Solvents of Low Nucleophilicity. II. Addition of Trifluoroacetic Acid to Alkenes and Cycloalkenes[1]

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Rates and products of addition of trifluoroacetic acid to the various hexenes and to cycloalkenes having five to eight carbon atoms were determined. The cations presumably formed during addition of trifluoroacetic acid to olefins underwent less hydride shift and less elimination than those formed by tosylate solvolysis.

It was recently found that trifluoroacetic acid adds to unbranched alkenes at a moderate rate at 25°.[2] In the study reported here rates of reaction of representative unbranched acyclic and cyclic olefins were determined. The results constitute the first quantitative information on reactivity as a function of olefin structure for addition of acids to unbranched olefins. Analysis of the products defined several features of the reaction path.

In the previous study[2] the approximate rate of addition of trifluoroacetic acid to 1-hexene at 25° was measured by a gas chromatographic method. In the present work rates of disappearance of various hexenes and cycloalkenes were measured by an iodine monobromide titrimetric method. The first order rate constants observed for the addition of trifluoroacetic acid to the various olefins are presented in Table I.

TABLE I

RATES OF ADDITION OF TRIFLUOROACETIC ACID TO HEXENES AND CYCLOALKENES AT 35°[a]

Olefin	$K \times 10^4$, sec.$^{-1}$
Cyclopentene	6.01
Cyclohexene	5.18
Cycloheptene	19.1
Cyclooctene	42[b]
1-Hexene[c]	2.35
cis-2-Hexene	3.02
trans-2-Hexene	1.66
cis-3-Hexene	3.99[d]
trans-3-Hexene	2.62

[a] The initial concentrations were 0.125 *M* in sodium trifluoroacetate and 0.1 *M* in olefin. Duplicate determinations were made. [b] This value may be in error by as much as 15% due to the formation of unreactive dimer as discussed in the Experimental. [c] $K \times 10^4$ in the absence of sodium trifluoroacetate was 2.30. Addition of 0.025 or 0.05 *M* sodium trifluoroacetate reduced the rate constant from 2.35 to 2.01×10^{-4}. Rate constants were independent of the salt concentration within the experimental precision, 5–10%. [d] Evaluated from the initial slope. The curved plot obtained in this case was attributed to isomerization of *cis*-3-hexene to *trans*-3-hexene or to 2-hexene.

From the observed Markownikoff orientation in the addition of trifluoroacetic acid to 1-hexene[2] and from the rate retardations observed for olefins containing electron-attracting substituents[3] it is clear that the addition reactions reported here are of the expected type involving addition of a proton to the olefin to give a cationic intermediate or transition state, as illustrated in Fig. 1 for cyclopentene.

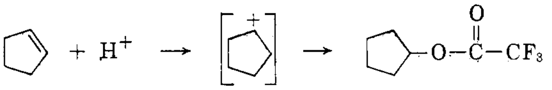

Fig. 1.—Addition of trifluoroacetic acid to cyclopentene

Discussion of Rates.—In the case of the cyclic olefins the most notable feature of the results is the fast rate of reaction observed for cycloheptene and cyclooctene, the latter of which exhibited a half-life of only 2.8 minutes, compared to 22.3 minutes for cyclohexene. In this connection it is of interest that the rate of solvolysis of cyclooctyl tosylate in acetic acid is larger than that of cyclohexyl tosylate by a factor of 191 at 70°.[4] Possible explanations of the fast rate of tosylate solvolysis are that (1) relief of steric strain (due to eclipsed hydrogens and other interactions) occurs in going from the saturated tosylate to a transition state resembling a trigonal carbonium ion[4,5] and (2) the rate may be enhanced by transannular hydrogen participation.[5] In the present case, addition to cyclooctene probably involves conversion of the olefin with two trigonal atoms to a cationic intermediate having one trigonal atom, followed ultimately by formation of a sterically unfavorable saturated cyclooctane derivative. This sequence presumably involves increasing steric repulsions at each stage.[6] Conceivably the steric interactions just mentioned would increase the energy of the transition state for addition and lead to a low rate. Since this result is not found it

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[1] (a) This paper is based in part on the M.S. research of G. Allen. (b) Presented at the 139th Meeting of the American Chemical Society, St. Louis, Mo., March, 1961.

[2] P. E. Peterson, *J. Am. Chem. Soc.*, **82**, 5834 (1960).

[3] P. E. Peterson and G. Allen, unpublished work.

[4] H. C. Brown and G. Ham, *J. Am. Chem. Soc.*, **78**, 2735 (1956).

[5] R. Heck and V. Prelog, *Helv. Chim. Acta*, **38**, 1541 (1955).

[6] The conversion of methylcycloalkenes to methylenecycloalkanes is also attended by a conversion of two trigonal carbons in the ring to one trigonal carbon in the ring. The very small equilibrium percentage of exocyclic isomer present at equilibrium in the case of the eight-, nine- and ten-membered rings has been attributed to the increased steric repulsions expected in the exocyclic isomer with only one trigonal center; see A. C. Cope, D. Ambros, E. Ciganek, C. F. Howell, and Z. Jacura, *J. Am. Chem. Soc.*, **82**, 1750 (1960). It should be noted, however, that in this case the seven-membered ring did not show the effect; furthermore, entropy effects made important contributions to the observed equilibrium constants.

seems likely that either steric factors are not reflected in the transition state for olefin additions (*cf.*, ref. 6) or that other factors (such as hydrogen participation, solvation energies, and entropy effects) are more important. Considering the cyclic olefins as a group it may be noted that the reactivity variation as a function of ring size is considerably smaller than in the case of tosylate solvolyses. Furthermore, the reactivity appears to be controlled by different factors or a different combination of factors from those affecting the formation of silver complexes or iodine complexes[7] or those affecting the heats of hydrogenation[8] or rates of addition of bis-3-methyl-2-butylborane[9] to cycloalkenes.

In the case of the acyclic olefins the reactivity variation as a function of structure is not large, but it may be noted that the *cis* olefins reacted faster than the corresponding *trans* isomers and that the 3-hexenes reacted faster than the corresponding 2-hexenes. The latter effect may be a manifestation of the greater stability of the 3-hexyl cation compared to the 2-hexyl cation as indicated by the rates of the corresponding tosylate solvolyses.[2] Only 3-hexene would give exclusively 3-hexyl cations upon addition of a proton.

Isomerization and Hydride Shift in the Addition of Trifluoroacetic Acid to 1-Hexene.—It was of interest to know whether the 2-hexyl cation formed from 1-hexene was identical with that formed from the solvolysis of 2-hexyl tosylate, since the reactions of secondary cations formed by solvolysis reactions are frequently (if not always) influenced by interactions with the leaving group. It was thought to be possible that, due to the low nucleophilicity of trifluoroacetic acid, the cationic intermediates from tosylate solvolyses in trifluoroacetic acid might react relatively slowly, allowing the tosylate group to be replaced by a solvent molecule to give the same solvated ion obtained from the addition of trifluoroacetic acid to the appropriate alkene. Accordingly, the per cents of elimination and hydride shift undergone by the 2-hexyl cation formed from 1-hexene (*cf.*, Fig. 2) were studied for comparison with the results from 2-hexyl tosylate solvolysis.

In order to find the relative amounts of reaction *via* the pathways shown in Fig. 2, the composition of the esters obtained from 1-hexene after a small per cent of reaction was determined (Table II), and the composition of the esters obtained from the other hexenes after complete reaction was determined (Table III), by gas chromatographic analysis.[9]

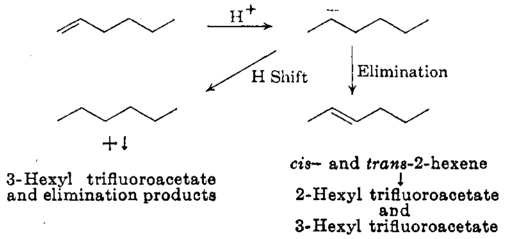

Fig. 2.—Modes of formation of 3-hexyl trifluoroacetate

TABLE II

VARIATION OF COMPOSITION OF TRIFLUOROACETATES FROM ADDITION OF TRIFLUOROACETIC ACID TO 1-HEXENE

Time (Min.)	3-Hexyl Trifluoroacetate, %
5[a]	10
10	12
14	9
50	14
100	17
1500	24

[a] The per cent reaction after 5 min. was 4.4% based on the measured rate constant, 1.50×10^{-4} sec.$^{-1}$, for this experiment at 0.5 *M* initial hexene concentration and 0.125 *M* sodium trifluoroacetate concentration in trifluoroacetic acid at 35°. The values obtained after five, ten, and fourteen minutes are regarded as being identical within experimental error. The hexyl trifluoroacetates were not isomerized under the reaction conditions.

TABLE III

COMPOSITION OF TRIFLUOROACETATES FROM ADDITION OF TRIFLUOROACETIC ACID TO HEXENES

Alkene	3-Hexyl Trifluoroacetate, %[a]
1-Hexene	23
cis-2-Hexene	58
trans-2-Hexene	58
cis-3-Hexene	78
trans-3-Hexene	77

[a] The other component is 2-hexyl trifluoroacetate.

The 3-hexyl trifluoroacetate present in the ester products formed from 1-hexene after a small per cent of reaction arises predominantly *via* the hydride shift pathway (Fig. 2), since at this early stage of reaction there is not yet enough 2-hexene (elimination product, Fig. 2) formed to contribute an appreciable proportion of 3-hexyl trifluoroacetate *via* the alternate pathway of addition to 2-hexene. The first entries in Table II accordingly show that about 10% of hydride shift occurred in the substitution products formed from the 2-hexyl cation which was formed in turn from 1-hexene.[10] This is considerably less than the value (22%) found for tosylate solvolysis.[2]

Accordingly the remaining 14% (24 − 10%) of 3-hexyl trifluoroacetate present after complete reaction must have arisen *via* addition to 2-hexene (or 3-hexene), since the hexyl trifluoroacetates were shown to be stable under the reaction conditions. The amount of 2-hexene which would have yielded this amount of 3-hexyl trifluoroacetate is 24% as calculated from the 58% yield reported in Table III. (Gas chromatographic evidence for the pres-

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[7] J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959).

[8] R. B. Turner and W. R. Meador, *ibid.*, **79**, 4133 (1957).

[9] H. C. Brown and A. W. Moerikofer, *ibid.*, **83**, 3417 (1961).

[9] A referee has suggested that 1,3-hydride shifts might explain our results. It has now been shown that 1,3-shifts are relatively unimportant compared to 1,2-shifts in addition of trifluoroacetic to 1-heptene (P. E. Peterson and R. E. Kelley, Jr., unpublished work). These results support the scheme of Fig. 2.

ence of 2-hexene is given in the Experimental.) Based on the assumption that 2-hexene would be the major elimination product from a 2-hexyl cation the per cent of elimination undergone by the cationic intermediate formed from 1-hexene must have been smaller (only slightly more than 24%) than that observed in the 2-hexyl tosylate solvolysis (86%). It may be concluded that contrary to the idea advanced earlier, trifluoroacetic acid as a solvent does not cause tosylate solvolysis and olefin addition reactions to proceed entirely *via* the same intermediate ion.

The comparatively small percentage of hydride shift and of elimination observed for the cationic intermediate from addition of trifluoroacetic acid to 1-hexene might be explained if both the tosylate solvolysis and olefin addition reactions proceed *via* an "encumbered"[11] 2-hexyl cation of the type shown below (Fig. 3). Here X and Y are both trifluoroacetic acid molecules (or trifluoroacetate ions) in the case of addition of trifluoroacetic acid to 1-hexene, while in the tosylate solvolysis reaction one of these groups is a toluenesulfonic acid molecule (or toluenesulfonate ion). On a statistical basis the ion in the latter reaction would be only half as likely as that in the former to react to form 2-hexyl trifluoroacetate, while the probability for hydride shift or for elimination of a proton to give an olefin might be similar in both cases. It is interesting that a similar cation specifically solvated with two solvent molecules has been proposed as the intermediate in the hydration of 1-butene and 2-butene and in the acid-catalyzed dehydration of 2-butanol in water.[12] Manassen and Klein believe that their proposed intermediate is different from that proposed by Taft for the hydration of isobutene, but in view of the recent modification of the Taft mechanism which involves the inclusion of an unspecified number of water molecules in the intermediate[11] it is not clear whether more than one mechanism is required to encompass the results obtained for branched and unbranched olefins.

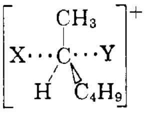

Figure 3

Effects of Added Acids and Bases.—The effect of added acids and bases on the rate of addition of trifluoroacetic acid to 1-hexene was briefly investigated. In the presence of added sulfuric acid and sodium hydrogen sulfate monohydrate the reaction was too fast to measure at 35°. The reaction rate was relatively insensitive to variation in concentration of added sodium trifluoroacetate as shown by the data in Table II. In a sample of redistilled trifluoroacetic acid the rate was essentially the same as that observed in the presence of sodium trifluoroacetate, but in a sample of unredistilled acid a 10% larger rate was observed. When the acidity of the latter acid was qualitatively tested using 2-nitrodiphenylamine as an indicator, the presence of a trace of strong acid was indicated. Accordingly subsequent rate determinations were carried out in distilled trifluoroacetic acid 0.125 *M* in sodium trifluoroacetate in order to ensure the absence of adventitious traces of acid.

The effect of added water was of interest, since small amounts of water in formic acid may change rates of acid-catalyzed reactions by factors of approximately ten,[13] and rates of acid-catalyzed reactions in acetic acid containing added strong acid are likewise strongly affected by traces of water.[14,15] Rates of addition of trifluoroacetic acid to 1-hexene were determined for solutions containing up to 16 ml. of added water per 100 ml. of solution, with the results shown in Fig. 4. As can be seen from Fig. 4, addition of up to 12 ml. of water per 100 ml. changed the rate constant for addition of trifluoroacetic acid to 1-hexene by a factor of approximately 1.5 or less. With increasing amounts of water the rate first increased and then decreased, approaching the unobservably small value expected for unbranched olefins in dilute aqueous solutions.

The general ease of manipulation resulting from the relative insensitivity of the rates of addition to

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(10) These statements are based on the assumption that the first two or three determinations in Table II were made at a sufficiently early time. The relatively constant value of the first three entries in Table II are an indication that such is the case, but the following more complex argument shows more conclusively that the assumption is true. As a first step in the argument, a maximum value will be found for the per cent elimination to 2-hexene, compared to substitution plus elimination to 2-hexene, undergone by the 2-hexyl cations formed from 1-hexene (in Fig. 2 the substitution reaction is not shown). To obtain this value it is temporarily assumed that all of the 24% of 3-hexyl trifluoroacetate present after complete reaction of 1-hexene arises *via* addition to 2-hexene (one of the two pathways in Fig. 2). The amount of 2-hexene which would have led to such a result is only 41%, based on the 58% yield of 3-hexyl trifluoroacetate reported in Table III. Accordingly the maximum ratio of elimination (to 2-hexene) to substitution undergone by the 2-hexyl cation is 41:59. Next it is noted that the five-minute analysis from Table II was made when 4.4% of ester had been formed; accordingly a maximum of about 3% of 2-hexene could have been present at this time, based on the 41:59 ratio just mentioned.

The *average* olefin composition over the five-minute period of reaction must have been at least about 98.5% of 1-hexene. Since the various hexenes react with trifluoroacetic acid at similar rates, the trifluoroacetates present at this stage must have been formed to an extent of about 98.5% directly from 1-hexene. The amount of 3-hexyl trifluoroacetate which would have been formed from the 1.5% of *cis*- or *trans*-2-hexene is only 0.9% based on the 58% yields shown in Table III. Accordingly the five-minute value of Table I represents the per cent of direct hydride shift in the cationic intermediate formed from 1-hexene. Actually this is also true of the ten-minute point, as can be shown by carrying through the same argument using the better value for per cent elimination which can be obtained (see discussion which follows) as soon as the per cent hydride shift is known.

(11) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *J. Am. Chem. Soc.*. **82**, 4729 (1960).

(12) J. Manassen and F. S. Klein, *J. Chem. Soc.*, 4203 (1960).

(13) P. D. Bartlett, C. E. Dills, and H. G. Richey, Jr., *J. Am. Chem. Soc.*, **82**, 5414 (1960).

(14) H. J. Gebhart, Jr., and K. H. Adams, *ibid.*, **76**, 3925 (1954).

(15) The trifluoroacetic acid used in the study reported here may have contained small amounts of water.

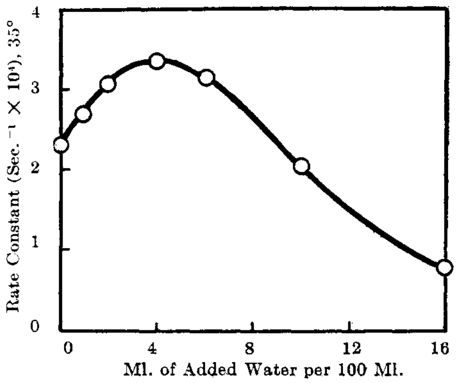

Fig. 4.—Effect of water upon rate of addition of trifluoroacetic acid to 1-hexene

changes in water concentration and trifluoroacetate ion concentration was one of the more striking features of the present investigation.

Experimental

Rate Determinations.—1-Hexene and cyclohexene were obtained from the Phillips Petroleum Co. *trans*-2-Hexene and *trans*-3-hexene were prepared by the published methods[16] involving reduction of the alkynes with sodium and ammonia. In our hands the volatile hexenes were lost unless a liquid ammonia filled cold finger condenser having a tube for removing condensate was used during the product isolation step. *cis*-2-Hexene and *cis*-3-hexene were prepared by the published methods[16] using the alkyne and Raney nickel. A commercial sample of cyclopentene turned deep red upon addition of trifluoroacetic acid. A sample prepared by pyrolysis of cyclopentanol turned light red. Accordingly, the latter material was distilled from a small amount of trifluoroacetic acid to give material which remained colorless upon addition of trifluoroacetic acid. Cycloheptene was obtained by phosphoric acid-catalyzed dehydration[17] of cycloheptanol. Cyclooctene was obtained from Light and Co., Colnbrook, Bucks, England. Other samples were obtained by hydrogenation of 1,5-cyclooctadiene and by phosphoric acid-catalyzed dehydration of cyclooctanol. All samples had similar infrared spectra and all showed the presence of small amounts of impurities upon gas chromatography. Trifluoroacetic acid (Matheson, Coleman and Bell or Allied Chemical) was distilled through a Vigreux column. Sodium trifluoroacetate was prepared by neutralization of the acid and evaporation of water in a vacuum desiccator. Iodine monobromide (Hanus reagent) was prepared by dissolving weighed amounts of iodine and bromine in acetic acid, omitting the adjustment to exactly equal amounts of iodine and bromine.[18] For a rate determination a sample of alkene suitable for preparing a 0.1 *M* solution was weighed in a 10- or 25-ml. volumetric flask, brought to 35.0°, and diluted to the volume of the flask with trifluoroacetic acid 0.125 *M* in sodium trifluoroacetate, also at 35°. Temperatures were measured on a thermometer calibrated by the Bureau of Standards. Aliquots (2 or 3 ml.) were withdrawn at intervals and added to 10 ml. of Hanus solution (0.05 molar in halogen) in 10 ml. of carbon tetrachloride. After 30 min., 10 ml. of 15% potassium iodide and 100 ml. of water was added, and the mixture was titrated with standard sodium thiosulfate.

Product Studies.—The relative amounts of 2-hexyl trifluoroacetate and 3-hexyl trifluoroacetate formed by addition of trifluoroacetic acid to the various hexenes was determined by gas chromatography as described previously.[2] In the case of the cyclic alkenes studies were confined to the product formed by reaction of cyclooctene with trifluoroacetic acid. This study was prompted by the finding that addition of trifluoroacetic acid to cyclooctene yielded a product containing double bonds which did not react with trifluoroacetic acid, but which did add halogen as shown by the titrimetric olefin determinations used in this study. In three determinations of the rate of addition of trifluoroacetic acid to cyclooctene the mole per cent of double bonds (per mole of cyclooctene used) determined after complete disappearance of cyclooctene was 16, 13, and 13%. These results and others given below can be explained by the assumption that some acid-catalyzed dimerization of cyclooctene occurred to produce 1-cyclooctylcyclooctene or cyclooctylidenecyclooctane which was too sterically hindered to add trifluoroacetic acid. In the determination of the rate constant for addition of trifluoroacetic acid to cyclooctene it was assumed that the unreactive dimer was all formed at the beginning of the rate determination when the olefin was present as a separate phase prior to the mixing of the reactants in the volumetric flask. Since this assumption may not be valid, the cyclooctene rate constant (Table II) is not as accurate as the constants for the other olefins.

Further characterization of the postulated dimer of cyclooctene was accomplished in a preparative experiment. Cyclooctene (22 g.) was added to 25 ml. of 0.125 *M* sodium trifluoroacetate in trifluoroacetic acid at 35°, and the mixture was diluted to 100 ml. with trifluoroacetic acid. Occasionally the mixture was removed from the 35° bath and shaken. The upper layer (initially cyclooctene) decreased in volume as the reaction mixture was shaken at intervals, and after 24 hr. had become slightly viscous and contained no cyclooctene (as shown by gas chromatography in a previous, preliminary experiment). The top layer was separated by means of a pipet; the 2.98 g. of material was washed with water and dried with magnesium sulfate to give a clear liquid. A sample was titrated with iodine monobromide. The apparent molecular weight based on the assumption that one double bond per molecule was present was found to be 208, compared to a value of 224 calculated for cyclooctylcyclooctene. A small amount of trifluoroacetate ester was present in the product, as shown by bands in the infrared spectrum at 1770, 1130, and 1215 cm.$^{-1}$. The discrepancy in the observed and expected molecular weights is in the direction to be expected if a small amount of diene was present in the dimer.

A second preparative experiment was carried out under conditions designed to maintain the cyclooctene concentration at a low value throughout the period of reaction. Cyclooctene (55 g.) was added dropwise with stirring to 100 ml. of trifluoroacetic acid and 5 ml. of 0.125 *M* sodium trifluoroacetate in trifluoroacetic acid at 70°. The addition required 1 hr. The product was cooled and washed with 100- and 10-ml. portions of 2 *M* potassium carbonate, dried with magnesium sulfate, and distilled to give 75.5 g. (67%) of cyclooctyl trifluoroacetate, b.p. 57–67° (3.4. mm.), which had an infrared spectrum identical with that of an authentic sample prepared from cyclooctanol and trifluoroacetic anhydride. The pot residue amounted to 7.84 g., and 8.83 g. of volatile material was collected from the Dry Ice–acetone cold trap. The latter material may have consisted of cyclooctane and bicyclo[3.3.0]octane in addition to any unchanged cyclooctene. Short path distillation of the pot residue at 1 mm. and a bath temperature of 230° or less gave 3.04 g. of material whose infrared spectrum was similar to that of the undistilled dimer reported above. Iodine monobromide titration gave an apparent molecular weight of 201. The volatility of the pot residue supports the formulation of this material as, in part, a dimer of cyclooctene.

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[16] K. N. Campbell and L. T. Eby, *J. Am. Chem. Soc.*, **63**, 216, 2683 (1941).

[17] A. C. Cope and P. E. Peterson, *ibid.*, **81**, 1643 (1959).

[18] A. Polgar and J. L. Jungnickel in "Organic Analysis," Vol. 3, Interscience Publishers, Inc., New York, 1956, pp. 224–225.

Isomerization of 1-Hexene.—Addition of trifluoroacetic acid 0.125 *M* in sodium trifluoroacetate to 1-hexene (initially 0.5 *M*) was carried out at 35°. Aliquots were removed after 5, 80, 170, and 240 min. and poured into an excess of 2 *M* potassium carbonate. The resulting solutions were extracted with small amounts of diethyl adipate in order to obtain the unchanged hexenes in a nonvolatile solvent. Gas chromatography of the solutions on an adiponitrile-firebrick column gave two peaks attributable to 1-hexene (or a mixture of 1-hexene and *trans*-2-hexene) and *cis*-2-hexene. The approximate amounts of the latter were 0, 10, 10, and 14%, respectively, for the aliquots mentioned above.

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The Disproportionation of Ethylbenzene-1-C_1^{14} under the Influence of Aluminum Bromide and Hydrogen Bromide[1]

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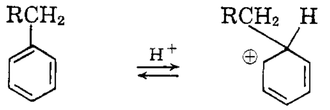
Ethylbenzene-1-C_1^{14} was disproportionated under the influence of aluminum bromide–hydrogen bromide at 0°. The distribution of activity in the benzene ring in ethylbenzene-C_1^{14} isolated from the reaction mixture after partial disproportionation indicates that a rapid prior equilibrium between ethylbenzene and its localized π-complex is not operative. The rearranged activity was found predominantly in the *meta* and *para* positions. A further necessary condition for this observation is that transalkylation (intermolecular shift of an ethyl group) is more rapid than intramolecular isomerization in ethylbenzene.

The general subject of the reactivity of alkyl substituted benzenes in the presence of Lewis acids or strong proton acids toward alkylating agents or in disproportionation studies has received wide interest in the literature. These reactions can all be considered to be examples of intra- or intermolecular alkylations and have numerous features in common.

The particular question of the mechanism of disproportionation reactions in alkylbenzenes has been carefully studied by Lien and McCaulay[3–5] and by Brown and Smoot.[6] Recently Streitwieser and Reif[7] have suggested another mechanism as possibly being operative in disproportionation reactions.

Studies which bear on the different aspects of the mechanism have been carried out by Roberts and co-workers.[8–10] This group has considered the question of rearrangements in the alkyl side chain during disproportionation by using carbon-14-labeled side chains. It had been demonstrated by Kinney[11] that there is no gross isomerization of an *n*-butyl group in the disproportionation of *n*-butylbenzene at 100° using aluminum chloride. The allied subject of "mixed" disproportionation[12] and alkylation[13,14] has been related to the disproportionation reaction in terms of reaction intermediates. Related intermediates can also be found to be suggested in the isomerization reactions of alkylbenzenes.[15–17] The intra- *vs.* intermolecular nature of the isomerization reactions has recently been investigated further by Allen.[18–21]

The mechanism proposed by McCaulay and Lien involved the formation of a sigma complex (stabilized by resonance) by addition of a proton from the strong proton acid HBF_4 (or $HF \cdot BF_3$) (equation 1)



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[1] Research performed under the auspices of the U. S. Atomic Energy Commission.

[2] International Coop. Administration Fellow, Brookhaven National Laboratory, 1958–1959.

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[7] A. Streitwieser, Jr., and L. Reif, *J. Am. Chem. Soc.*, **82**, 5003 (1960).

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[13] H. C. Brown and H. Jungk, *J. Am. Chem. Soc.*, **78**, 2182 (1956).

[14] H. Jungk, C. R. Smoot, and H. C. Brown, *J. Am. Chem. Soc.*, **78**, 2185 (1956).

[15] G. Baddeley, G. Holt, and G. Voss, *J. Chem. Soc.*, 100 (1952).

[16] (a) D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246 (1952). (b) *Cf.* D. A. McCaulay and A. P. Lien, *J. Am. Chem. Soc.*, **73**, 2013 (1951) for relative basicities of the methylbenzenes.

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