of β-bromoethylbenzene. During the addition the temperature rose to, but not over, 20°. After one hour the reaction mixture was poured onto ice with stirring to precipitate the sulfonyl chloride which was washed with ice-water and taken up in ether. The ether solution was washed with dilute sodium bicarbonate and dried. The residue remaining on evaporation of the ether was dissolved in 350 ml. of cold 95% ethanol. To this solution was added slowly a solution of 224 g. of potassium hydroxide in one l. of 95% ethanol. This reaction mixture was refluxed one hour and filtered. The solid thus collected was washed with an additional 500 ml. of hot ethanol and filtered. The combined filtrates were cooled to −20° to precipitate the crude product. This crude product was taken up in the minimum quantity of hot water and filtered. The filtrate was extracted with benzene and cooled to precipitate the product. A final recrystallization from 95% ethanol gave 66.5 g. (30%) of potassium *p*-vinylbenzenesulfonate.

Anal. Calcd. for $C_8H_7KO_3S$: S, 14.42. Found: S, 14.37.

The monomer was stored at −20° and recrystallized from ethanol just prior to use. It was free from halide ion and was converted to its toluidine salt, m.p. 189–190°.

Anal. Calcd. for $C_{15}H_{17}NO_3S$: neut. equiv., 291.35. Found: neut. equiv., 290.8.

Polymerization of Potassium *p*-Vinylbenzenesulfonate in Dimethylformamide Solution.—A solution of 1.56 g. of potassium *p*-vinylbenzenesulfonate and 0.156 mg. (0.01%) of *t*-butyl peracetate in 15 ml. of dimethylformamide was heated under an oxygen-free nitrogen atmosphere at 109° for 22 hours. The polymer began to precipitate from the solution within 10 minutes at reaction temperature. The precipitated polymer, along with an additional amount of polymer precipitated by the addition of an equal volume of ether, was washed with ether and vacuum dried to give 1.5 g. of polymer. This procedure was repeated using 1.56 mg. (0.1%) and 15.6 mg. (1.0%) of *t*-butyl peracetate initiator.

All of these polymers were hygroscopic solids soluble in water and alcohol. Viscosities were determined on samples vacuum dried at 56° to constant weight. The viscosity data are given in Fig. 1. The addition of 9–17% of divinylbenzene to this polymerization procedure gave cross-linked, insoluble polymers.

Cross-linked Copolymers of Styrene and Potassium *p*-Vinylbenzenesulfonate.—A mixture of 6.66 g. (0.03 mole) of potassium *p*-vinylbenzenesulfonate, 0.77 g. (0.00592 mole 10%) of divinylbenzene, 0.43 g. (0.00408 mole) of styrene, 100 ml. of dimethylformamide and 0.78 mg. (0.01%) of *t*-butyl peracetate was heated at 89° with stirring under oxygen-free nitrogen for 22 hours. All ingredients had dissolved within 5–10 minutes and the copolymer began to precipitate in 25–30 minutes. The precipitate, along with an additional quantity of polymer precipitated by the addition of ether, was washed with ether and dried to give 7.15 g. of the 75/25 copolymer.

Using a similar procedure but with varying quantities of monomers 6.41 g. of 50/50 copolymer and 10.03 g. of 25/75 copolymer were obtained. The 50/50 copolymer was also prepared without addition of the ether-precipitated copolymer in 6.07 g. yield.

The capacities and swelling ratios of these copolymers were determined as previously described.[1] Difficulties were encountered in converting these resins to the acid form because they were too fine to wash in a column. The degree of swelling was also determined by weighing the resins before and after swelling with water to determine the weight of water absorbed.

TABLE I

Copolymer composition[a]	Yield, %	Swelling ratio	Capacity Calcd.	Capacity Obsd.	Sulfur Calcd.	Sulfur Found
75/25	91	6.3	4.56	4.18	14.63	14.22, 14.08
50/50	94	4.1	3.47	3.53	11.11	11.35, 11.40
50/50[b]	91	..	3.47	3.49	11.11	11.45, 11.63
25/75	92	3.3	2.02	2.03	6.67	6.69, 6.84

[a] The ratio is that of the moles of potassium *p*-vinylbenzenesulfonate to moles of styrene plus moles of divinylbenzene. [b] Without added ether precipitated copolymer.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Heats of Reaction of Pyridine and Nitrobenzene with Boron Trifluoride, Trichloride and Tribromide; the Relative Acceptor Properties of the Boron Halides[1,2]

BY HERBERT C. BROWN AND ROBERT R. HOLMES[3]

RECEIVED OCTOBER 27, 1955

The 1:1 molecular addition compounds of boron trifluoride, trichloride and tribromide with pyridine and of the trichloride and tribromide with nitrobenzene were prepared and characterized. The molar heats of reaction of the three boron halides with nitrobenzene were determined, calorimetrically in the case of the chloride and bromide, and from Henry's law constants in the case of the fluoride. The molar heats of reaction of pyridine with these boron halides in nitrobenzene solution were also determined calorimetrically. From the resulting data, the relative bond dissociation energies of the pyridine–boron trihalides addition compounds were calculated, providing a measure of the relative strengths of the boron trihalides as Lewis acids. The results reveal that the acceptor properties increase in the order: $BF_3 < BCl_3 < BBr_3$. The order is opposite to that which would be predicted on the basis of the relative electronegativities of the halogens and suggests that resonance contributions must play a dominant role in determining the relative acceptor properties of the boron halides.

The boron trihalides are typical Lewis acids or electron-pair acceptors. Numerous 1:1 molecular addition compounds formed by the reaction of these halides with organic bases have been described.[4,5]

An examination of the available data suggests that the coördinating ability of the boron halides must increase with increasing atomic weight of the halogen, $BF_3 < BCl_3 < BBr_3 < [BI_3]$. For example, no evidence could be found for the existence of a compound between boron trifluoride and arsine, even at temperatures as low as −120°,[6] whereas addition compounds of arsine with boron trichloride[7] and boron tribromide[8] are stable with respect to dissociation at temperatures near 0°. Similarly, phosphorus trichloride forms a 1:1 addition com-

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[1] The Catalytic Halides. XIV.

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

[3] Research assistant (1951–1953) on a grant from the Atomic Energy Commission for the study of "Chemistry of Polyvalent Metal Halides."

[4] H. S. Booth and D. R. Martin, "Boron Trifluoride and Its Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1949.

[5] D. R. Martin, *Chem. Revs.*, **34**, 461 (1944).

[6] D. R. Martin and R. Dial, THIS JOURNAL, **72**, 852 (1950).

[7] A. Stieber, *Compt. rend.*, **195**, 610 (1932).

[8] A. Stock, *Ber.*, **34**, 949 (1901).

pound with boron tribromide, but fails to react with either the corresponding fluoride or chloride.[9]

On the basis of the relative electronegativities of the various halogens, the opposite order would have been predicted for the relative acid strengths of the boron trihalides. Accordingly, it appeared of interest to investigate the phenomenon further by obtaining quantitative data for the reaction of the boron halides with typical organic bases. In pursuit of this objective the molar heats of reaction of boron trifluoride, trichloride and tribromide with nitrobenzene and with pyridine have been measured. In the course of the study various molecular addition compounds of the boron halides with these bases have been prepared and characterized.

Results

The solubility of boron trifluoride in nitrobenzene is quite high, far greater than would be expected for an inert solute. This suggests the probable formation of an unstable 1:1 addition compound between the two components. However, the dissociation pressure must be quite high, considerably greater than could be handled in the glass vacuum apparatus. We therefore made no further attempt to isolate this derivative.

The remaining addition compounds were synthesized by mixing the two components at low temperatures, with the more volatile component in excess, and then removing the excess of the more volatile component at an appropriate temperature. Only 1:1 compounds were observed to form at room temperature.[10]

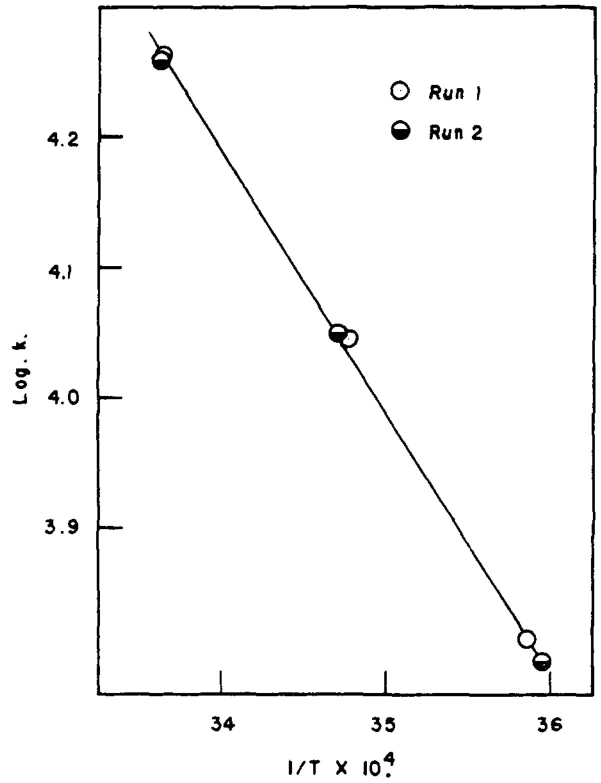

Fig. 1.—Variation with temperature of the Henry's law constants for the solubility of boron trifluoride with temperature.

The pyridine derivatives are white, crystalline solids with sharp melting points, whereas the nitrobenzene products are yellow and melt with dissociation or decomposition. The observed data are summarized in Table I.

TABLE I

PHYSICAL CONSTANTS FOR THE 1:1 MOLECULAR ADDITION COMPOUNDS OF NITROBENZENE AND PYRIDINE WITH THE BORON HALIDES

Compound–boron halide	M.p., °C.	Vapor pressure Mm.	Vapor pressure °C.
Nitrobenzene– trifluoride	[d]		
Nitrobenzene– trichloride[a]	57–58 (dissoc.)	95	25.5
Nitrobenzene– tribromide	63–64 dec.	8	24.5
Pyridine– trifluoride[b]	47–48		
Pyridine– trichloride[c]	113–114		
Pyridine– tribromide	128–129		

[a] M.p. 45–47°: C. Kinney and C. Mahoney, *J. Org. Chem.*, 8, 526 (1943). [b] M.p. 45°: P. A. van der Meulen, and H. A. Heller, THIS JOURNAL, 54, 4404 (1932). [c] M.p. 114.5–115.0°: W. Gerard and M. F. Lappert, *J. Chem. Soc.*, 1020 (1951). [d] Highly dissociated at 25°.

In a sealed ampule, nitrobenzene–boron tribromide melts at 63–64° to a red liquid. After a minute or so at 65–70°, the red liquid solidifies to a red solid. The change is irreversible. After a day or two, the sample loses its red color and becomes light tan. This phenomenon was not examined further.

The solubility of boron trifluoride in nitrobenzene was measured at several temperatures and the data used to calculate the heat of solution. Typical results are summarized in Table II and shown graphically in Fig. 1.

TABLE II

MEAN VALUES OF THE HENRY'S LAW CONSTANTS FOR BORON TRIFLUORIDE IN NITROBENZENE

Determination 1		Determination 2	
Temp., °C.	Henry's law constant k, mm. $\times 10^{-3}$	Temp., °C.	Henry's law constants k, mm. $\times 10^{-3}$
5.68	6.51	5.25	6.25
14.50	11.1	15.03	11.2
24.10	18.3	24.10	18.1

The heats of solution of liquid boron trichloride and bromide in dilute nitrobenzene solution (0.1 to 0.2 *M*) were determined calorimetrically. The results are summarized in Table III.

TABLE III

MOLAR HEATS OF SOLUTION OF THE BORON HALIDES IN NITROBENZENE AT 25°

Halide	Heat of solution, $-\Delta H$, kcal./mole
Boron trifluoride (g.)	9.24 ± 0.12[a]
Boron trifluoride (liq.)	6.7 ± .5[b]
Boron trichloride (liq.)	8.7 ± .2
Boron tribromide (liq.)	12.5 ± .2

[a] *From Henry's law constants (Table II).* [b] Calculated using a value of 2.5 kcal./mole for the heat of vaporization of boron trifluoride, as estimated from data for the heat of solution of boron trifluoride in *n*-pentane: M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 34, 11 (1938).

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(9) R. R. Holmes, Ph.D. Thesis, Purdue Univ., 1953.

(10) It has recently been observed that at lower temperatures (−30 to −80°) the addition compounds of pyridine with the boron halides are capable of adding a second mole of the boron halide.

The heats of reaction of pyridine with boron trifluoride in nitrobenzene solution had been determined previously to be 25.0 kcal./mole.[11] We measured, therefore, the heats of reaction of pyridine (in nitrobenzene solution) with boron trichloride and boron tribromide (each in nitrobenzene solution). The results are summarized in Table IV.

TABLE IV

MOLAR HEATS OF REACTION OF THE BORON HALIDES WITH PYRIDINE IN NITROBENZENE SOLUTION AT 25°

Halide	Heat of reaction, $-\Delta H$, kcal./mole
Boron trifluoride (ref. 11)	25.0 ± 1.0
Boron trichloride	30.8 ± 0.2
Boron tribromide	32.0 ± 0.2

Discussion

The various thermodynamic quantities are summarized in Table V. The high heats of solution of the boron halides in nitrobenzene must mean that the boron halides are essentially in the form of their addition compounds, $C_6H_5NO_2:BX_3$. Consequently, the data are presented as molar heats of reaction.

TABLE V

HEAT OF REACTION OF THE BORON HALIDES WITH NITROBENZENE AND WITH PYRIDINE AT 25°

Reaction	Heat of reaction, $-\Delta H$, kcal./mole
$BF_3(g) + C_6H_5NO_2(liq.) = C_5H_5NO_2:BF_3(soln.)$	9.24 ± 0.12
$BF_3(liq.) + C_6H_5NO_2(liq.) = C_6H_5NO_2:BF_3(soln.)^a$	6.7 ± .5
$BCl_3(liq.) + C_6H_5NO_2(liq.) = C_6H_5NO_2:BCl_3(soln.)$	8.7 ± .2
$BBr_3(liq.) + C_6H_5NO_2(liq.) = C_6H_5NO_2:BBr_3(soln.)$	12.5 ± .2
$BF_3(soln.) + C_5H_5N(soln.) = C_5H_5N:BF_3(soln.)$	25.0 ± 1.0
$BCl_3(soln.) + C_5H_5N(soln.) = C_5H_5N:BCl_3(soln.)$	30.8 ± 0.2
$BBr_3(soln.) + C_5H_5N(soln.) = C_5H_5N:BBr_3(soln.)$	32.0 ± 0.2
$BF_3(liq.) + C_5H_5N(soln.) = C_5H_5N:BF_3(soln.)$	31.7 ± 1.5
$BCl_3(liq.) + C_5H_5N(soln.) = C_5H_5N:BCl_3(soln.)$	39.5 ± 0.4
$BBr_3(liq.) + C_5H_5N(soln.) = C_5H_5N:BBr_3(soln.)$	44.5 ± 0.4

[a] The addition compound is probably somewhat dissociated in solution.

The heat evolved in the reaction of pyridine with the boron halide, with both components in nitrobenzene solution, must represent the heat of the displacement reaction

$$C_5H_5N + X_3B:O_2NC_6H_5 \longrightarrow C_5H_5N:BX_3 + C_6H_5NO_2$$

The large heats observed, in the neighborhood of 30 kcal./mole, provide a measure of the enormous difference in the strengths of the two bases, pyridine and nitrobenzene. The fact that the heat of this reaction increases from 25 kcal./mole for the fluoride, to 30.8 for the chloride, to 32.0 for the bromide is interesting. It suggests that the difference in the heats of reaction of two bases with Lewis acids may increase with increasing acid strength.

The gaseous state would be best for comparing the relative strengths of the three boron halides under consideration here. However, calculation of the heats of the reaction, $Base(g) + BX_3(g) \rightarrow Base:BX_3(g)$, would require a knowledge of the heats of sublimation of the various addition compounds. These data are not now available.

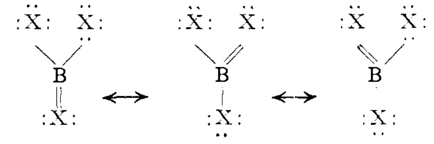
Since the boron halides are relatively non-polar liquids or gases, it appears that the liquid state of these materials should provide an alternative satisfactory reference state. Table V summarizes the available data for the reactions, $Base\ (soln.) + BX_3\ (liq.) = Base:BX_3\ (soln.)$.

It can be observed that with both nitrobenzene and pyridine as reference bases the heat of reaction increases with increasing atomic weight of the halogens. In other words, the acid strengths toward these bases increase in the order $BF_3 < BCl_3 < BBr_3$.

The electronegativities of the halogens decrease with increasing atomic weight. On the basis of the inductive effect the strongest acid would have been expected to be boron trifluoride, followed by the chloride and bromide in order.

The same order would have been anticipated on the basis of the various steric requirements of the different boron halides However, the bases utilized in the present study were selected so as to minimize this factor and steric effects presumably are not of importance in the present results.

In order to account for the observed order, it appears necessary to bring resonance in as the major contributing factor in influencing acid strength. The marked shortening of the boron–fluorine bond distance observed in boron trifluoride led Pauling to suggest that resonance structures of the following type must contribute strongly to boron trifluoride.[12]



Since resonance structures of this kind are not possible in the molecular addition compounds, such resonance will tend to reduce the tendency of the boron halide to add to a lone pair.

The ability to form double bonds appears to decrease sharply in the heavier elements. Resonance of this kind should be therefore of lesser importance in the chloride and still smaller importance in the bromide. It must be assumed that these resonance interactions are sufficiently large so as to reverse the trend expected from the relative inductive effects of the different halogens.

In the case of central atoms from later periods, such as aluminum and gallium, such resonance contributions should be smaller. In this case the order predicted on the basis of the inductive contributions of the halogens may be observed. Unfortunately, in these cases the comparison of acid strengths is rendered difficult by the internal association of the metal halides. However, we hope to undertake a study of this question.

Experimental Part

Materials.—Pyridine (Matheson) was distilled through a 52-plate column and stored over calcium hydride in sealed ampules. It was 99.9% pure as estimated from its cooling curve. It exhibited the following constants: b.p. 114.5° at 738 mm., m.p. −41.75°, $n^{20}D$ 1.5100.

Purification of the nitrobenzene has been previously described.[13]

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[11] H. C. Brown and R. H. Horowitz, THIS JOURNAL, **77**, 1730 (1955).

[12] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1948, p. 238.

[13] H. C. Brown and R. R. Holmes, THIS JOURNAL, **77**, 1727 (1955).

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.

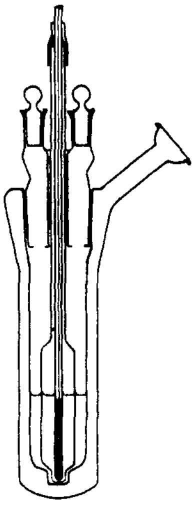

Fig. 2.—Silvered-wall, vacuum-jacketed calorimeter.

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]

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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).