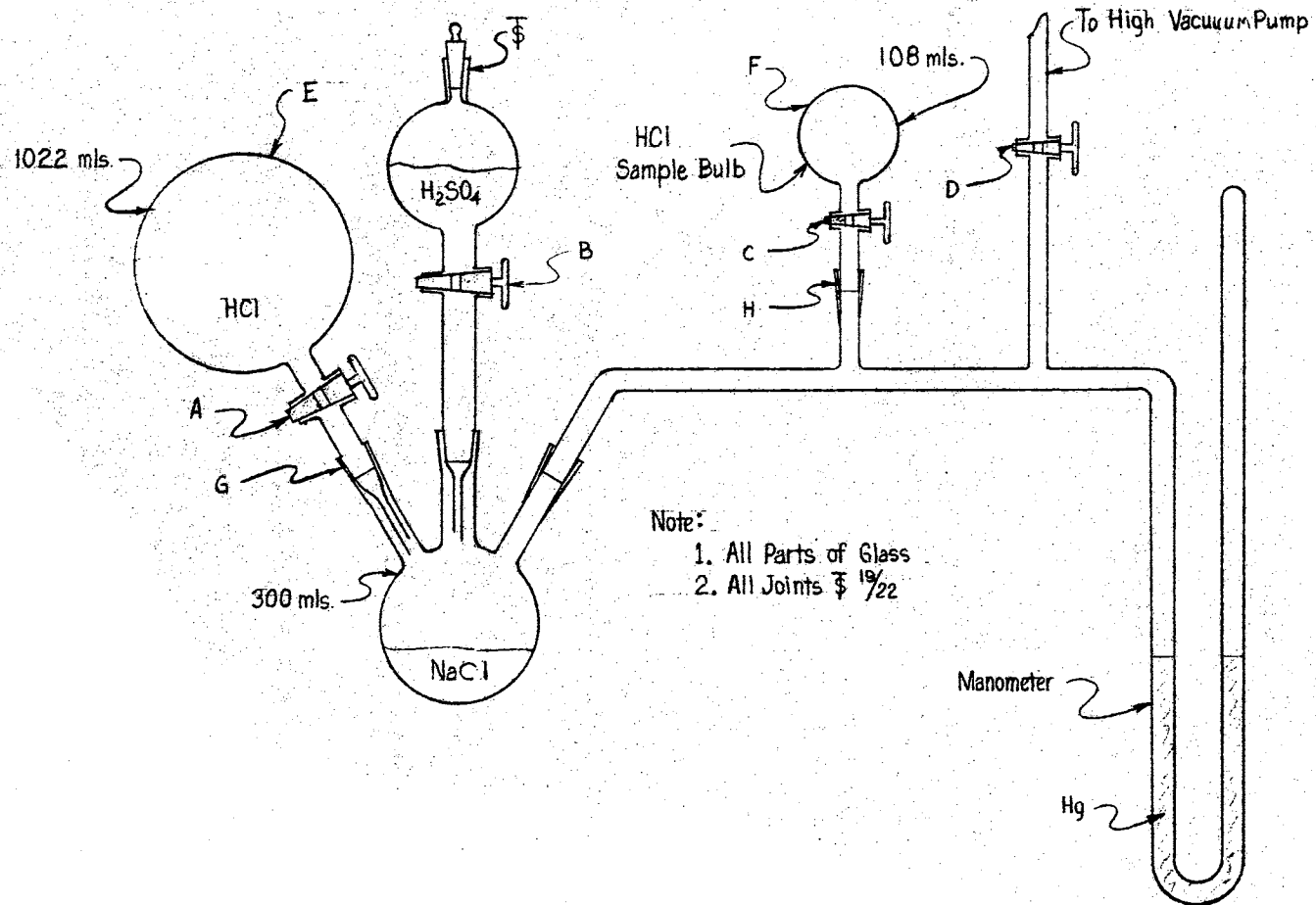
Preparation of Hydrogen Chloride-t.

Tritium chloride gas was prepared using the apparatus shown in Figure III. Stopcock B was closed. Stopcocks A, C, and D were opened and the system was evacuated to 1 micron pressure. Stopcock D was then closed and the system checked for leaks. When the manometer reading showed no change at the end of 1 hour, stopcock B was opened permitting a solution of 4 ml. of water-t ($250\mu\text{c./ml.}$) in pure sulfuric acid to drop on 5 g. of sodium chloride.

When the manometer indicated a pressure of 741 mm of mercury, stopcocks A, B, and C were closed and D was opened thus passing the excess hydrogen chloride-t up the hood. When the system had once again attained a pressure of 1 micron the system was opened to the atmosphere and bulbs E and F detached at G and H respectively. The stem of bulb F was immersed in 40 ml. of standard sodium hydroxide solution and stopcock D was then opened. When 30 ml. of base had risen in the bulb, D was closed, inverted and a slight pressure of nitrogen applied. Bulb E was then placed in its original position, stopcock D opened and the solution forced out of the bulb into the remaining 10 ml. of standard base. Bulb F was washed three times with 10 ml. of water in this manner. The excess base was titrated with standard hydrochloric acid solution to a phenolphthalein end-point and diluted to 100 ml. Four 1-ml. samples were assayed as previously described; calculation showed that the hydrogen chloride-t had a specific activity of $44.89\mu\text{c./mmole.}$ Since bulb E contained 1022 ml., calculation shows that 40.46 mmole of hydrogen

Figure III

Apparatus For Producing Tritium Chloride



chloride-t was collected.

EXCHANGE REACTIONS

The p-t-ethylbenzene and benzene system.

Since the original aim of this experiment was not to obtain kinetic data, temperature control was not stringently maintained. However, every possible precaution was taken to maintain anhydrous conditions. The reaction was performed in a 300-ml. three-neck flask previously dried at 120° for 18 hrs. Upon removal from the drying oven the flask was capped on one side and immediately connected to a source of dry nitrogen in a room maintained at 10°. This flow of dry nitrogen was maintained throughout the operation. Stirring was effected by a magnetic stirrer.

Two hundred ml. of dry 1,2,4-trichlorobenzene was placed in the flask by dropping this material through the nitrogen stream with a separatory funnel. An ampoule of aluminum bromide previously dried in a desiccator was dropped into the flask and broken with a dry stirring rod. A light-brown solution resulted which in 10 minutes had turned dark brown in color. An equimolar solution of p-t-ethylbenzene in benzene was then prepared by placing in a dry previously tared 100-ml. separatory funnel, through a stream of dry nitrogen approximately 15 g. of benzene. The nitrogen source was disconnected and the funnel capped, weighed and the weight recorded. The balance was preset and weighing as rapidly as possible sufficient p-t-ethylbenzene was dropped into the funnel to obtain an equimolar solution. The funnel was capped and the exact weight recorded. This was done to minimize the amount of water in the system.

The flask and the separatory funnel were allowed to stand at 10° for 4 hrs. At this time the contents of the separatory funnel were allowed to drop into the flask and the time recorded. No change in the color of the complex resulted. Samples were withdrawn at 80, 120, 480, 960, and 1820 seconds and treated as described previously. Each sample was withdrawn using a previously dried pipette to avoid contamination of the remaining solution. Results of the analysis of the samples may be found in Table I. No assay was made of the 980-second and 1820-second samples.

Control Experiment.

Since the results obtained would rely on the assumption that no exchange occurs during the separation procedure, the first step was to prove this assumption correct. This was done by dissolving benzene-t and chlorobenzene in 1,2,4-trichlorobenzene and subjecting the solution to the separation procedure.

Forty-two ml. of a solution containing 33.8 mmole of benzene-t (8.21 μ c./mmole) and 39.13 mmole of chlorobenzene dissolved in 303.6 mmole of 1,2,4-trichlorobenzene was subjected to the separation procedure. Fractions boiling at 78-79°, 131-132°, and 212-213° were collected having refractive indices respectively of 1.4993, 1.5420, and 1.560. Analysis of these materials showed no transfer of activity from benzene-t to chlorobenzene or the solvent.

The Benzene-t and Chlorobenzene System.

This reaction was expected to produce kinetic data; therefore, the three-neck flask was placed in a 15° \pm 0.1° thermostated bath. The

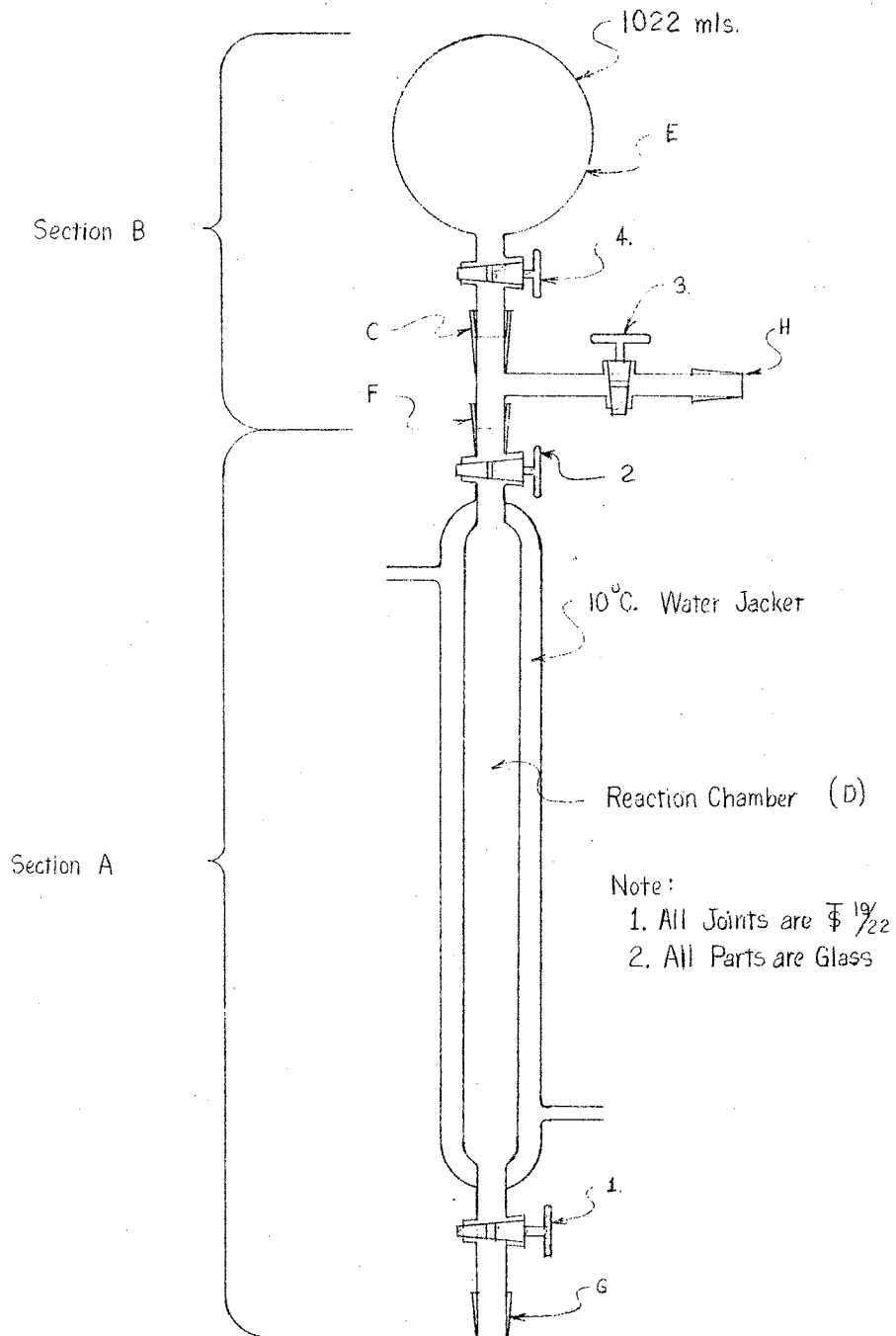
procedure was the same except that the funnel was inverted and allowed to cool to 15°C in the bath prior to addition. The complex produced by the aluminum bromide and 1,2,4-trichlorobenzene had the same color and no change was apparent on adding the chlorobenzene and benzene-t solution. In this case samples were withdrawn at 1, 2, 4, 8, 16, 32, and 64 minutes. These samples were treated and analyzed as previously described. Results of these analyses may be found in Table II.

The Tritium Chloride and Benzene System.

This experiment was performed utilizing the equipment shown on Figure IV. A solution of 1,2,4-trichlorobenzene and benzene were weighed as described previously in part A. Approximately 60 g. of this solution was placed in a dry separatory funnel with a ground-glass joint. To this funnel was also added a weighed amount of aluminum bromide in an ampoule. The ampoule was subsequently broken and the aluminum bromide allowed to dissolve. When solution was complete, the funnel was attached to section A at point F. Section A was attached to the vacuum line and evacuated up to the stopcock in the funnel. Stopcock 1 was then closed and the funnel opened. As the last drop of solution passed into reaction chamber D, stopcock 2 was closed. Section A was then removed from the line and cooled by pumping a liquid at $10^{\circ} \pm 0.10^{\circ}$ through the outer chamber. The remainder of the original 1,2,4-trichlorobenzene solution was attached to bulb E at point C, using a funnel identical to the one described above. Bulb E has a known volume and contains hydrogen chloride-t at a known pressure and radioactivity. A pressure of 4 lb. of nitrogen was applied at the top of the funnel. The funnel was opened and stopcock 4 was opened, thus forcing all the remaining solution in

Figure IV

Apparatus For Conducting The Tritium Chloride - Benzene Exchange



bulb E. Bulb E was allowed to achieve a pressure of 4 lb. of nitrogen, stopcock 4 was then closed and the funnel was detached.

Bulb E was placed in 10° bath for 45 minutes and then attached to section A as shown in Figure IV. The assembled apparatus was attached to the vacuum line, stopcock 3 opened and the volume between stopcocks 2 and 4 evacuated. Stopcock 3 was then closed and the apparatus detached from the line. Stopcocks 2 and 4 were opened in that order and the contents of bulb E were forced into the reaction chamber. Stopcock 2 was closed as the last drop of liquid passed into the reaction chamber. Stopcock 4 was closed immediately thereafter. Bulb E was detached and the remaining hydrogen chloride-t was analyzed as previously described. As soon as possible, the reaction chamber was vigorously shaken to insure homogeneity and samples were withdrawn at 3, 6, 12, 32, and 64 minutes, with the aid of nitrogen pressure applied at point F.

These reaction mixtures were separated and assayed in the usual manner. The results of these analyses may be found in Table III. From assay of the remaining hydrogen chloride-t in bulb E and correcting for the volume of the assembly apparatus, calculation shows that 12.47 mmole of hydrogen chloride-t at 44.89 μ c./mmole entered the reaction chamber.

Immediately upon contact of the solution in bulb E to the solution in reaction chamber D, a deep-red color developed which at the end of 1 hr. had attained a reddish-brown color.

The use of this technique is justified by the data of Kenner, Polanyi, and Szego (16) who showed that only a very slight exchange occurs when benzene is placed in contact with deuterium chloride in the absence of a Friedel-Crafts catalyst.

RESULTS

The readings on the vibrating reed electrometer were obtained in millivolts, which were converted to microcuries per millimole by means of the equation:

$$\mu\text{c./mmole} = \frac{(\text{reading in millivolts}) (A) (B)}{\text{mmoles of sample}}$$

The quantity A has the value of 8.75×10^{-4} for tritium in methane using an electrometer resistance of 10^{12} ohms. The quantity B is an experimentally determined factor which gives the percentage of the total volume of the gas contained in the combustion tube which is transferred to the ionization chamber. At least three assays were made on each sample thus obtaining the average specific activity entered in the tables of results.

TABLE I

THE p-t-ETHYLBENZENE-BENZENE EXCHANGE

<u>p-t</u> -Ethylbenzene	0.2036 mole
Benzene	0.2033 mole
1,2,4-Trichlorobenzene	1.7035 mole
Aluminum Bromide	0.0328 mole

Time, sec.	Sample	Refractive Index 25°	Boiling Point, °C.	Specific Activity, μc./mmole
0	Ethylbenzene	1.4993	134-136	4.47
0	Benzene	1.4990	78-79	0
0	1,2,4-Trichlorobenzene	1.5690	212-213	0
80	Ethylbenzene	1.4993	134-136	1.70
80	Benzene	1.4990	78-79	2.45
80	1,2,4-Trichlorobenzene	1.5690	212-214	0.06
120	Ethylbenzene	1.4933	134-137	2.46
120	Benzene	1.4990	78-79.5	2.44
120	1,2,4-Trichlorobenzene	1.5690	212-214	0.07
240	Ethylbenzene	1.4993	134-137	2.41
240	Benzene	1.4990	78-79	sample lost
240	1,2,4-Trichlorobenzene	1.5690	212-214	0.08
480	Ethylbenzene	1.4993	135-136	2.51
480	Benzene	1.4990	79-80	2.46
480	1,2,4-Trichlorobenzene	1.5690	212-214	0.08

TABLE II

THE BENZENE-t EXCHANGE WITH CHLOROBENZENE

Aluminum Bromide	0.01933 mole
Benzene- <u>t</u>	0.1672 mole
Chlorobenzene	0.2308 mole
1,2,4-Trichlorobenzene	1.8968 mole

Time, min.	Sample	Refractive Index 25°	Boiling Point, °C.	Specific Activity uc./mmole
0	Benzene	1.4990	78-79	8.21
0	Chlorobenzene	1.5240	132-133	0.00
0	1,2,4-Trichlorobenzene	1.5686	212-214	0.00
1	Benzene	1.4990	78-79	4.13
1	Chlorobenzene	1.5240	132-133	2.05
1	1,2,4-Trichlorobenzene	1.5687	212-214	0.00
2	Benzene	1.4990	79-80	4.16
2	Chlorobenzene	1.5240	132-133	2.53
2	1,2,4-Trichlorobenzene	1.5690	212-214	0.007
4	Benzene	1.4990	78-79	4.19
4	Chlorobenzene	1.5240	132-134	2.61
4	1,2,4-Trichlorobenzene	1.5691	212-214	0.080
8	Benzene	1.4990	78-79.5	4.05
8	Chlorobenzene	1.5241	131-135	2.23
8	1,2,4-Trichlorobenzene	1.5686	212-214	0.079

TABLE II (Continued)

Time, min.	Sample	Refractive Index 25°	Boiling Point, °C.	Specific Activity $\mu\text{C./mmole}$
16	Benzene	1.4990	78-79	3.90
16	Chlorobenzene	1.5240	132-133	2.84
16	1,2,4-Trichlorobenzene	1.5690	212-214	0.058
32	Benzene	1.4990	78-79	3.67
32	Chlorobenzene	1.5240	132-134	2.88
32	1,2,4-Trichlorobenzene	1.5690	212-214	0.082
64	Benzene	1.4990	78-79	3.58
64	Chlorobenzene	1.5240	132-134	2.97
64	1,2,4-Trichlorobenzene	1.5690	213-214	0.081

TABLE III

THE TRITIUM CHLORIDE AND BENZENE EXCHANGE

Aluminum Bromide	0.00742 mole
Benzene	0.2048 mole
Hydrogen chloride- <u>t</u>	0.01247 mole
1,2,4-Trichlorobenzene	0.6503 mole
Initial hydrogen chloride- <u>t</u>	44.89 $\mu\text{c.}/\text{mmole}$

Time, min.	Sample	Refractive Index 25°	Boiling Point, °C.	Specific Activity, $\mu\text{c.}/\text{mmole}$
0	Benzene	1.4990	78-79	0
0	1,2,4-Trichlorobenzene	1.5690	212-215	0
3	Benzene	1.4990	78-79	1.57
3	1,2,4-Trichlorobenzene	1.5690	212-214	0.1165
6	Benzene	1.4990	78-79	1.46
6	1,2,4-Trichlorobenzene	1.5690	212-214	0.173
16	Benzene	1.4990	78-79	1.45
16	1,2,4-Trichlorobenzene	1.5690	212-214	0.265
32	Benzene	1.4990	78-79	1.27
32	1,2,4-Trichlorobenzene	1.5690	212-214	0.304
64	Benzene	1.4990	78-80	1.14
64	1,2,4-Trichlorobenzene	1.5687	212-215	0.319
128	Benzene	1.4990	78-80	1.12
128	1,2,4-Trichlorobenzene	1.5688	212-214	0.414

DISCUSSION OF RESULTS

The results indicate that tritium is completely exchanged between p-t-ethylbenzene and benzene at 10° under these conditions within 80 seconds. The exchange between benzene-t and chlorobenzene reaches equilibrium at 15° within one minute. Tables I and II indicate that no significant exchange is observed from the donor molecules to the solvent in the absence of hydrogen chloride.

Table III indicates that the exchange of tritium between hydrogen chloride-t and benzene is complete in 3 minutes at 10° and that significant exchange between hydrogen chloride-t and 1,2,4-trichlorobenzene occurs which is not complete in 128 minutes.

Comparison of the Tables I, II, and III indicate that a different complex is formed when anhydrous hydrogen chloride is present. This is supported by the remarkable change in color which occurs when hydrogen chloride is allowed to contact the solution containing the dissolved catalyst. This observation corroborates the report of Thomas (25) that aluminum chloride will not form a complex with aromatic hydrocarbons unless hydrogen chloride or some other halogen acid is present.

The lack of exchange with 1,2,4-trichlorobenzene as shown in Tables I and II and the low rate of exchange shown in Table III indicates that as the acidity of the aromatic hydrocarbon decreases the rate of exchange decreases.

The extreme rapidity of these exchanges is difficult to reconcile with existing knowledge. The rapidity in the more acidic aromatic

hydrocarbons is remarkably analogous to the exchange in aqueous solutions. Any mechanism which shows as a rate-determining step, the displacement of a hydrogen atom from the aromatic ring (24,13,22) is now untenable since the hydrogen atom itself is in constant motion between the various molecules.

If the π complex postulated by Brown and Brady (2) forms initially, then this complex must be sufficiently strong to cause expulsion of a hydrogen atom from the aromatic nucleus. The π complex must in fact be strong enough to cause the reaction between benzene- t and chlorobenzene to attain equilibrium in one minute. The subsequent formation of a σ complex (2) in which the catalyst is attached to a specific carbon atom on the aromatic nucleus is of doubtful meaning since the π complex is presumably able to cause dislocation of a hydrogen atom from a specific carbon atom. Brown and Brady (2) were able to show however that the rate of alkylation of aromatic hydrocarbons by alkyl halides is dependent on the rate of formation of the σ complex.

A satisfactory mechanism of Friedel-Crafts reactions should take into account the data of Lebedev, (17,18), Brown and co-workers (2,3,4, 5,6), the extreme rapidity of exchange of aromatic hydrogen atoms, and the role of hydrogen chloride in the reaction.

The role of hydrogen chloride in the reaction might be determined with a system utilizing tritium chloride, aluminum bromide and 1,2,4-trichlorobenzene. This should have the advantages of providing a homogeneous solution, a simple three-component system, a measurable rate of exchange and obtaining exact amounts of each component used.

The exchange reactions might be further studied with a system containing tritium labeled chlorobenzene in the presence of

1,2-dichlorobenzene, 1,2,4-trichlorobenzene and aluminum bromide. Both these systems should provide reliable kinetic data which might elucidate a mechanism of this very interesting and complex reaction.

CONCLUSIONS

The results of the various exchange reactions lead one to conclude that the more acidic aromatic hydrocarbons exchange aromatic hydrogen atoms at a very rapid rate in the presence of catalytic amounts of aluminum bromide at 15°.

It can be further concluded from this study that the presence of hydrogen chloride enhances the catalytic effect of the aluminum bromide.

Application of the above knowledge to previous work suggests that these rapid exchanges proceed through the π complex postulated by Brown and co-workers (2,3,5,6).

SUMMARY

Tritiated hydrogen chloride, benzene and p-t-ethylbenzene have been prepared and isolated. These were subjected to Friedel-Crafts conditions using aluminum bromide as the catalyst and 1,2,4-trichlorobenzene as the solvent in various experiments. Tritium was shown to exchange between the more acidic aromatic hydrocarbons at a very rapid rate. Tritium was also shown to exchange between tritium chloride and aromatic hydrocarbons at a very rapid rate.

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