for 1 hr. with 10% sodium hydroxide solution (10 ml.). The solution was neutralized with sulfuric acid and evaporated to dryness and the solid extracted with ethanol. Evaporation of the ethanol gave solid material (0.098 g.) shown spectroscopically to be unchanged potassium trifluoromethylfluoroborate.

[Contribution from the Thiokol Chemical Corporation, Reaction Motors Division, Thiokol Chemical Corporation, Denville, New Jersey]

Fluorination of Ammonia

By Scott I. Morrow, Donald D. Perry, Murray S. Cohen and Carl Schoenfelder

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The reaction of fluorine and ammonia was reinvestigated in packed copper reactors under varying conditions of stoichiometry. The results qualitatively confirmed the earlier work of Ruff for the reaction in which an excess of fluorine was employed, but in the present study the use of excess ammonia produced dinitrogen tetrafluoride, difluoramine and dinitrogen difluoride in addition to the previously obtained nitrogen trifluoride. The products were identified by infrared and mass spectrometric analysis. A mechanism for the reaction is suggested, which explains the formation of these products and is consistent with previously advanced fluorination mechanisms.

Introduction

The vapor phase reaction of ammonia and fluorine was originally investigated by Ruff and Hanke[1] in an unpacked T-shaped copper reactor with both an excess of fluorine and an excess of ammonia. The products in both cases were reported to be nitrogen trifluoride and ammonium fluoride (Equation 1), although the presence of other nitrogen fluorides was postulated. Yields of nitrogen trifluoride of about 6% were obtained,

$$4NH_3 + 3F_2 \longrightarrow NF_3 + 3NH_4F \qquad (1)$$

but the main reaction was evidently the formation of nitrogen and hydrogen fluoride (Equation 2). The latter then combined with unreacted ammonia to form ammonium fluoride (Equation 3).

$$2NH_3 + 3F_2 \longrightarrow N_2 + 6HF \qquad (2)$$

$$HF + NH_3 \longrightarrow NH_4F \qquad (3)$$

We have reinvestigated this reaction to obtain more detailed information on reaction conditions, utilizing techniques such as the copper reactor packing of Fredenhagen and Cadenbach[2] and a reactor of modified design to supplement studies in the T-shaped reactor. The reaction was also explored under conditions which might be expected to yield difluoramine and monofluoroamine. Although difluoramine was first reported by Ruff and Staub,[3] recent work on its synthesis and characterization[4,5] has shown that the material described by the original authors was not difluoramine.

Our results not only confirmed those of Ruff and Hanke[1] on the preparation of nitrogen trifluoride but also showed that dinitrogen tetrafluoride, dinitrogen difluoride (difluorodiazine) and difluoramine can be obtained when an excess of ammonia is used. A preliminary report on the formation of dinitrogen tetrafluoride in this reaction has already been made.[6] Dinitrogen difluoride has previously been prepared by Haller,[7] and its structure has been determined by Bauer[8] and by Colburn, *et al.*[9]

Experimental

Reagents.—The fluorine used in this work was obtained from the Pennsalt Chemical Corporation, Philadelphia, Pennsylvania. Ammonia was supplied by the Matheson Company, East Rutherford, New Jersey. The Molecular Sieves were Linde Type 4-A, made by the Linde Company, Division of Union Carbide Corporation.

Apparatus.—A double valve system was used to control the flow of fluorine from the pressure storage cylinder. The gas was passed through a tube filled with sodium fluoride pellets to remove hydrogen fluoride impurity and thence through an orifice-type or glass, float-type flow meter to the reactor system. A stainless steel blowout manometer filled with fluorocarbon oil (Fluorolube, Hooker Electrochemical Company) was located in the fluorine feed line between the sodium fluoride tube and the flow meter. Fluorine was diluted with dry, oxygen-free nitrogen before entering the reactor. Ammonia was passed over a bed of soda lime and through a −23° trap to remove moisture, before it was diluted with nitrogen and fed into the reactor. When the T-shaped copper reactor was used, fluorine was introduced through the side arm and ammonia through the bottom port of the reactor. This reactor was made of a 12-inch section of two-inch diameter copper pipe, having a three-inch long side arm located four inches from the ammonia inlet. Figure 1 shows the method of introducing the gases into the homogeneous reactor. This reactor was made of a 36-inch length of two-inch diameter copper pipe. Copper gauze or copper shot was used for packing in both reactors. The temperature in the reaction zone was measured by means of a thermocouple inserted in a well in the side of the reactor. Effluent gases from the reactors were passed through −78° and −196° traps to recover products and unreacted ammonia. All of the connecting tubing in the reactor system was copper; the cold traps were machined from bar-stock Kel-F to fit standard stainless steel AN fittings. All of the valves were Hoke stainless steel needle valves. A burner filled with wood charcoal was situated in the exit line from the cold traps to convert fluorine to fluorocarbons when the apparatus was passivated by sweeping it with fluorine or when excess fluorine was used in the reaction.

Calibration of Fluorine Flow Meters.—The fluorine flow meters used in this work were calibrated by displacing nitrogen with fluorine from a long, narrow vertical copper tube. At low rates of flow for short periods of time no fluorine passed into the system in which the nitrogen was collected and measured. The amount of nitrogen displaced from the tube, measured by the displacement of water, gave a direct measure of the amount of fluorine passing through the meter.

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(1) O. Ruff and E. Hanke, *Z. anorg. u. allgem. Chem.*, **197**, 394 (1931).

(2) K. Fredenhagen and G. Cadenbach, *Ber.*, **67**, 928 (1934).

(3) O. Ruff and L. Staub, *Z. anorg. u. allgem. Chem.*, **198**, 32 (1931).

(4) E. A. Lawton and J. Q. Weber, This Journal, **81**, 4755 (1959).

(5) A. Kennedy and C. B. Colburn, *ibid.*, **81**, 2906 (1959).

(6) S. I. Morrow, D. D. Perry and M. S. Cohen, *ibid.*, **81**, 6338 (1959).

(7) J. F. Haller, Ph.D. Thesis, Cornell University, September, 1942.

(8) S. H. Bauer, This Journal, **69**, 3104 (1947).

(9) C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger and C. O. Parker, *ibid.*, **81**, 6397 (1959).

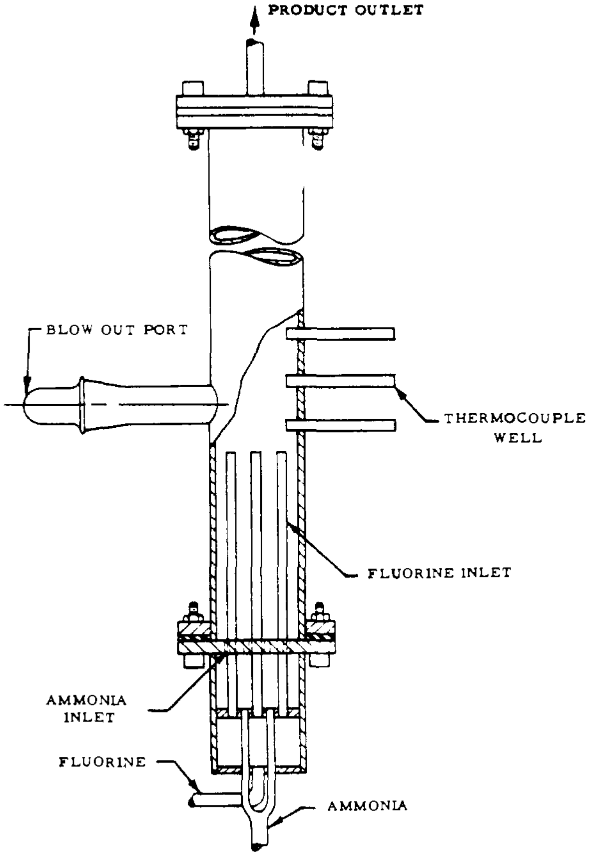

Fig. 1.—Homogeneous reactor.

Separation of Products.—In the experiments with excess fluorine, in which nitrogen trifluoride was the only gaseous product, the unreacted fluorine and nitrogen condensed in the −196° product trap were pumped off in a vacuum at this temperature. Since nitrogen trifluoride has a vapor pressure of less than a millimeter of mercury at this temperature,[10] only trace amounts were lost during the short pumping periods used.

In the experiments with excess ammonia unreacted ammonia was removed either by condensation at −78°, by adsorption, or by countercurrent scrubbing. Adsorbents used were granular, anhydrous calcium chloride or Linde Type 4-A Molecular Sieves. Scrubbing was accomplished by passing the product gases upward through a column packed with glass wool and wet with a continuous downward stream of distilled water. The water wash was collected in a receiver at the bottom of the column and the amount of unreacted ammonia determined by analysis of this aqueous solution. In no case was any ammonia detected in the products when these adsorption or scrubbing techniques were used.

Nitrogen trifluoride and dinitrogen tetrafluoride were separated by distilling the former at −142° to a −196° trap in a vacuum. Samples of dinitrogen tetrafluoride isolated in this way sometimes contained traces of hexafluoroethane. Traces of nitric oxide also may have been present. The latter is believed to be responsible for the blue color of the condensed liquid at low temperatures. In experiments where dinitrogen difluoride was obtained, it was found in the nitrogen trifluoride fraction. Two methods of isolating pure dinitrogen difluoride were investigated, but neither was completely successful. In the first method the mixture was fractionated at −186° (liquid argon) to remove the more volatile nitrogen trifluoride. This procedure effected considerable concentration of the dinitrogen difluoride. It has been found in more recent work in this Laboratory that dinitrogen difluoride can be fractionally condensed at −186° in a vacuum from a mixture with nitrogen trifluoride to give nearly pure material. The second procedure involved fractional distillation in a low temperature Podbielniak column. A 48.5 millimole sample of nitrogen trifluoride which contained dinitrogen difluoride was distilled in the column, and most of the nitrogen trifluoride was removed. The sample of dinitrogen difluoride obtained (4 millimoles) was still not completely pure, however. Use of larger quantities of material would undoubtedly give better results in the low temperature distillation in the Podbielniak column.

Although infrared spectra provided evidence for the formation of difluoramine in several experiments, it was possible to isolate and positively identify it in only one case. In this experiment the first product trap, held at −78°, contained approximately two ml. of a liquid, which exploded when it was cooled to −196°. It is probable that difluoramine (b.p. −23.6°) was present in this fraction, since it is known to detonate when undergoing solid–liquid phase transitions.[4,5] The products collected in the next two traps, held at −196°, were then fractionated in a vacuum from −142, −110 and −78°. The two millimole sample of material which was retained was shown to be an equimolar mixture of ammonia and difluoramine by infrared analysis.

Analysis.—Nitrogen trifluoride was analyzed by infrared spectroscopy and mass spectrometry. Mass spectrometric analysis of the combined products from the reactions using excess fluorine showed that the mixture contained 88.25% nitrogen trifluoride, 9.40% carbon tetrafluoride and 2.35% nitrous oxide. Dinitrogen tetrafluoride was analyzed by infrared spectroscopy, since infrared data on it were available.[11] Dinitrogen difluoride was identified by mass spectrometry and infrared analysis. On the basis of the infrared data it was possible to show that both the *cis* and *trans* isomers were present.[9] The *trans* isomer is stable upon prolonged storage in mixtures with nitrogen trifluoride in a stainless steel bomb. However, the *cis* isomer decomposed upon prolonged storage in a bomb, evolving a non-condensable gas which was apparently nitrogen. Difluoramine was identified by infrared spectroscopy on the basis of its known absorption bands.[6] The amount present in the mixture with ammonia was determined by calibration of the infrared spectrophotometer with pure ammonia at different pressures. By means of Beer's law it was possible to determine the pressure of ammonia in the unknown sample and thus to ascertain the concentration of the difluoramine. Aqueous solutions of ammonia were analyzed by the standard steam distillation method Ammonium fluoride was identified by infrared and elemental analysis.

Results

Reaction occurred smoothly in all of the experiments without the application of heat. The reaction was exothermic and caused a temperature rise in the reaction zone of as much as 18°. The only volatile nitrogen fluoride isolated when excess fluorine was used was nitrogen trifluoride. As indicated in Table I, dinitrogen tetrafluoride, difluoramine and dinitrogen difluoride were also isolated in the reactions in which excess ammonia was used. Yields reported in the table are based on the quantity of fluorine converted to the product in question. The only explosions which occurred were during work-up of the product samples. The explosions were attributed to the presence of difluoramine in the products, since it was shown to be present in one case where an explosion occurred. Difluoramine is known to explode on occasion when it is frozen.[4,5] Use of adsorbents such as water, calcium chloride and Linde Molecular Sieves eliminated these explosions.

Variations in the composition of the products was due not only to differences in the ratio and flow rates of reactants but also to the condition of the

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(10) L. Pierce and E. L. Pace, *J. Chem. Phys.*, **23**, 551 (1955).

(11) C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).

TABLE I

REACTION CONDITIONS AND YIELDS IN FLUORINATION OF AMMONIA

Type reactor	Time, hr.	$NH_3:F_2$, molar ratio	$N_2:F_2$, molar ratio	F_2 rate, l. STP/hr.	NH_3 rate, l. STP/hr.	Total N_2 rate, l. STP/hr.	N_2F_4, m*M*	NF_3, m*M*	N_2F_4, % yield	NF_3, % yield
T[a]	..	1.1:1	5.1 to 20:1	1.2 to 2.3	1.3 to 2.5	11.9 to 23.8	0	160	0	22.8[b]
T	1.5	1.5:1	5:1	1.6	2.5	8.4	4.6	17.8	8.4	24.3
T	2.9	1.5:1	5:1	1.6	2.5	8.4	1.7	30.4	1.6	21.2[c]
H[a]	2.5	1.5:1	5:1	2.1	3.3	11.1	6.8	29.6	5.8	18.9[d]
H	4.0	1.5:1	5:1	2.1	3.3	11.1	9.2	48.5	4.9	19.3[d]
H	2.0	1.5:1	5:1	2.1	3.3	11.1	2.3	24.8	2.4	19.8[d]
T	1.7	1.5:1	5.1	1.6	2.5	8.4	5.5	8.9	9.0	10.9
T	1.4	1.8:1	5:1	1.4	2.5	7.6	4.7	7.9	10.8[e]	13.6
T	2.0	1.8:1	5:1	1.4	2.5	7.6	5.3	19.6	8.6	24.0
H	2.0	2:1	5:1	2.1	4.4	11.1	1.6	29.3	1.7	23.4[d]

[a] T = T-shaped reactor; H = homogeneous reactor. [b] Average of 5 experiments. When calculated on basis of equation 1, a yield of 56.1% is obtained. [c] Difluoroamine was identified as one of the products of this reaction. No absorbent was used to remove unreacted ammonia. [d] Dinitrogen difluoride was obtained in these experiments. [e] Yield is 26.8% when calculated on basis of equation 6.

copper packings in the reactor. For instance, a significant amount of difluoramine was obtained only with a copper gauze packing which had been used a total of 5 hr. in previous experiments. When used packings were removed from the reactors, they were not only coated with ammonium fluoride in the reaction zone but also showed variations from the original color. It was suspected that the packings played a catalytic role in the reaction. Difluoramine was detected in the product from the T-shaped reactor but only when no absorbent for ammonia was used. Both T-shaped and homogeneous reactors produced dinitrogen difluoride, dinitrogen tetrafluoride and nitrogen trifluoride.

The amount of unreacted ammonia recovered when water scrubbing was used varied from 23.6 to 36.7% of the amount originally used. Tests of these solutions for fluoride ion showed that there was essentially no absorption of fluorinated products by the water. When calcium chloride and Linde Molecular Sieves were used to remove ammonia from the product gases, significant evolution of heat occurred in these beds, which was probably due to the heat of absorption of ammonia.

Discussion

The ammonia–fluorine reaction was investigated under conditions of stoichiometry which would be expected to lead to the formation of difluoramine or monofluoramine. Formation of these compounds should require an excess of ammonia. The formation of dinitrogen tetrafluoride and dinitrogen difluoride in the reaction was somewhat more unusual, but it can be explained on the basis of Bigelow's theories on the mechanism of fluorination reactions.[12]

Ruff's equation for the preparation of nitrogen trifluoride from fluorine and ammonia requires a

$$4NH_3 + 3F_2 \longrightarrow NF_3 + 3NH_4F \qquad (1)$$

1.33:1::$NH_3:F_2$ molar ratio. Since he apparently obtained the best results with an excess of fluorine over that required by Equation 1, we investigated reactions with a 1.1:1::$NH_3:F_2$ ratio. A series of five experiments made in this way gave only nitrogen trifluoride and ammonium fluoride, although some nitrogen may have been formed and not detected. The remainder of the study was made with excess ammonia, under conditions expected to lead to the formation of difluoramine or monofluoramine, according to Equations 4 and 5, respectively

$$3NH_3 + 2F_2 \longrightarrow NHF_2 + 2NH_4F \qquad (4)$$

$$2NH_3 + F_2 \longrightarrow NH_2F + NH_4F \qquad (5)$$

The ammonia–fluorine molar ratio corresponding to Equation 4 is 1.5:1, for Equation 5, 2:1. An experiment employing the stoichiometry of Equation 4 gave some difluoramine. However, in the single experiment made according to Equation 5 there was no evidence of monofluoramine in the products. Dinitrogen tetrafluoride and dinitrogen difluoride were also obtained in experiments with ammonia–fluorine ratios of 1.5:1 to 2:1. The equation for formation of dinitrogen tetrafluoride requires a 1.6:1 stoichiometry and that for dinitrogen difluoride a 2:1 stoichiometry

$$8NH_3 + 5F_2 \longrightarrow N_2F_4 + 6NH_4F \qquad (6)$$

$$8NH_3 + 4F_2 \longrightarrow N_2F_2 + 6NH_4F \qquad (7)$$

The fact that dinitrogen tetrafluoride, dinitrogen difluoride and difluoramine were obtained in addition to nitrogen trifluoride when $NH_3:F_2$ ratios of 1.5:1 to 2:1 were used can best be explained by assuming that the mechanism involved is similar to that postulated by Bigelow[12] for the fluorination of hydrocarbons. The initial step in such a reaction is the thermal or catalytic formation of fluorine atoms from molecular fluorine

$$F_2 \rightleftharpoons 2F\cdot \qquad (8)$$

Since the dissociation energy of fluorine (37 kcal./mole) is less than that of chlorine and bromine,[13] it is reasonable to expect fluorine atoms to be present, particularly in the presence of metals such as copper which might catalyze the above dissociation. The next step in the proposed chain mechanism involves the reaction of ammonia and a fluorine atom

$$NH_3 + F\cdot \longrightarrow NH_2\cdot + HF \qquad (9)$$

The amino radical then reacts with fluorine

$$NH_2\cdot + F_2 \longrightarrow NH_2F + F\cdot \qquad (10)$$

Subsequent steps (Equations 11–14) lead to the formation of nitrogen trifluoride

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(12) L. A. Bigelow, *Chem. Revs.*, **40**, 51 (1947).

(13) M. G. Brown, *Trans. Faraday Soc.*, **55**, 9 (1959).

$$NH_2F + F\cdot \longrightarrow NHF\cdot + HF \quad (11)$$
$$NHF\cdot + F_2 \longrightarrow NHF_2 + F\cdot \quad (12)$$
$$NHF_2 + F \longrightarrow NF_2\cdot + HF \quad (13)$$
$$NF_2\cdot + F_2 \longrightarrow NF_3 + F\cdot \quad (14)$$

The formation of dinitrogen tetrafluoride can be explained by the combination of two difluoramino radicals

$$2NF_2\cdot \longrightarrow N_2F_4 \quad (15)$$

while difluoramine could be formed as shown in Equation (12). The formation of dinitrogen difluoride can then occur by reaction of the $NF_2\cdot$ and $NHF\cdot$ radicals followed by elimination of hydrogen fluoride from the trifluorohydrazine formed

$$NHF\cdot + NF_2\cdot \longrightarrow [NHF\text{-}NF_2] \longrightarrow N_2F_2 + HF \quad (16)$$

The fact that dinitrogen difluoride yields were of the order of 5% or less is in accord with the relatively low order of probability of collision of these two radicals. Although these mechanisms are not rigorously proven by the experimental data, they fit the existing theory for such reactions and also give a logical explanation of the results.

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[CONTRIBUTION FROM THE ROHM & HAAS CO., REDSTONE ARSENAL RESEARCH DIVISION, HUNTSVILLE, ALA.]

The Direct Synthesis of Difluoramine[1]

BY JEREMIAH P. FREEMAN, AL KENNEDY AND CHARLES B. COLBURN

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Difluoramine, HNF_2, was prepared in yields up to 75% by the reduction of tetrafluorohydrazine with mercaptans, preferably thiophenol. Arsine also was useful in this reaction.

Recently three groups have reported the isolation of difluoramine, HNF_2, as a by-product of various fluorination reactions: (1) from the passage of nitrogen trifluoride saturated with water vapor over a heated bed of arsenic (trace quantities)[2]; (2) from the fluorination of urea and subsequent decomposition of intermediate products[3]; (3) and from the fluorination of ammonia (trace quantities).[4]

A new, direct and simple method has now been found that produces difluoramine in good yield. Heating tetrafluorohydrazine,[5] N_2F_4, with thiophenol in an evacuated bulb produces difluoramine in 74% yield. The product was readily purified by fractional condensation in a high vacuum line. A second distillation removed the last traces of N_2F_4 and difluoramine of 99% purity (mass spectrometer) was obtained. The material remaining in the reaction bulb was unreacted thiophenol and diphenyl sulfide. The over-all reaction then is

$$N_2F_4 + C_6H_5SH \longrightarrow 2HNF_2 + C_6H_5SSC_6H_5$$

Higher reaction temperatures led to further reaction and the production of nitrogen. Similar results were obtained when metal bombs rather than glass reactors were used. Aliphatic mercaptans were not as useful as thiophenol because they also caused the reduction of tetrafluorohydrazine to nitrogen. Interestingly, glass vessels could not be used for the aliphatic mercaptan reactions.

The earlier synthesis based on nitrogen trifluoride, water and arsenic suggested the intermediacy of tetrafluorohydrazine and arsine. Further experiments showed that this mixture did indeed yield difluoramine. Arsine reacted slowly with tetrafluorohydrazine in a steel reactor at room temperature but more conveniently at 50° to produce arsenic and difluoramine (52% yield). After several successful reactions, the reaction began to occur explosively. A new reactor was then used and all subsequent reactions occurred at a normal rate. The explosive reaction may have been caused by air which leaked into this system.

Nitrogen trifluoride did not react with arsine under similar conditions up to temperatures of 175°. Above 175°, the arsine decomposed while the nitrogen trifluoride remained unreacted.

The difluoramine was identified by its infrared spectrum and mass spectral cracking pattern.[2] Amounts up to two liters (S.T.P.) have been stored in Pyrex vessels for long periods without decomposition. However, old vacuum systems which have become etched or which contained unknown residual materials could not be used for storage, nor could metal bombs. In these systems difluoramine reverted to tetrafluorohydrazine.

Experimental[6]

Thiophenol and Tetrafluorohydrazine.—Twelve milliliters (0.107 mole) of thiophenol was placed in a 1-l. round-bottomed flask equipped with a magnetic stirrer and attached to a vacuum line. The thiophenol was degassed and 483 cc. (0.0215 mole) of tetrafluorohydrazine[5] was condensed in using a liquid nitrogen cold bath. The resulting mixture was allowed to warm to room temperature and then was immersed in an oil-bath. The mixture was stirred for 4 hours at a bath temperature of 50°. The bath was then removed and the flask allowed to cool to room temperature. The contents were then distilled *in vacuo* through a series of U-tubes cooled at −80°, −128° (methylcyclohexane slush) and −196°, respectively. The product retained in the

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(1) This research was carried out under Army Ordnance Contract DA-01-021-ORD-5135.

(2) A. Kennedy and C. B. Colburn, THIS JOURNAL, **81**, 2906 (1959).

(3) E. A. Lawton and J. Q. Weber, *ibid.*, **81**, 4755 (1959).

(4) S. I. Morrow, D. D. Perry, M. S. Cohen and C. W. Schoenfelder, Abstracts, 137th Meeting, American Chemical Society, Cleveland, Ohio, April 1960, p. 11-M.

(5) C. B. Colburn and A. Kennedy, THIS JOURNAL, **80**, 5004 (1958).

(6) All gas volumes mentioned were measured at standard conditions of pressure and temperature.