Boron trifluoride was purified by preparation of the addition compound with anisole, followed by regeneration at higher temperatures. The gas exhibited a vapor pressure of 298 mm. at −111.8° with a molecular weight of 68.1 as compared to the calculated value of 67.8.

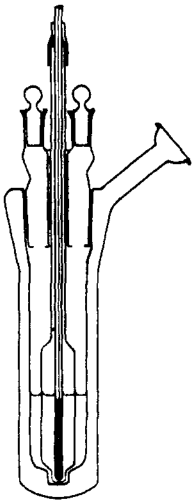
Fig. 2.—Silvered-wall, vacuum-jacketed calorimeter.

Boron trichloride (Matheson) could be readily purified by regeneration from the nitrobenzene addition compound. A typical procedure follows. The addition compound (10 g.) was prepared in the vacuum system by passing boron trichloride gas over nitrobenzene at 10°. After reaction was complete, there was present a crystalline yellow solid. The volatile impurities were pumped off at −20° and the boron trichloride recovered by warming the addition compound to 50°. A trap at −78° was used to remove entrained nitrobenzene. The product was then fractionated by passing it through traps maintained at −78.5, −111.7 and −196°. The material in the −111.7° trap was tensiometrically homogeneous and exhibited a vapor pressure of 476 mm. at 0°.

Boron tribromide was a sample previously prepared by the reaction of bromine with calcium boride and purified by distillation in an all-glass fractionation column, b.p. 90.2° at 748 mm., vapor pressure 19.0 mm. at 0°.

Apparatus.—Because of the corrosive nature of the boron halides, it was deemed desirable to modify the calorimeter previously described[11] by utilizing ground joints for all closures. The final design is shown in Fig. 2.

In the previous design a small well containing mercury was used to separate the two chambers. Although this device was perfectly satisfactory for boron trifluoride, we observed that a reaction took place between mercury and nitrobenzene solutions of boron trichloride and tribromide. The mercury well was therefore replaced by a thin glass bulb sealed to the bottom of the inner movable chamber. The reaction was initiated by pressing this chamber down slightly, crushing the thin bulb dividing the two solutions. Otherwise the operational procedure was identical with that previously described.[11]

After each chemical run the apparatus was calibrated electrically.[9] From the temperature rise (corrected for heat losses using a simplified graphical method[14]), the amount of material reacted and the calibration value, the heat of reaction was calculated.

The heats of solution of the boron trichloride (~1 g.) and boron tribromide (~2 g.) in nitrobenzene were determined as follows. The boron halides were sealed in weighed, fragile glass ampules, so selected as to contain negligible vapor space. The bulbs and sealed-off portions were weighed to obtain the amount of boron halide present in the ampule. This was placed in the calorimeter with 99.80 ml. of nitrobenzene. After temperature equilibrium had been reached, the bulb was crushed beneath the surface of the nitrobenzene. The subsequent calorimetric procedure was identical with that previously described for the determination of the heats of reaction of addition compounds.[11]

A minimum of three determinations were made for each of the calorimetric studies. The average values with the mean deviations are reported in Tables III and IV.

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[14] E. Lawton, Ph.D. Thesis, Purdue University Library, 1952.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Disproportionation of the Alkylbenzenes under the Influence of Hydrogen Bromide and Aluminum Bromide; the Nature of the Transition State in Disproportionation Reactions[1,2]

BY HERBERT C. BROWN AND CHARLES R. SMOOT[3]

RECEIVED OCTOBER 26, 1955

The disproportionation of alkylbenzenes under the influence of aluminum bromide and hydrogen bromide has been studied in a homogeneous system ($6RAr:HBr:Al_2Br_6$) at 0°. Toluene is not altered by these conditions; however, the higher alkylbenzenes undergo rapid conversion to benzene, di- and trialkylbenzenes in a series of reversible reactions. The equilibrium concentrations were determined and equilibrium constants calculated for the disproportionations of ethyl-, *n*-propyl-, isopropyl- and *t*-butylbenzenes. The rates at which equilibria are attained were determined for ethyl- and isopropylbenzene at 0°. The alkylbenzenes are very rapidly converted to benzene and dialkylbenzenes, the latter being converted much more slowly to trialkylbenzenes. At equilibrium the tri- and monoalkylbenzenes predominate. The dialkylbenzenes are mainly the *meta* isomers, although the amount of the *para* isomer present increases with increasing branching of the alkyl group. The trialkylbenzenes are the 1,3,5-isomers exclusively. The order of migratory aptitudes for alkyl groups is *t*-butyl > isopropyl > ethyl > methyl. Similar disproportionation studies were made in the system: ($5C_6H_6 + RAr$):$HBr:Al_2Br_6$. In this system equilibrium is attained in less than one minute. The products are benzene and dialkylbenzene, with no trialkylbenzene being detected. A mechanism is proposed for the disproportionation, involving a nucleophilic displacement by an aromatic on a highly reactive localized π-complex (unstable intermediate), the latter being in mobile equilibrium with a more stable σ-complex of the alkylbenzene undergoing disproportionation.

The disproportionation of alkylbenzenes to higher and lower homologs has been studied by numerous investigators,[4] but until recently there were many conflicting reports concerning the reaction. Lien and McCaulay[5] recently reported a careful study of the disproportionation of alkylbenzenes in the hydrogen fluoride–boron trifluoride system which clarified many of the discrepancies previously reported. They proposed a mechanism which adequately accounts for the orientation and configuration of the alkyl groups, as well as the role of the catalyst in disproportionation reactions.

In connection with a recent study of the Friedel-Crafts reaction of higher alkyl halides under the influence of aluminum bromide, results were obtained which could not be interpreted by any reasonable mechanism for the alkylation stage. It appeared that disproportionation of the alkylation products was occurring in this system under the

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[1] The Catalytic Halides. XV.

[2] Based upon a thesis submitted by Charles R. Smoot in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Standard Oil Company (Indiana) Fellow at Purdue University, 1952–1954.

[4] D. V. Nightingale, *Chem. Revs.*, **25**, 329 (1939).

[5] A. P. Lien and D. A. McCaulay, THIS JOURNAL, **75**, 2407 (1953).

conditions of the alkylation reaction. Consequently, a study of the disproportionation of alkylbenzenes under the influence of aluminum bromide and hydrogen bromide was undertaken.

It appeared desirable to operate in a homogeneous system under conditions very similar to those used in the alkylation studies. Accordingly, the experiments were carried out using the system,[6] 6RAr: HBr:Al_2Br_6. The initial studies were performed with pure alkylbenzenes in order to establish the products formed, their equilibrium concentrations and the approximate rates at which equilibrium is attained. Similar studies were performed in benzene solution ($5C_6H_6$ + RAr:HBr:Al_2Br_6) utilizing concentrations identical to those which should be present at the completion of a typical alkylation reaction ($6C_6H_6$:RBr:Al_2Br_6). In this manner it was hoped to gain a better understanding of the mechanism of the alkylation reaction through knowledge of the subsequent disproportionation reactions.

Results

In the disproportionation experiments utilizing excess alkylbenzene, aluminum bromide was dissolved in the alkylbenzene at 0° in a molar ratio of 1 to 6 and the reaction initiated by addition of hydrogen bromide (1 mole per mole of Al_2Br_6). Samples were removed periodically from the homogeneous reaction mixture and quenched by addition to ice. The composition of the samples was determined by infrared analysis. Samples of 1 g. were utilized for the analysis and the compositions of mono-, di- and trialkylbenzenes determined. The results are reported in terms of moles per 1-g. sample since mole fractions could not be calculated (benzene was used as solvent for the analyses and its concentration could not be determined). After the reaction mixture was at equilibrium, the reaction was discontinued and the equilibrium concentrations of each component determined by rectification. The di- and trialkylbenzenes obtained in the final rectification were used as standards for the infrared analyses. As their purity was not established, the relative changes of concentration are more significant than the absolute values.

Rates of Disproportionation.—Toluene was treated with aluminum bromide and hydrogen bromide at 0° for eight days. No appreciable disproportionation was observed and the toluene was recovered unchanged. Infrared analyses indicated that less than 0.1% *m*-xylene was present. It is apparent that the disproportionation of toluene is immeasurably slow at this temperature, even though other alkylbenzenes are rapidly converted to benzene and higher alkylated products under the same conditions.

At 0° under these conditions ethylbenzene is rapidly converted to benzene and diethylbenzene and the latter, in turn, is more slowly converted into trialkylbenzene. The changes in concentrations of the various components are shown in Fig. 1; it is apparent that the concentration of diethylbenzene passes through a maximum after about 20 minutes. The rate of formation of triethylbenzene is considerably slower and approximately 25 hours are required to reach the equilibrium concentration.

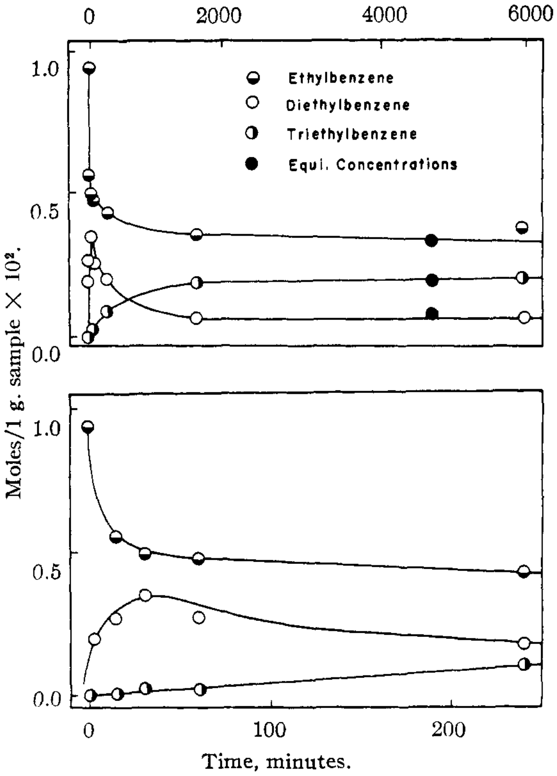

Fig. 1.—Rate of disproportionation of ethylbenzene under the influence of aluminum bromide and hydrogen bromide at 0°.

The disproportionation of isopropylbenzene is considerably faster, about 100 times the rate of ethylbenzene. The changes in concentration of mono-, di- and triisopropylbenzenes in the disproportionation reaction are shown in Fig. 2. It is apparent that the concentration of diisopropylbenzene has already passed through a maximum when the first sample was removed at 10 minutes. The rate of formation of triisopropylbenzene is quite rapid and its equilibrium concentration is reached after several hours. Due to the complexity of the kinetics of bimolecular, consecutive reactions, it was not possible to calculate absolute rate constants for these reactions.

Similar studies were carried out with *n*-propyl- and *t*-butylbenzene, but it was not possible to follow the rates in these cases. The infrared bands due to the products from the disproportionation of *n*-propylbenzene were broad and quite weak, and it was not possible to analyze the hydrocarbon mixtures. However, it was possible to establish that no isopropylbenzene was formed in the reaction. The final equilibrium concentrations were determined by rectification of the product.

On addition of the hydrogen bromide to the *t*-butylbenzene–aluminum bromide solution, a yellow solid was precipitated. After a short time, the entire solution was semisolid. Samples were removed from the heterogeneous mixture, but the data for the analyses were quite erratic, presumably

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[6] H. C. Brown and W. J. Wallace, THIS JOURNAL, **75**, 6268 (1953).

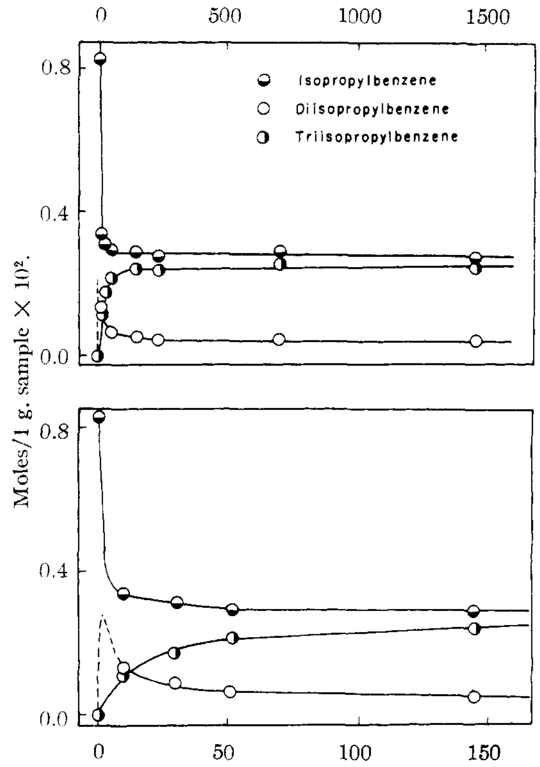

Fig. 2.—Rate of disproportionation of isopropylbenzene under the influence of aluminum bromide and hydrogen bromide at 0°.

the result of non-representative sampling. The results indicated, however, that the reaction was very close to equilibrium shortly after the addition of the hydrogen bromide. The solid precipitated from the reaction mixture was either 1,3,5-tri-*t*-butylbenzene or its σ-complex.[7] The reaction appears to be considerably faster than the corresponding reaction of isopropylbenzene.

The disproportionation experiments were also studied in benzene solution to provide data more directly applicable to the alkylation studies. Aluminum bromide (1 mole) was dissolved in 5 moles of benzene and 1 mole of the monoalkylbenzene and treated with 1 mole of hydrogen bromide at 0°. Samples were removed periodically and analyzed by infrared. However, with isopropyl- and *t*-butylbenzene, the reaction was at equilibrium when the first sample was removed at 1 minute. Only dialkylbenzenes were formed and no trialkylbenzenes were observed. The dialkylbenzenes contained approximately 10% *p*-diisopropyl- and 40% *p*-di-*t*-butylbenzene.

There was one serious complication in the use of benzene as the reaction medium for disproportionation studies. The reactions could be studied only over a period of several hours, as the σ-complex of benzene is relatively unstable and undergoes slow side reactions, with the formation of a high-boiling, tarry residue. When benzene was treated with hydrogen bromide–aluminum bromide for eight days at 25°, only 32% of the initial benzene was recovered. The remainder was converted to a high-boiling tarry material.[8] It appears that the σ-complex of benzene may be sufficiently reactive to alkylate another molecule of benzene, leading to the formation of higher polymers.

Equilibria in Disproportionation.—The disproportionation of alkylbenzenes to benzene and dialkylbenzene has been shown previously[5] to be an equilibrium reaction and apparent equilibrium constants were calculated for ethylbenzene. In the present study the dialkylbenzene reacted further to yield the trialkyl derivative. These products arise from a series of reversible reactions which may be written[9]

$$2RC_6H_5 \rightleftarrows C_6H_6 + R_2C_6H_4 \qquad (1)$$

$$RC_6H_5 + R_2C_6H_4 \rightleftarrows C_6H_6 + R_3C_6H_3 \qquad (2)$$

The apparent equilibrium constants for reactions 1 and 2 are defined as

$$K_1 = N_{\text{benzene}}\, N_{\text{dialkylbenzene}}/N^2_{\text{alkylbenzene}}$$

$$K_2 = N_{\text{benzene}}\, N_{\text{trialkylbenzene}}/N_{\text{alkylbenzene}}\, N_{\text{dialkylbenzene}}$$

where N is the mole fraction. The values of K_1 and K_2 for the disproportionation of a series of alkylbenzenes are shown in Table I.

TABLE I

DISPROPORTIONATION OF ALKYLBENZENES AT 0°

Reactants[a] RC_6H_5	Reactants[a] Al_2Br_6	R	Products, mole % C_6H_6	Products, mole % RC_6H_5	Products, mole % $R_2C_6H_4$	Products, mole % $R_3C_6H_3$	Equil. constant K_1	Equil. constant K_2
0.376	0.0634	Ethyl[b]	39.9	31.3	6.9	21.9	0.28	4.0
.600	.101	Ethyl	35.7	36.0	8.2	20.1	.23	2.4
.664	.117	*n*-Propyl	42.1	26.2	13.1	18.5	.80	2.3
.280	.0487	*i*-Propyl[b]	35.4	30.5	4.9	29.2	.19	6.9
.678	.1135	*i*-Propyl	43.3	30.4	6.4	20.2	.30	4.5
.542	.0902[c]	*i*-Propyl	31.1	44.4	13.4	11.1	.21	0.58
.290[d]	.296	*i*-Propyl	90.4	5.8	3.8		10	
.682	.1106	*t*-Butyl	35	46	16	3	0.27	

[a] Moles: equal molar quantities of hydrogen bromide and aluminum bromide (Al_2Br_6) were used unless otherwise noted. [b] 25°. [c] 0.06 mole of hydrogen bromide. [d] Benzene, 1.63 moles, was used as solvent.

With ethyl-, *n*-propyl- and isopropylbenzene, the reaction occurs readily, yielding only benzene, mono-, di- and trialkylbenzenes. With *t*-butylbenzene a slow side reaction was observed even at 0°, leading to the formation of a high boiling, tarry residue on rectification. This decomposition is quite slow and is observed only after several days at 0°. This decomposition of *t*-butylbenzene is probably similar to that observed by McCaulay and Lien[10] in their study of the action of hydrogen fluoride–boron trifluoride on *t*-butylbenzene at 45°. These authors noted the formation of isobutane, β-alkylstyrenes and higher boiling tars in the reaction.

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(7) The 1,3,5-tri-*t*-butylbenzene was identified by its characteristic absorption peaks at 11.48 and 14.04 μ; D. A. McCaulay, A. P. Lien and P. H. Launer, THIS JOURNAL, **76**, 2354 (1954). The absorption peak at 11.48 μ was used for the quantitative analyses of this component.

(8) The high-boiling, tarry residue was partially rectified at 0.28 mm. and three separate fractions obtained: I, b.p. 66–68°, d^{20}_4 0.9402, n^{20}_D 1.5264; II, b.p. 143–145°, d^{20}_4 1.0581, n^{20}_D 1.4899; and III, b.p. 200–220°, n^{20}_D 1.6167. The boiling points suggest that the compounds have the empirical formulas $(C_6H_6)_2$, $(C_6H_6)_3$ and $(C_6H_6)_4$, but no further work was done to establish the nature of the products.

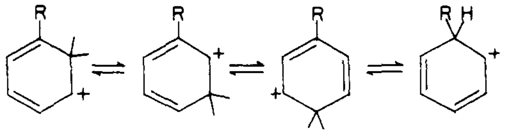
(9) A third reaction leading to the formation of trialkylbenzene can also be written: $2R_2C_6H_4 \rightleftarrows RC_6H_5 + R_3C_6H_3$. However, the equilibrium constant for this reaction can be derived from the expressions for reactions 1 and 2.

(10) D. A. McCaulay and A. P. Lien, THIS JOURNAL, **75**, 2411 (1953).

Although the dialkylbenzenes formed in these studies were predominantly the *meta* isomers, some of the *para* isomer was observed in each case. There appeared to be a gradual increase with increasing branching of the alkyl group in the amount of the *para* isomer present at equilibrium. Thus, with ethyl-, isopropyl- and *t*-butylbenzenes, the dialkylbenzenes were estimated to contain 5, 10 and 40% of the *para* isomer, respectively.

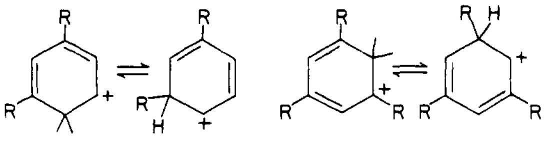
Discussion

From the data in Figs. 1 and 2 it is apparent that the monoalkylbenzenes disproportionate very rapidly to dialkylbenzenes, which are in turn relatively slowly converted to trialkylbenzenes. The large difference in the rates of disproportionation of mono-, di- and trialkylbenzene can be accounted for in terms of the relative stabilities of the σ-complexes which are formed. With monoalkylbenzenes four different σ-complexes may be formed,[11] but only IV will lead to disproportionation.



I II III IV

Similar equilibria can be written for the σ-complexes of *m*-di- and 1,3,5-trialkylbenzenes.

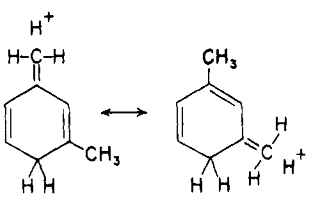


V VI VII VIII
(plus 2 isomeric structures)

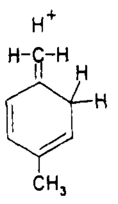
It has been previously postulated[5,10] that the rate-determining step in the reaction is an attack by another aromatic on σ-complexes of the type IV, VI or VIII. Thus, the rate of reaction will depend upon the concentration of free aromatic and also upon the concentration of the σ-complex with the proton attached at the substituted position. As additional alkyl groups are added to the ring, the basicity of the unsubstituted positions increases markedly and the relative concentrations of σ-complexes with the proton attached at the substituted positions decrease very rapidly.[12] As less of the di- and trialkylbenzenes are free to participate in nucleophilic substitution, and as less of the desired σ-complex is present at equilibrium, the rate of disproportionation decreases rapidly in going from mono- to di- to trialkylbenzene.

Values for the apparent equilibrium constants, K_1 and K_2, are shown in Table I. These are only apparent equilibrium constants as they are influenced by the concentration of the catalyst. This is especially true for K_2, since most of the trialkylbenzenes were present as their σ-complexes. The values for K_1 are similar to those observed in the hydrogen fluoride–boron trifluoride system,[5] where values of 0.21 to 0.30 were observed for ethylbenzene. Also, similar to the results of McCaulay and Lien in the hydrogen fluoride–boron trifluoride system,[5] the use of excess catalyst results in a large increase in the apparent equilibrium constant, K_1, and inhibits the formation of trialkylbenzene. Thus, the value for K_1 calculated for the disproportionation of isopropylbenzene in benzene solvent with excess catalyst is 10 and no triisopropylbenzene was observed in the product. The large increase in the apparent equilibrium constant, K_1, is attributed to the formation of a stable σ-complex with the catalyst. The removal of the diisopropylbenzene shifts the equilibrium in reaction (1) to the right, resulting in a larger observed value for K_1. Moreover, since the diisopropylbenzene is essentially completely converted to its σ-complex, it cannot be further alkylated to form triisopropylbenzene.

With increasing branching of the alkyl group, the amount of *para* isomer in the dialkylbenzene fraction increased sharply relative to the *meta* derivative. This decrease in the stability of the *m*-dialkylbenzene with respect to the *para* can be accounted for in terms of the difference in the hyperconjugative ability of a carbon–hydrogen bond as compared to a carbon–carbon bond. The great stability of the σ-complexes of *m*-dialkylbenzene is usually attributed[13] to the greater stabilization of the *m*-isomer through hyperconjugative contributions of the two alkyl groups. Thus, for the most stable σ-complex of *m*-xylene, six resonance forms can be written, as both methyl groups can engage in hyperconjugative resonance simultaneously (IX); whereas in the corresponding σ-complex of *p*-xylene only three such forms can be written with only one methyl group capable of hyperconjugative stabilization of the ion X.



IX



X

Hyperconjugation is more important in carbon–hydrogen than in carbon–carbon bonds.[14] Consequently, gradual replacement of the α-hydrogen atoms with methyl groups should lead to a considerable decrease in the difference in stability of the σ-complexes from the *m*- and *p*-dialkylbenzenes. On this basis it can be predicted that the *meta/para* basicity ratios of dialkylbenzenes should decrease rapidly with increasing branching of the alkyl groups.

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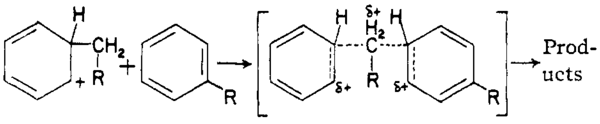
[11] It should be recognized that various resonance structures can be written for each of the isomeric σ-complexes. Only one of the possible resonance structures for each isomer is shown.

[12] The partial basicity factors with hydrogen fluoride–boron trifluoride have been calculated for the *ortho*, *meta* and *para* positions [F. E. Condon, THIS JOURNAL, **74**, 2528 (1952), from data of D. A. McCaulay and A. P. Lien, *ibid.*, **73**, 2013 (1951)]. Assuming these factors to be correct, the partial basicity factor for the methyl-substituted position was estimated to be 1.7 from the basicity of hexamethylbenzene. Using these partial basicity factors, the equilibrium concentrations of the σ-complexes with the proton attached to the substituted position were calculated to be: toluene, 0.48%; *m*-xylene, 0.0084%; mesitylene, 0.00011%.

[13] D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

[14] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

Mechanism of Disproportionation.—In order to account for the retention of structure of the migrating alkyl group, the inertness of neopentylbenzene under conditions where ethylbenzene is rapidly disproportionated, and the observed second-order kinetics, McCaulay and Lien[5,10] have proposed a displacement mechanism for alkylbenzene disproportionation. In this mechanism the rate-determining step is a nucleophilic attack by an aromatic on the rearward side of the alkyl group of the σ-complex XI.



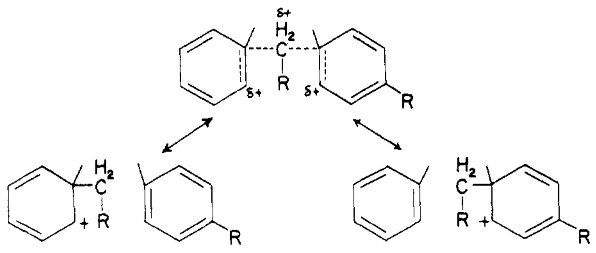
XI Transition State

They explain the order of alkyl group reactivity, *i.e.*, *t*-butyl > isopropyl > ethyl > methyl, by stabilization of the transition state through hyperconjugative interactions with the α-methyl groups.

This mechanism provides a highly satisfactory interpretation for almost all of the known facts about the disproportionation reaction. However, it appears necessary to introduce one modification in order to account for the enormous effect of α-substitution on the rate of the disproportionation reaction.

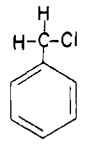
For example, the transfer of an ethyl group may be estimated to be approximately 10^7 faster than that of a methyl group.[15] It does not appear possible to attribute to hyperconjugative stabilization a difference in rates of this magnitude, *unless a very high degree of positive character is developed at the reaction center.*

If a partial σ-bond is developed with the attacking aromatic before bond rupture occurs, with a gradual shift of the alkyl group from one ring to the second as a single stage process, only a small partial positive charge would be expected at the reaction center since the transition state would be stabilized by resonance with both rings (XII).

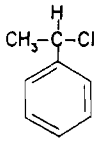


(3 resonance forms) XII (3 resonance forms)

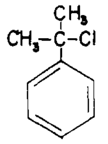
Arguments can be presented to support the conclusion that resonance interaction with the aromatic ring should be far more important than hyperconjugative interactions with α-alkyl groups. For example, the replacement of one of the methyl groups in *t*-butyl chloride by a phenyl group (XV) results in an increase in the rate of solvolysis by a factor greater than 1,000.[16] Similarly, the replacement of the α-hydrogen atoms in benzyl chloride (XIII) by methyl groups (XIV, XV) increases the rate of the unimolecular solvolysis by relatively small factors, in the range of 10 to 100.[16,17]



XIII



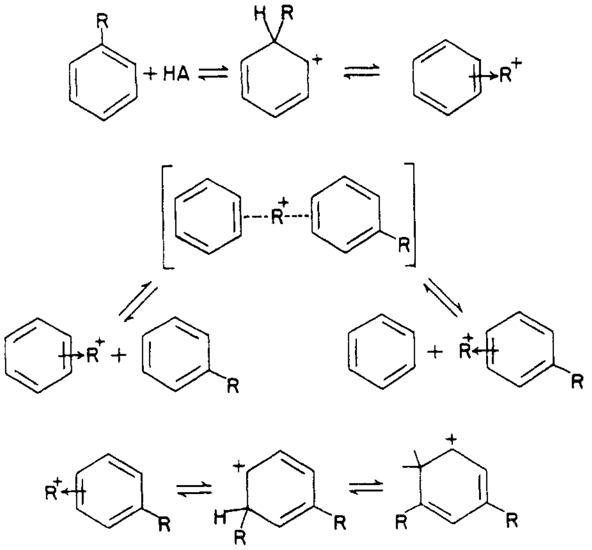
XIV



XV

Consequently, in the transition state for the disproportionation reaction, where resonance interactions with both rings should be possible, it does not appear reasonable to attribute increases in rate of 10^7 to the increased hyperconjugative stabilization made possible by the replacement of an α-hydrogen atom by a methyl group.

In order to account for the very large difference in rates with varying alkyl groups, the following modification in the mechanism of Lien and McCaulay is suggested. It is proposed that the σ-complex of the aromatic is first equilibrated with a localized[18] π-complex of higher energy. The localized π-complex undergoes a rearward nucleophilic attack by another aromatic in a rate-determining stage. The rate of reaction is determined, therefore, both by the concentration of the π-complex and the rate at which it is attacked by another aromatic. The sequence of steps in the mechanism (XVI) is[19]



XVI

According to this mechanism, as R is changed from methyl to *t*-butyl, the equilibrium concentra-

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[15] The energy of activation for the disproportionation of *m*-xylene is 10 kcal. greater than that for the isomerization of the xylene.[5] As the disproportionation of ethylbenzene is faster than the isomerization of the xylenes, it is at least 10^7 faster than the disproportionation of *m*-xylene.

[16] M. Grayson, Ph.D. Thesis, Purdue University Library, 1952.

[17] G. M. Bennett and B. Jones, *J. Chem. Soc.*, 1816 (1935).

[18] For a discussion of the role of "localized" *versus* "unlocalized" π-complexes in isomerization reactions together with pertinent references see H. C. Brown and H. Jungk, THIS JOURNAL, **77**, 5579 (1955).

[19] Only that σ-complex is shown in which the proton has been added to the ring carbon holding the alkyl group. This σ-complex is undoubtedly less stable than the isomeric species. However, it is the only one which should lead to disproportionation. Finally, only one resonance form of the σ-complexes is indicated, but it should be recognized that they are stabilized by resonance.

tion of the π-complex will greatly increase because of the great increase in stability of the carbonium ion, R^+. As the carbonium ion is transferred from one π-complex to a new aromatic ring, forming another π-complex in the rate-determining step, it cannot be stabilized significantly by resonance with the aromatic ring. The stabilization by hyperconjugation affects the rate, not primarily by stabilization of the transition state, but rather by increasing the equilibrium concentration of the localized π-complex present in the reaction mixture. This increase in the concentration of the π-complex with increased branching of the alkyl group must be so large that it far overshadows the smaller differences in the ease with which these alkyl groups can participate in bimolecular displacement reactions. Only in the case of the neopentyl group does the large steric factor in bimolecular displacements[20,21] result in a controlling effect on the reaction rate.

The mechanism outlined above is related to that proposed for isomerization of the alkylbenzenes.[18,22,23] The same order of reactivity is observed in isomerization of *p*-alkyltoluene as in disproportionation. A small equilibrium concentration of the localized π-complex is established. This is either relatively rapidly converted to the *meta* σ-complex in the isomerization reaction or it more slowly transfers its alkyl group to another aromatic ring in the disproportionation reaction. A careful study of the effect of the structure of the alkyl group on the rates of isomerization and disproportionation under identical reaction conditions should provide a test of the proposal that both reactions proceed through identical localized π-complexes. Unfortunately, such a study will be very difficult experimentally.

Experimental Part

Materials.—The highest purity, commercially available hydrocarbons were rectified through a column rated at 70 plates. Constant boiling center cuts were collected and stored over calcium hydride. The materials utilized exhibited constant refractive indices ($n^{20}D$) as follows: benzene, 1.5008; toluene, 1.4985; ethylbenzene, 1.4954; *n*-propylbenzene, 1.4915; isopropylbenzene, 1.4912; *t*-butylbenzene, 1.4920.

Aluminum bromide was prepared as described in a previous paper in this series.[18] It was stored in a specially constructed flask from which it could be removed without coming into contact with moist air. Anhydrous hydrogen bromide (Mathieson Chemical Co.) was dried and used without further purification.

Procedure for the Disproportionation of Alkylbenzenes.—A typical disproportionation experiment with the pure alkylbenzene is described. Distilled aluminum bromide (53.9 g., 0.101 mole) was dissolved in 63.5 g. (0.600 mole) of ethylbenzene and the solution cooled to 0–5° in a water–ice-bath (some aluminum bromide precipitated). After five minutes 0.104 mole of hydrogen bromide was added rapidly to the solution. The catalyst dissolved immediately and the homogeneous solution was dark amber-red in color; 4-ml. samples were withdrawn by a pipet and quenched by addition to water at 3, 8, 15, 30 and 60 minutes after the hydrogen bromide had been added. Several more samples were removed at longer intervals: 4.0, 17.4 and 25.5 hours. After 1 day, the color had changed to a light reddish-orange and remained as such.

After maintaining the reaction mixture at 0° for eight days, it was quenched by addition to ice, the organic product washed with water and finally dried over calcium hydride. The product was fractionated. It contained 6.84 g. (0.0874 mole, 35.7 mole %) of benzene, 9.39 g. (0.0885 mole, 36.0 mole %) of ethylbenzene, 2.69 g. (0.0201 mole, 8.2 mole %) of *m*-diethylbenzene and 8.07 g. (0.0495 mole, 20.1 mole %) of 1,3,5-triethylbenzene.

The aliquots which had been removed at varying time intervals were dried and analyzed by infrared.

In the disproportionation experiments where benzene was used as solvent, a similar procedure was used with minor changes. The aluminum bromide was dissolved in benzene in a 1-to-5 molar ratio and the hydrogen bromide added. The homogeneous solution was cooled to 0–5° and the alkylbenzene added to initiate the reaction.

Analysis of Samples by Fractionation.—The products from the disproportionation studies were dried and fractionated in a micro Todd column with a stainless steel spiral. A high reflux ratio was used between constant boiling fractions to ensure sharp separations. A plot of ml. distillate *versus* distillation temperature was prepared and used to determine the relative quantities of each component.

Infrared Analyses.—The infrared spectra were obtained with a Perkin–Elmer double beam spectrophotometer. The products obtained from rectification of the final reaction product were used as standards, and the spectra of these standards were used to assign the absorption peaks in the unknown samples to the proper components. The compositions of the samples were calculated from the relative intensities of the various absorption peaks as compared to the same peaks in the known standards.[24]

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