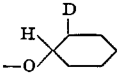
methyl group deuterium content in the experiment in question to that present in the exchange experiment. Subtracting these corrections from the observed over-all deuterium change gives the deuterium change due to the reduction reaction itself. The data in Table V have been calculated in this manner.

Since the acetone produced during the reaction is effectively removed into the fractionating column as soon as it is formed and is therefore unavailable for complete exchange, the corrections applied are probably somewhat too high as is evidenced by the negative values in columns 2 and 5 of Table V.

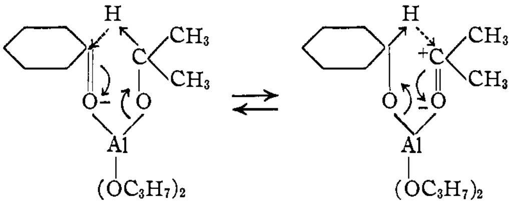
TABLE V

REDUCTION OF CYCLOHEXANONE–CORRECTED FOR EXCHANGE

Experiment	Δ Moles D as CH_3 —OCD CH_3 $\times 10^4$	Δ Moles D as CH_2D —OCH CH_3 $\times 10^4$	Moles D as CH_2D O=C CH_3 $\times 10^4$	Moles D as  $\times 10^4$	Moles D as  as $\times 10^4$
1	49.5	1.4	3.5	58.4	−6.5
2	37.4	−6.0	3.4	47.0	−6.2
3	40.1	−4.2	2.6	51.5	−6.2
4	37.8	−3.6	0.0	28.2	3.2
5	35.0	−2.2	0.5	27.9	0.9

Although the individual determinations of deuterium content have an absolute error of only ±0.002 mole per cent. deuterium oxide, it is necessary to determine the change in deuterium content of the carbinol positions by difference, thus giving these quantities a relative probable error of 5–6%. Since the data in Table V are also computed by difference, the probable error here is increased to about 10%. Unavoidable systematic errors are also present due to the difference in initial deuterium concentration between the exchange experiment and the reduction experiments and to the absence of enolizable ketone during the exchange experiment.[12] Taking these factors into account, the agreement between the amount of deuterium lost from the carbinol carbon atom of the isopropoxide and that appearing on the carbinol carbon atom of the cyclohexanol must be considered satisfactory. Any appreciable involvement of the methyl group hydrogen atoms in the reduction is unlikely in view of the fact that the amount of deuterium lost from the methyl group is essentially the same during the reduction as during the exchange reaction.

The above data indicate that hydrogen atoms are transferred during the Meerwein–Ponndorf reaction predominantly if not solely from the carbinol carbon atom of the alkoxide to the carbonyl carbon atom of the ketone. This is entirely consistent with the proposed mechanism involving the activated complex



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[12] A more complete discussion of errors is given in the Ph.D. thesis of E. D. Williams, Jr., University of Pennsylvania, 1952.

PHILADELPHIA, PENNA.

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Disproportionation of Alkylbenzenes. I. Product Distribution and Rate Studies

BY A. P. LIEN AND D. A. MCCAULAY

RECEIVED NOVEMBER 24, 1952

The disproportionation of alkylbenzenes has been studied with hydrogen fluoride–boron trifluoride catalysts to determine the effect of catalyst concentration on the distribution of reaction products and on the rate of disproportionation. Excess hydrogen fluoride and minor amounts of boron trifluoride partially convert ethylbenzene into benzene, some diethylbenzene and much triethylbenzene; equilibrium lies on the side of undisproportionated ethylbenzene. With excess boron trifluoride, ethylbenzene is 95% disproportionated to benzene and diethylbenzene; no triethylbenzene is formed, and the diethylbenzene is exclusively the meta isomer. Rate studies on *m*-xylene show that migration of alkyl groups is much slower than with ethylbenzene. The rate of disproportionation is a function of temperature and of boron trifluoride concentration and appears to fit a second-order curve. The amount of mesitylene in the trimethylbenzene fraction increases with increasing boron trifluoride concentration and approaches 100% under relatively mild conditions. The dependence of product distribution and of rates of alkylbenzene disproportionation upon boron trifluoride concentration is attributed to preferential complex formation with the starting material and to resulting variations in the amount of hydrocarbon present in the catalyst phase.

The disproportionation of alkylbenzenes to higher and lower homologs with Friedel–Crafts catalysts has been the subject of numerous investigations.[1] As in the field of aromatic alkylation and isomerization, there have been conflicting reports concerning the orientation and configuration of the alkyl group in the disproportionation products. The role of the catalyst and the reaction mechanism have also been subjects of much speculation.[1]

Because recent studies involving HF–BF_3 catalyst systems helped to explain some of the anomalies and apparent discrepancies in the field of methylbenzene isomerization,[2] similar techniques have been applied to the related reaction of disproportionation. The isomerization studies had shown that the acidity and amount of catalyst markedly affect the course of the reaction; a highly acidic catalyst selectively combines with the most basic alkylbenzene isomer and thereby allows isomerization to give an almost quantitative yield of that isomer. Because disproportionation re-

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

[2] D. A. McCaulay and A. P. Lien, THIS JOURNAL, **74**, 6246 (1952).

quires more vigorous conditions than isomerization,[2,3] it was decided to determine the effect of catalyst acidity and catalyst concentration, not only on orientation of the disproportionated alkyl groups, but also on the relative distribution of the homologous polyalkylbenzenes. A further point of interest in the present work was the intermolecular migration of ethyl as well as methyl groups, because ethylbenzene is rapidly disproportionated into benzene and diethylbenzene under conditions that do not affect the xylenes.[2,4]

The present paper deals principally with the distribution of the disproportionation products and with the rate of the reaction. The next paper in the series will describe the disproportionation of alkylbenzenes with longer side chains and will go more deeply into the mechanism of the reaction. Ethylbenzene was chosen for the product distribution investigation because it is sufficiently reactive to be studied under relatively mild conditions. The xylenes were chosen for the rate studies because the methyl group migrates more slowly than the ethyl group and because, of all the methylbenzenes, the xylenes disproportionate at the most convenient rate for measurement. Inasmuch as isomerization of the xylenes occurs much more rapidly than disproportionation and gives *m*-xylene as the principal product, this isomer was used as the starting material for the rate measurements.

Experimental

The ethylbenzene, diethylbenzene and *m*-xylene were Eastman Kodak Co. White Label grade and, after spectrometric analysis, were used without further purification. The hydrogen fluoride and boron trifluoride were commercial grades of 99.6 and about 99% purity, respectively, and were obtained from the Harshaw Chemical Company.

The experiments were carried out in the manner previously described.[2] The hydrocarbon was stirred with the hydrogen fluoride and boron trifluoride under controlled conditions and, after a predetermined time, the phases were separated. The hydrocarbon products of both phases were fractionated through a column of thirty theoretical plates. Fractions of individual carbon number were analyzed by either infrared or ultraviolet absorption.

Disproportionation Product Distribution

Results of the experiments pertinent to product distribution in disproportionation are presented in Table I. Run 1 shows that, in the presence of excess boron trifluoride, ethylbenzene is about 95% converted into benzene and diethylbenzene at 0°. The diethylbenzene fraction was found by infrared analysis to contain 99–100% *m*-diethylbenzene. For the disproportionation reaction

$$2C_6H_5C_2H_5 \rightleftarrows C_6H_6 + C_6H_4(C_2H_5)_2$$

the apparent equilibrium constant is defined as

$$K = N_{\text{benzene}}N_{\text{diethylbenzene}}/N^2_{\text{ethylbenzene}}$$

where N is the mole fraction. The value of K calculated from this experiment is 89. The remaining three runs, in which minor amounts of boron trifluoride were used, give much lower values for K. In runs 2 and 3, with ethylbenzene, the values are 0.21 and 0.23, respectively; in run 4, in which the starting materials were benzene and diethylbenzene, K is 0.30. The true value of K, in the presence of 0.1 to 0.2 mole of boron trifluoride, is therefore within the range 0.21 to 0.30.

TABLE I

DISPROPORTIONATION OF ETHYLBENZENE

	Run 1	Run 2	Run 3	Run 4
Feed composition, mole %				
Benzene	0	0	0	75
Ethylbenzene	100	100	100	0
Diethylbenzene	0	0	0	25
BF_3, moles/mole hydrocarbon	0.9	0.1	0.17	0.1
HF, moles/mole hydrocarbon	10	6	6	6
Temperature, °C.	0	16	66	16
Reaction time, min.	60	60	60	960
Product distribution, mole %				
Raffinate	0	87.9	[a]	90.8
Extract	100	12.1	[a]	9.2
Raffinate composition, mole %				
Benzene	....	27.9	....	66.4
Ethylbenzene	....	52.4	....	37.6
Diethylbenzene	....	19.7[b]	....	6.0[c]
Triethylbenzene	....	0.0	....	0.0
Total		100.0		100.0
Extract composition, mole %				
Benzene	41	12.2	....	33.4
Ethylbenzene	5	20.4	....	14.0
Diethylbenzene[d]	54	17.2	....	7.4
Triethylbenzene[e]	0	50.2	....	45.2
Total	100	100.0		100.0
Combined-product composition, mole %				
Benzene	41	25.9	35.4	58.6
Ethylbenzene	5	48.5	41.3	32.7
Diethylbenzene	54	19.5	10.9	5.5
Triethylbenzene	0	6.1	12.4	3.2
Apparent equil. const., K	89	0.21	0.23	0.30

[a] Phases not separated. [b] 75% *m*-diethylbenzene. [c] 60% *m*-diethylbenzene. [d] Exclusively the 1,3-isomer. [e] Exclusively the 1,3,5-isomer.

The increase of 300- to 400-fold in apparent equilibrium constant and the predominant production of *m*-diethylbenzene obtained with excess boron trifluoride are attributed to the preferential formation of a complex of *m*-diethylbenzene with HF–BF_3. The formation of this complex lowers the concentration of uncomplexed diethylbenzene and allows the disproportionation reaction to approach completion

$$2C_6H_5C_2H_5 \rightleftarrows C_6H_6 + C_6H_4(C_2H_5)_2 \underset{[m\text{-}C_6H_4(C_2H_5)_2\cdot H]^+BF_4^-}{\overset{\text{HF–BF}_3}{\rightleftarrows}}$$

The thermodynamic equilibrium constant must therefore be computed from concentrations in the hydrocarbon phase, rather than from the total product distribution, because of complex formation in the extract phase. The constants calculated from the raffinate compositions of Runs 2 and 4 are 0.20 and 0.28; this range for ethylbenzene is very close to the value of 0.15 to 0.22 for toluene obtained by Pitzer and Scott.[5] The equilibrium con-

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(3) G. Baddeley, G. Holt and D. Voss, *J. Chem. Soc.*, 100 (1952).

(4) A. P. Lien and D. A. McCaulay, U. S. Patent 2,528,893 (Nov. 7, 1950).

(5) K. S. Pitzer and D. W. Scott, THIS JOURNAL, **65**, 813 (1943).

TABLE II

DISPROPORTIONATION OF *m*-XYLENE

6 moles HF per mole xylene; 30 minutes reaction time

Temperature, °C.	66	80	80	100	100	100	120	120	120	120	120[a]	120[a]
BF_3, moles per mole xylene	1.1	0.09	0.65	0.0	0.06	0.66	0.0	0.08	0.28	0.55	0.13	0.60
Products, mole %												
Toluene	0	1	2	0	4	20	3	15	26	32	4	8
Xylenes	100	98	94	100	91	58	94	67	47	34	91	82
Trimethylbenzene	0	1	3	0	5	22	3	18	27	34	5	10
Composition of trimethylbenzenes, %												
Hemimellitene (1,2,3-)	...	...	...	...	....	0	0	0	0	0	....	....
Pseudocumene (1,3,4-)	...	...	...	...	....	Trace	65	40	10	Trace	....	....
Mesitylene (1,3,5-)	...	...	...	...	....	100	35	60	90	100	....	....

[a] 3 minutes reaction time.

stant for the disproportionation of any monoalkylbenzene is likely to be considerably less than one.

In runs 2, 3 and 4, triethylbenzene was formed along with the other products of simple disproportionation, whereas none was produced in run 1. This striking difference is explained by the supposition that, in the presence of excess boron trifluoride, diethylbenzene exists in the form of a positively charged cation

$$[m\text{-}C_6H_4(C_2H_5)_2\cdot H]^+BF_4^-$$

An ethyl group migrating from ethyl- or diethylbenzene bears a positive charge and hence will not react with another cation, but it will attack the uncomplexed benzene and ethylbenzene. With a deficiency of boron trifluoride, considerable diethylbenzene remains uncomplexed and will react with a migrating ethyl group to form triethylbenzene.

Disproportionation Rate

Results of the experiments made to investigate the effect of catalyst concentration on rate of disproportionation are given in Table II. At 66° in the presence of excess HF–BF_3, no conversion of xylene occurred—in sharp contrast to the almost complete disproportionation of ethylbenzene at 0°. The composition of the trimethylbenzene product of disproportionation is dependent on the boron trifluoride concentration. In the runs with little or no boron trifluoride, a mixture of mesitylene and pseudocumene was obtained; with sufficient boron trifluoride, isomerization gave almost pure mesitylene. These findings are exactly as already predicted from the previous isomerization study.[2]

The maximum xylene conversion, in runs with a deficiency of boron trifluoride, was about 30%, and, in runs with high boron trifluoride concentration, was about 65%. The thermodynamic equilibrium constant for the disproportionation reaction calculated from the free energies of formation of toluene, the xylenes and the trimethylbenzenes[6] is 1.17, corresponding to about 70% disproportionation. Excess boron trifluoride would be expected to increase this value to at least 95%. Equilibrium was therefore not reached in these runs, and the extent of participation of the reverse reaction was probably small.

In general, the rate of disproportionation increases with increasing boron trifluoride concentration and with temperature. The effect of boron trifluoride concentration at various temperatures is shown graphically in Fig. 1, where $(1/N) - 1$ is plotted against the moles of boron trifluoride per mole of xylene.[7] N is defined as the mole ratio of unconverted xylene. After an initial increase in disproportionation, the rate at each temperature is proportional to the boron trifluoride concentration.

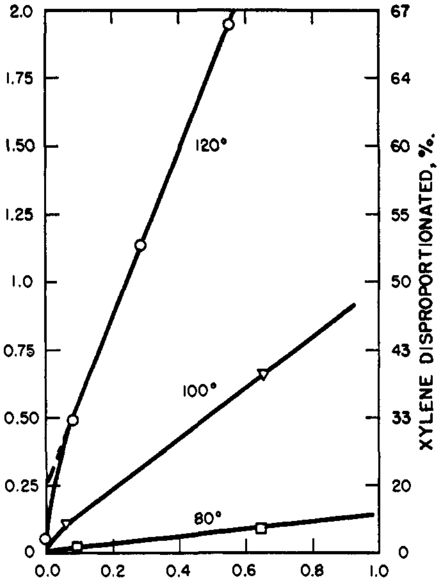

Fig. 1.—Effect of BF_3 on xylene disproportionation.

The amount of aromatic hydrocarbon in the acid layer has also been found to vary linearly with the boron trifluoride concentration.[2] Thus, the rate of disproportionation is directly related to the amount of hydrocarbon dissolved in the catalyst phase. The main function of the boron trifluoride activator, therefore, is to bring more hydrocarbon into solution in the acid phase, where it is dispropor-

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(6) W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **37**, 95 (1946).

(7) The assumption is made that the reaction is bimolecular, for reasons that will be given in paper II of this series. The formula for the velocity constant for a bimolecular reaction, $k = x/ta(a - x)$ (where a is the initial concentration of the reactant, and x is the amount reacted at time t), becomes $k = 1/t((1/N) - 1)$ when N, the mole fraction of unconverted xylene, is substituted for $1 - x$ and 1 is substituted for a. The quantity $(1/N) - 1$, at constant time, is thus proportional to the reaction rate constant.

tionated at a rate dependent upon the temperature.[8]

An approximation of the activation energy for the disproportionation of *m*-xylene was calculated from the change in reaction rate with temperature. In Fig. 2, the logarithms of the 30-minute values of $(1/N) - 1$ from Fig. 1 were plotted against the reciprocal of the absolute temperature. Straight lines that best fit the two sets of points were drawn, and an average activation energy of 23 kcal. was calculated from the slopes. This value is about 10 kcal. higher than that calculated for the *p*-xylene isomerization reaction.[2]

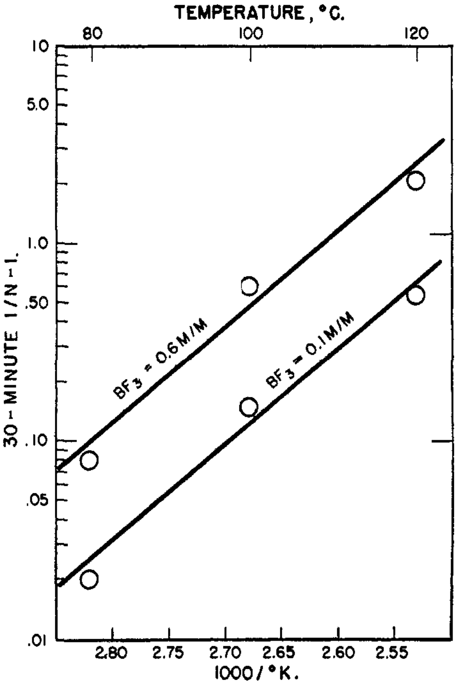

Fig. 2.—Effect of temperature on rate of disproportionation.

The last two runs in Table II were made with reaction times of 3 minutes, instead of the 30 minutes used in the other runs. A plot of $(1/N) - 1$ against contact time constructed from these data and from the 30-minute results at 120° is given in Fig. 3. The disproportionation can be represented within experimental error by straight lines through the origin. The reaction, therefore, appears to fit a second-order rate curve.

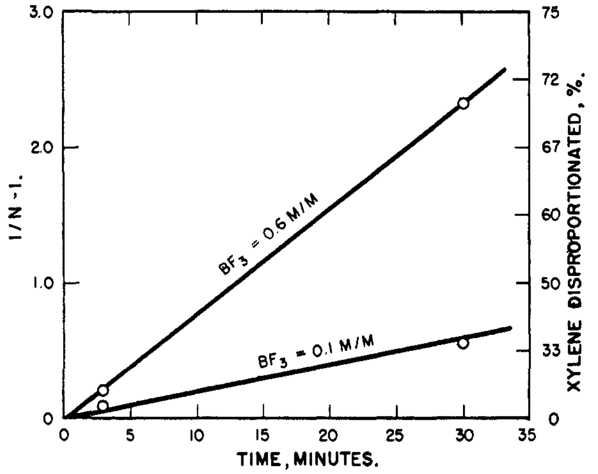

Fig. 3.—Effect of time on xylene disproportionation at 120°.

Conclusion

A highly acidic catalyst, such as HF–BF_3, preferentially forms complexes with the more basic aromatic hydrocarbons present and thereby affects the course of alkylbenzene disproportionation reactions. Thus, complex formation with the dialkylbenzene product of monoalkylbenzene disproportionation not only increases several-hundredfold the apparent equilibrium constant for the reaction, but also inhibits further reaction of the dialkylbenzene with migrating alkyl groups to form trialkylbenzenes. Complex formation also affects the rate of disproportionation by controlling the amount of hydrocarbon present in the catalyst phase.

WHITING, INDIANA

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(8) Extrapolation to zero mole of boron trifluoride gave the values 1, 4 and 20% disproportionation of xylene for pure hydrogen fluoride at 80, 100 and 120°, respectively. Actually, no disproportionation at 100° and only 6% at 120° were obtained in the runs made with no added boron trifluoride. The difference between the actual and extrapolated activity of hydrogen fluoride is probably due to the presence of small amounts of impurities, such as water, which are more basic than the aromatic hydrocarbon. A small amount of boron trifluoride combines with and removes these basic compounds and gives the hydrogen fluoride the acidity and catalytic activity exemplified by the extrapolated curves.