sulfonic acid in nitrobenzene were made up with the aid of hypodermic syringes. The pyridine compound or methanesulfonic acid was drawn up into the syringe. This was weighed. Approximately the amount desired was transferred to a 250-ml. volumetric flask containing 200 ml. of nitrobenzene. The syringe and remaining contents were reweighed to obtain the precise amount transferred. The solution in the volumetric flask was then diluted to volume. These solutions were then transferred to the calorimeter by means of pipets, taking great precautions to minimize exposure to moisture.

The precision attained is indicated by the observed heats of reaction of methanesulfonic acid with 2-picoline in a series of eight different measurements: 18.44, 18.41, 18.35, 18.41, 18.31, 18.19, 18.08, 18.54 kcal./mole. These lead to the mean value of 18.34 ± 0.11 kcal./mole, reported as 18.3 kcal./mole in Table IV.

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Displacement Reactions. V. The Heat of Reaction of Pyridine with Boron Trifluoride. A Convenient Calorimeter for Measuring the Heat of Formation of Molecular Addition Compounds

BY HERBERT C. BROWN AND RAYMOND H. HOROWITZ[1,2]

RECEIVED JULY 8, 1954

A simple calorimeter has been developed for determining the heat of formation of molecular addition compounds in solution with an accuracy of 1%. The calorimeter has been applied to the determination in nitrobenzene of the heat of reaction of pyridine with boron trifluoride and with a number of addition compounds of boron trifluoride:

$$C_5H_5N(\text{soln.}) + BF_3(\text{soln.}) = C_5H_5N{:}BF_3(\text{soln.}) \quad -\Delta H = 25.0 \text{ kcal./mole}$$

$$C_5H_5N(\text{soln.}) + (CH_2)_5O{:}BF_3(\text{soln.}) = C_5H_5N{:}BF_3(\text{soln.}) + (CH_2)_5O(\text{soln.}) \quad -\Delta H = 12.2 \text{ kcal./mole}$$

It is convenient that the heat of the latter reaction is essentially independent of the concentration of the reactants over the range, 0.086 – 0.17 *M*. The heat of reaction increases to 14.1 and 15.9 kcal./mole for the corresponding addition compounds of ethyl and *n*-butyl ether. The heat of reaction of pyridine with benzonitrile–boron trifluoride and anisole–boron trifluoride are very similar to the value obtained with dissolved boron trifluoride, and it is concluded that these addition compounds must exist largely dissociated in the nitrobenzene solution.

The development of techniques for the precise determination of thermodynamic data for the dissociation of molecular addition compounds in the vapor phase has been described in earlier papers.[3] These techniques have been highly satisfactory in their application to the study of molecular addition compounds which exhibit a measurable dissociation in the vapor phase over a convenient temperature range.[4]

However, there exist many addition compounds which are either too stable or too unstable to be studied by this method. A calorimetric procedure which would permit the determination of the heats of formation in solution of molecular addition compounds which cannot be handled by the vapor phase technique should be very useful. Accordingly we decided to undertake the development of a simple calorimetric procedure which would permit the determination of the heats of formation with a precision of approximately 1%.

It was proposed to utilize the calorimeter for the estimation of the strains in selective series of addition compounds of pyridine bases containing bulky 2-alkyl substituents. These strains were to be compared with the strains estimated for the reactions of these pyridine bases with alkyl halides.[5] Since the data for the latter reactions were obtained with nitrobenzene as solvent, this substance was used also for the calorimeter studies.

The addition compound formed by pyridine and boron trifluoride is a compound of such low volatility that its study by vapor phase dissociation appears to offer major difficulties.[6] Moreover, the compound is very sensitive to moisture. Consequently, a study of the heat of formation of the compound was undertaken to provide a rigorous test of the proposed procedure.

Results and Discussion

The calorimeter which was finally developed consisted of a Dewar vessel in which there was a central receptacle which dipped into a small pool of mercury, thereby providing two compartments of equal volume for the solutions of the two reactants (Fig. 1). In the outer compartment there was placed a standard solution of pyridine in nitrobenzene; in the inner compartment, a solution of boron trifluoride in nitrobenzene or, preferably, a solution of tetrahydropyran–boron trifluoride in nitrobenzene. Since the concentration of the pyridine in the solution could be established with greater accuracy, the boron trifluoride component usually was used in excess.

The calorimeter was immersed in a water-bath at 24°. As soon as the thermometer in the central chamber reached the temperature of the water-bath, the air in the double wall of the vessel was pumped out to insulate the reaction chamber. The solutions were now allowed to react by raising and lowering the central reaction chamber at a standardized rate and observing the increase in temperature.

The solubility of boron trifluoride in nitrobenzene is relatively low. Such solutions fumed badly in the

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(1) Based upon a thesis submitted by Raymond H. Horowitz in January, 1951, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Research Fellow at Purdue University, 1948–1951, under a contract with the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

(3) H. C. Brown, M. D. Taylor and M. Gerstein, THIS JOURNAL, **66**, 431 (1944); H. C. Brown and M. Gerstein, *ibid.*, **72**, 2923 (1950).

(4) H. C. Brown, H. Bartholomay, Jr., and M. D. Taylor, *ibid.*, **66**, 435 (1944); H. C. Brown and M. D. Taylor, *ibid.*, **69**, 1332 (1947); H. C. Brown and G. K. Barbaras, *ibid.*, **69**, 1137 (1947); **75**, 6 (1953).

(5) H. C. Brown and A. Cahn, *ibid.*, **77**, 1715 (1955).

(6) P. A. van der Meulen and H. A. Heller, *ibid.*, **54**, 4404 (1932).

presence of air and were difficult to handle for the calorimetric measurements. Addition compounds of boron trifluoride provided more satisfactory sources of the halide for reaction with the base. The reactions of pyridine with a number of addition compounds of boron trifluoride were examined in order to select the most convenient carrier for these studies.

It is clear that to be a suitable carrier an addition compound should either be readily available or synthesized. It should be easily purified and its stability should be such as to provide a quantitative transfer of boron trifluoride to pyridine and related bases. Moreover, the donor which is liberated in the reaction should not interfere with the calorimetric measurements.

Ethyl ether–boron trifluoride is commercially available and easily purified by distillation under reduced pressure. It transfers boron trifluoride quantitatively to pyridine with a molar heat of reaction of 14.1 kcal. Unfortunately, the evaporation from the solution of the ethyl ether formed in the reaction causes appreciable thermal changes. The heat of reaction of *n*-butyl ether–boron trifluoride with pyridine is somewhat greater, 15.9 kcal./mole, indicating a somewhat less stable donor–acceptor interaction in this compound. The lower volatility of *n*-butyl ether avoided the difficulty previously encountered with ethyl ether. However, the difficulties involved in the purification of the addition compound (*n*-butyl ether–boron trifluoride cannot be distilled without decomposition) led us to abandon the use of this compound. Dioxane–boron trifluoride was too insoluble in nitrobenzene to be utilized.

The application of the addition compound of tetrahydropyran with boron trifluoride overcame these difficulties. The transfer of boron trifluoride is satisfactorily quantitative, with $-\Delta H = 12.2$ kcal./mole; the compound is readily purified by distillation under reduced pressure, and the volatility of the liberated tetrahydropyran (b.p. 88° at 760 mm.) is sufficiently low that no difficulties were encountered with thermal changes due to evaporation.

The addition compounds of boron trifluoride with anisole and benzonitrile also were examined briefly. These compounds were much less stable and their solutions in benzene fumed badly. The heats of reactions with pyridine were so high as to indicate essentially complete dissociation in nitrobenzene solution. In the case of benzonitrile certain irregularities in the heat changes were observed. These may have arisen from the trimerization of the benzonitrile to the triazine under the catalytic influence of the boron trifluoride. The results are summarized in Table I.

In view of these results, tetrahydropyran–boron

TABLE I

HEAT OF REACTION OF PYRIDINE WITH VARIOUS SOURCES OF BORON TRIFLUORIDE IN NITROBENZENE SOLUTION

Donor	Formula of addition compound	Heat of reaction $-\Delta H$ (kcal./mole)
Tetrahydropyran	$(CH_2)_5O:BF_3$	12.2
Ethyl ether	$(C_2H_5)_2O:BF_3$	14.1
n-Butyl ether	$(n\text{-}C_4H_9)_2O:BF_3$	15.9
Dioxane	$O(CH_2CH_2)_2O:BF_3$[a]	
Anisole	$C_6H_5(CH_3)O:BF_3$	25.3
Benzonitrile	$C_6H_5CN:BF_3$	23.8
Nitrobenzene	$C_6H_5NO_2:BF_3$[b]	25.0

[a] Insoluble in nitrobenzene. [b] The heat of solution of boron trifluoride in nitrobenzene is greater than would be expected for simple solution. The solution of the gas may be accompanied by the formation of an unstable addition compound.

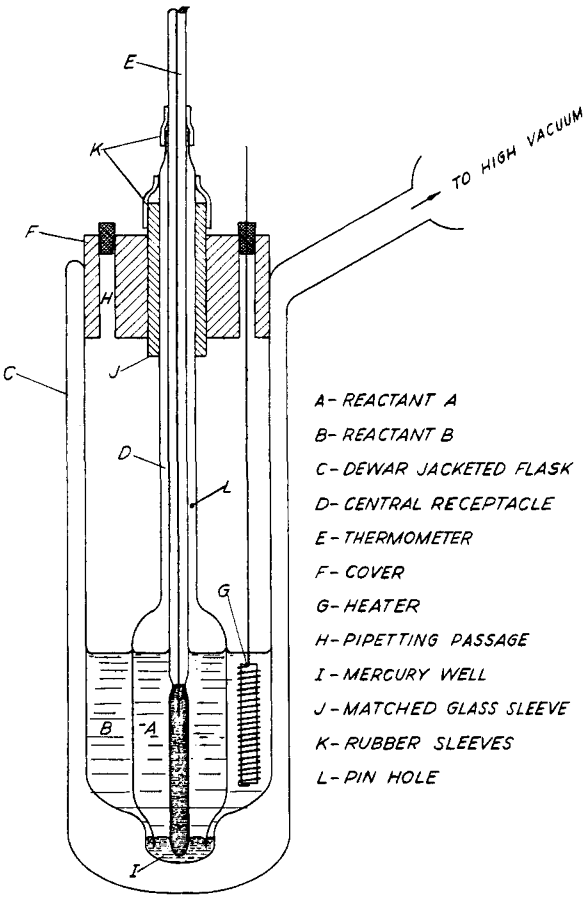

Fig. 1.—Diagram of the mercury-well calorimeter.

TABLE II

MOLAR HEAT OF REACTION OF PYRIDINE WITH TETRAHYDROPYRAN–BORON TRIFLUORIDE IN NITROBENZENE SOLUTION

Pyridine, *M*	THP:BF₃, *M*	Temp. rise,[a] °C.	Heat of reaction $-\Delta H$ (kcal./mole)
0.08644	0.130	0.709	12.27
.08644	.130	.699	12.10
.08644	.130	.700	12.11
.1297	.160	1.060	12.23
.1297	.160	1.050	12.11
.1297	.160	1.060	12.23
.1728	.200	1.414	12.24
.1728	.200	1.424	12.33
.1728	.200	1.430	12.38
.1728	.200	1.393	12.06
.1728	.200	1.403	12.15
.1728	.200	1.413	12.23
.1728	.350	1.400	12.12
.1728	.350	1.400	12.12

[a] Corrected by −0.03° as discussed in Experimental Part.

trifluoride was selected as the most satisfactory of the available carriers.

A detailed study was then made of the heat of reaction of pyridine with tetrahydropyran–boron trifluoride over a range of concentration. The heat of reaction was determined to be 12.19 ± 0.08 kcal./mole. The value was not affected by changes in the concentration of the reactants. The data in Table II will illustrate the precision attained.

The direct measurement of the heat of reaction of a nitrobenzene solution of boron trifluoride with pyridine resulted in a value of 25.0 ± 0.6 kcal. Because of the difficulties in handling the solution of boron trifluoride in nitrobenzene, the precision attainable was much less than in the case of the addition compound. We hope to improve the procedure to permit a more precise value of this quantity to be obtained.

From the two thermochemical equations

$$C_5H_5N(\text{soln.}) + BF_3(\text{soln.}) = C_5H_5N{:}BF_3(\text{soln.}) \qquad -\Delta H = 25.0 \text{ kcal./mole}$$

$$C_5H_5N(\text{soln.}) + (CH_2)_5O{:}BF_3 = C_5H_5N{:}BF_3(\text{soln.}) + (CH_2)_5O(\text{soln.}) \qquad -\Delta H = 12.2 \text{ kcal./mole}$$

we can obtain the equation

$$(CH_2)_5O(\text{soln.}) + BF_3(\text{soln.}) = (CH_2)_5O{:}BF_3(\text{soln}). \qquad -\Delta H = 12.8 \text{ kcal./mole}$$

The heat of reaction of boron trifluoride with tetrahydropyran has not been measured directly. However, the heat of dissociation of tetrahydrofuran–boron trifluoride has been measured in the gas phase and found to be 13.4 kcal./mole.[7] The difference in the heat of dissociation of the boron trifluoride addition compounds of the two cyclic ethers would have been expected to be quite similar, with the tetrahydrofuran derivative slightly the more stable of the two.[8] Consequently, if one may attempt to generalize from a single example, it appears that the heat of formation of addition compounds in solution may be of the same order of magnitude as the heat of reaction in the vapor phase.

We hope to examine the generality of this conclusion by an examination of the heats of reaction of a selected group of addition compounds which can be studied by both techniques. However, in addition to the example mentioned above, there are sound theoretical reasons for expecting that the heats of formations of addition compounds will not differ greatly in the gas phase and in solution. It follows that the heat of dissociation of pyridine–boron trifluoride, previously reported[6] to be 51 kcal./mole from dissociation studies in the temperature range from 313–356°, must be seriously in error. The true value must be much closer to the 25.0 kcal./mole observed in the present study with relatively small corrections to obtain the true gas phase value.

Experimental Part

Materials.—Nitrobenzene (du Pont technical grade) was distilled at atmospheric pressure. The center fractions were stored over calcium hydride. Pyridine was distilled through a 70-plate column and the material, b.p. 114.0° (745 mm.), collected. Standard solutions of the pyridine in nitrobenzene were prepared, standardized by titration,[6] and stored over calcium hydride.

The tetrahydropyran (du Pont technical grade) was dried over calcium hydride and then passed through a column of silica gel to remove olefinic impurities. The product was fractionated through a column and the fractions with constant properties (b.p. 85.0° at 731 mm., n^{20}_D 1.4201) collected and used to prepare the addition compound. Boron trifluoride was passed into tetrahydropyran until no more heat was evolved. The gain in weight was the theoretical for a 1:1 compound. The product, tetrahydropyran–boron trifluoride, was distilled under vacuum (b.p. 65.0° at 4 mm.) in an all-glass apparatus. The center cuts were collected in glass ampules and sealed under nitrogen. The entire operation was carried out with careful exclusion of moisture. Prepared in this way the product appeared stable and showed no evidence of chemical change over a period of several months.

Apparatus and Procedure.—Since consistently reproducible results could be obtained only by careful attention to a number of precautions, the experimental procedure will be described in detail.

The glass components of the calorimeter (Fig. 1) were cleaned and dried overnight in an oven at 110°. The calorimeters were assembled hot and allowed to cool as a stream of dry nitrogen flowed through the vessels. Eight ml. of mercury was then poured into the central well through a long stemmed funnel inserted in the opening at E. After the funnel was removed and the opening stoppered, each calorimeter was placed in the water-bath with its Dewar jacket connected to a vacuum line through the ball joint.

At this point 50.00 ml. of the standard solution of pyridine in nitrobenzene was transferred to the outer calorimeter chamber by means of a pipet inserted through H, with the minimum possible exposure to the atmosphere. Similarly 50.00 ml. of the standard solution of tetrahydropyran–boron trifluoride was introduced into the central chamber through the thermometer opening at E. In this opening a Taylor calorimetric thermometer (18–28° in $^1/_{100}$°) was inserted and the opening sealed by means of the rubber sleeve K.

When the thermometer was sensibly constant at the water-bath temperature, the air in the Dewar jackets was evacuated. The solutions were now allowed to mix and react by raising and lowering the central chamber. For the next 15 to 20 minutes, the central chamber was raised and lowered at a regular rate of four times per minute. At the end of each down stroke, care was taken to agitate the mercury in the well and, at the same time, induce a rotatory motion to the solution. Time–temperature data were recorded every minute of the run. The cooling curves were plotted and extrapolated back to zero time in order to determine the temperature rise for the reaction.

It should be pointed out that the calorimeter was designed so that 50.00 ml. filled the two chambers, A and B, to an identical depth, sufficient to cover the bulb of the thermometer. Moreover, the central receptacle contained a small opening L which permitted equalization of the air pressures in the two chambers.

At the end of the run, air was admitted to the Dewar jackets and the calorimeters were permitted to attain water-bath temperature. At this point the jackets were again evacuated and current was passed through the heater G for the electrical calibration. During the electrical calibration, the rates of stirring and temperature rise were maintained as close to those of the chemical run as possible. The electric heater was constructed of manganin wire on a threaded Teflon cylinder. In the solution zone, Teflon spacers served to prevent contact between the bare copper lead wires.

The molar heat of reaction was calculated with the aid of the expression

$$\Delta H(\text{cal.}) = 20\Delta TS/N$$

The electrical equivalent S was determined by dividing the electrical energy input by the temperature rise it produced. In the expression ΔT is the temperature rise observed in the chemical run, N is the molarity of the pyridine solution (used in deficiency) and the factor 20 arises from the use of 50 ml. of solution.

It was observed that the mixture of a 50.00 ml. of a nitrobenzene solution of the carrier with an equal volume of ni-

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(7) H. C. Brown and R. M. Adams, THIS JOURNAL, **64**, 2557 (1942). It should be pointed out that this value was obtained by relatively crude methods before we had developed the precision dissociation tensimeters. We hope to re-examine the dissociation of the ether-boron fluoride compounds by the more precise methods now available.

(8) H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950).

trobenzene resulted in a temperature rise of 0.03°. This increase was independent of the concentration. It therefore was concluded that the increase in temperature must not be due to any heat of dilution, but rather to a reaction of the carrier with trace amounts of a basic impurity present in the nitrobenzene. Since the carrier always was used in excess, a correction of −0.03° always was applied to the observed temperature rise.

A detailed study was made of the heat equivalent of the calorimeter filled with 100 ml. of nitrobenzene and filled with nitrobenzene containing the typical reaction products pyridine–boron trifluoride, tetrahydropyran and excess carrier. A total of 24 determinations with pure nitrobenzene gave the value for the electrical equivalent of the calorimeters of 74.7 ± 0.5 cal./deg. With the reaction products present, a total of 9 determinations gave the value of 74.8 ± 0.5 cal./deg. Moreover, there was evident no dependence on the concentration of the reagents (0.096–0.29 *M*). It therefore was concluded that the heat capacity of the solutions must be very similar to the heat capacity of the nitrobenzene.

Typical data illustrating the precision attained are presented in Table II.

To further test the reliability of the procedure, the heat capacity of nitrobenzene and the heat of reaction of sodium hydroxide and hydrochloric acid were determined. Three determinations gave for the heat capacity of nitrobenzene at 24° the value 0.355 ± 0.003 cal./deg. g., as compared to values of 0.347,[9] 0.362,[10] 0.352[11] reported in the literature. For the heat of reaction of sodium hydroxide with hydrochloric acid at 23.88°, five determinations gave the value 13.70 ± 0.07 kcal./mole as compared to the literature value of 13.62.[12]

These results support the conclusion that the calorimetric procedure should be capable of giving data on the heats of formation of molecular addition compounds in solution with a precision of 1%.

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(9) G. Schulze, *Verhandlungen der Physikalischen Gesellschaft zu Berlin*, **14**, 189, 258, 244 (1912).

(10) G. S. Parks and S. S. Todd, *J. Chem. Phys.*, **2**, 440 (1934).

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(12) T. W. Richards and A. W. Rowe, THIS JOURNAL, **44**, 684 (1922).

LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

Steric Effects in Displacement Reactions. VI. The Heats of Formation of the Addition Compounds of Boron Trifluoride with the Monoalkylpyridines. A Linear Relationship Involving Sterically Hindered Reactants[1]

BY HERBERT C. BROWN AND RAYMOND H. HOROWITZ[2]

RECEIVED JULY 8, 1954

The heats of reaction of the monoalkylpyridine bases with tetrahydropyran–boron trifluoride have been measured in nitrobenzene solution. The presence of a methyl group in the 3- or 4-position increases the heat of reaction from 12.2 kcal./mole observed for pyridine to 12.5 for 3-picoline and 12.7 for 4-picoline. Changes in the structure of the alkyl group (alkyl = methyl, ethyl, isopropyl, *t*-butyl) in the 3- or 4-position has little further effect on the stability of the addition compounds. These heats of reactions therefore parallel the pK_a values of the bases—the stronger the base the larger the heat of reaction with tetrahydropyran–boron trifluoride. In the 2-position the opposite effect is observed. Whereas the methyl group in 2-picoline results in an increase in the strength of the base, there is observed with this base a decreased heat of reaction with tetrahydropyran–boron trifluoride ($-\Delta H$ = 10.5 kcal./mole). The effect becomes increasingly important with 2-ethyl ($-\Delta H$ = 9.9), 2-isopropyl ($-\Delta H$ = 8.9), and 2-*t*-butyl ($-\Delta H$ = 2.0). The decrease is attributed to steric strains in the addition compounds arising from the conflicting steric requirements of the 2-alkyl groups and the boron trifluoride group. A plot of the heat of reaction data for these pyridine bases *vs.* the activation energy data for the reaction of the bases with methyl iodide reveals a reasonably good linear relationship. It is concluded that to obtain such linear relationships with sterically hindered reactants it is necessary to compare reactions with similar steric requirements.

The energies of activation of the reactions of 2-alkylpyridines with methyl iodide increase with the increasing bulk of the 2-substituent. These increases are attributed to steric strains in the activated complex arising from the conflicting steric requirements of the 2-substituent and the methyl group of the iodide.[3]

The bulk of the 2-substituent has but a small effect upon the pK_a value[4] and upon the heat of reaction of methanesulfonic acid with these bases.[5] It is considered that in these reactions the steric requirements of the proton are so small that there is no significant steric interaction with the bulky 2-substituents.

As a test of this interpretation it appeared desirable to examine the effect of the steric requirements of the 2-substituents on the reaction of these pyridine bases with a reference acid of moderate steric requirements. Boron trifluoride offered a number of advantages for such a study. Accordingly, it was decided to measure the heat of reaction of this acid with the monoalkylpyridines.

Results

In the previous paper there was described a calorimeter which was developed for the determination of the heat of reaction of pyridine with boron trifluoride and with tetrahydropyran–boron trifluoride, both in nitrobenzene solution.[6] In this study, the use of the carrier resulted in much better precision.

We were interested primarily in differences in the heats of reaction of the pyridine bases with boron trifluoride. These differences are as easily determined from the data for the reaction of the pyridine bases with tetrahydropyran–boron trifluoride as from data for the direct reaction of these bases with boron trifluoride. In view of the greater precision attainable by the use of a carrier, it was decided to measure the heats of reaction of the pyridine bases with tetrahydropyran–boron trifluoride.

Typical data are summarized in Table I.

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(1) Based upon a thesis submitted by Raymond H. Horowitz in January, 1951, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Research Fellow at Purdue University, 1948–1951, under a contract with the Office of Naval Research for the study of "Steric Strains in Chemical Reactions."

(3) H. C. Brown and A. Cahn, THIS JOURNAL, **77**, 1715 (1955).

(4) H. C. Brown and X. R. Mihm, *ibid.*, **77**, 1723 (1955).

(5) H. C. Brown and R. R. Holmes, *ibid.*, **77**. 1727 (1955).

(6) H. C. Brown and R. H. Horowitz, *ibid.*, **77**, 1730 (1955).