and the CX_4 type is consistently more soluble in the less polar solvents.

The extremely low solubilities of CCl_2F_2 and CCl_3F in aniline as compared to their solubilities in dimethylaniline and aliphatic amines support the suggestion made in an earlier paper that there is considerable association in primary aromatic amines.[2b]

The solubilities of $CHCl_2F$ in nitro compounds and nitriles show that these groups act as donor centers although when they are attached to a phenyl group[2b] they are much less effective donors than when attached to an alkyl group. A rather surprising case of solubility above the calculated amount was found in the case of $CHCl_2F$ in mesitylene.

Summary

The solubilities of CCl_2F_2 and of CCl_3F have been measured over a range of pressures in a wide variety of organic solvents. In practically every case the solubility was lower than that calculated from Raoult's law. These observations support the earlier postulation that intermolecular association through hydrogen bonding is an important factor in producing solubility of hydrogen containing halogenated methanes.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF DUKE UNIVERSITY]

The Action of Elementary Fluorine on Organic Compounds. VI. The Vapor Phase Reaction between Ethane and Fluorine in Progressively Varying Proportions

BY JOHN D. CALFEE,[1] NOBUKAZU FUKUHARA AND LUCIUS A. BIGELOW

In a preceding communication (IV),[2] we have described preliminary experiments dealing with the vapor phase fluorination of ethane over a copper gauze catalyst, and the subsequent isolation of hexafluoroethane and other products. The present report describes a further study of this important reaction in which ethane and fluorine reacted in progressively varying proportions, and the more important products subsequently were separated and rectified. In each case, a perfectly quiet continuous change took place, which could be duplicated readily in every essential respect.

The Apparatus.—The fluorination chamber consisted of a section of brass pipe filled with small squares of 20-mesh copper gauze, essentially the same as that described before.[2] However, two tubes filled with sodium fluoride were used instead of one to absorb hydrogen fluoride, and special precautions were taken to make certain that no air whatever was drawn into the apparatus when the condensing trap was cooled with liquid air. Also, the quantities of the reacting gases were measured carefully; the ethane by means of a calibrated flowmeter, and the fluorine through the known electrical efficiency of the generator, recently measured by Lewis[3] and shown to be nearly constant at about 80% during most of the life of the charge. Furthermore, the products were not passed through potassium hydroxide solution, but were distilled directly, since

in general the ethane was in excess; thus no free fluorine was present.

The complete Booth–Podbielniak low-temperature rectification unit which was used to separate the products was constructed according to the principles described by Booth and Bozarth.[4] A diagram of the apparatus as adapted to our work, to be described in this and subsequent papers, is illustrated in Fig. 1. The unit consisted of three main parts, first, the boiler OO, the Podbielniak low-temperature column M, and the control manometer S with its contacts 1 and 2, together with the liquid air supply O and other accessories. Beyond the control valve K were the collecting system UU, VV, T, with manometers, and the melting point apparatus W. Finally came the gas density balance FF, with its thermostat, and an absolute manometer AA to measure accurately the pressures in the balance, as well as in any part of the receiving system. The temperature at the head of the column was measured by means of a thermocouple F, in connection with a recording potentiometer; and the boiler as well as the melting point apparatus was provided with a magnetic stirrer. The operating technique for this type of unit, together with the theoretical considerations involved, have been described before.[4]

Results and Discussion.—Four separate fluorinations of ethane were made in the manner already described, and the products condensed and rectified. There were isolated carbon tetrafluoride (b. p. −128°), two azeotropic mixtures, A and B, with constant boiling points, constant molecular weights, but wide melting ranges, ethane (b. p. −88°), hexafluoroethane (b. p. −78°), and some higher boiling material.

When azeotrope B (b. p. −96°, mol. wt. 64) was passed repeatedly through a 10% sodium hydroxide solution,

(1) This paper, and also III and IV of this series, have been constructed wholly or in part, from Mr. Calfee's Doctorate Thesis, presented to the Graduate School of Duke University in May, 1938.

(2) Calfee and Bigelow, THIS JOURNAL, **59**, 2072 (1937).

(3) Hubert M. Lewis, unpublished work.

(4) Booth and Bozarth, *Ind. Eng. Chem.*, **29**, 476 (1937).

dried and redistilled, it boiled at −92°, with a mol. wt. of 62. The difference was due undoubtedly to the removal of a small amount of impurity, presumably carbon dioxide, which could have come from the generator. No evidence was found to indicate the presence of silicon tetrafluoride in this product, but when the sample boiling at −92° was mixed with considerable carbon dioxide and distilled again, it boiled from −98° to −96°. The azeotrope was shown by direct synthesis to consist of ethane and hexafluoroethane, in the approximate molecular ratio of 2:1, since a known mixture of these compounds had a constant boiling point of −92°, and a constant mol. wt. of 64.

Azeotrope A was less simple, however. Its boiling point was −104° at atmospheric pressure (mol. wt. 54), −91 to −90° at 1140 mm. (mol. wt. 52) and −108° at 390 mm. (mol. wt. 52). It did not contain ethylene (b. p. −103°), since it was inert to bromine; and it was not a mixture of ethane and fluoroform, which yielded an azeotrope boiling at −96° (mol. wt. 46).

When it was passed through a 10% solution of sodium hydroxide ten times, dried and redistilled, silica was deposited immediately in the alkaline solution, and the remaining material separated sharply into two fractions, one boiling at −92° (mol. wt. 62), and the other at about −87° (mol. wt. 31). These properties correspond to those of azeotrope B and ethane, respectively. From this it was clear that azeotrope A consisted of ethane, hexafluoroethane and silicon tetrafluoride, in the approximate molecular ratio of 6:1:1, corresponding to an average mol. wt. of 53.

Table I gives the collected results of the fluorinations in the form of a comparison of the volume ratios of the reacting gases with the quantities of the various fractions separated, these last being expressed in liquid volume % of the total condensate obtained in the same run.

TABLE I

THE COLLECTED RESULTS OF THE LOW TEMPERATURE FRACTIONATION OF THE FLUORINATED ETHANE

Liquid volume per cent. of:	Gas volume ratios of fluorine to ethane			
	1:1	2.3:1	4:1	6:1
Carbon tetrafluoride	5	12	21	12
Azeotrope A	11	17	21	18
Azeotrope B	31	52	14	0
Ethane	42	0	0	0
Hexafluoroethane	0	6	32	41
Residue b. p. > −78°	12	17	14	29

The total volumes of liquid condensate obtained in these runs were 88, 40, 28 and 17 ml., respectively, on a twenty-hour operating basis, and previous to rectification. The figures in the table are to be considered as semi-quantitative, since the measurement of liquid volumes at low temperatures had to be made on a comparison basis, the error being estimated as not greater than ± 3 units in the
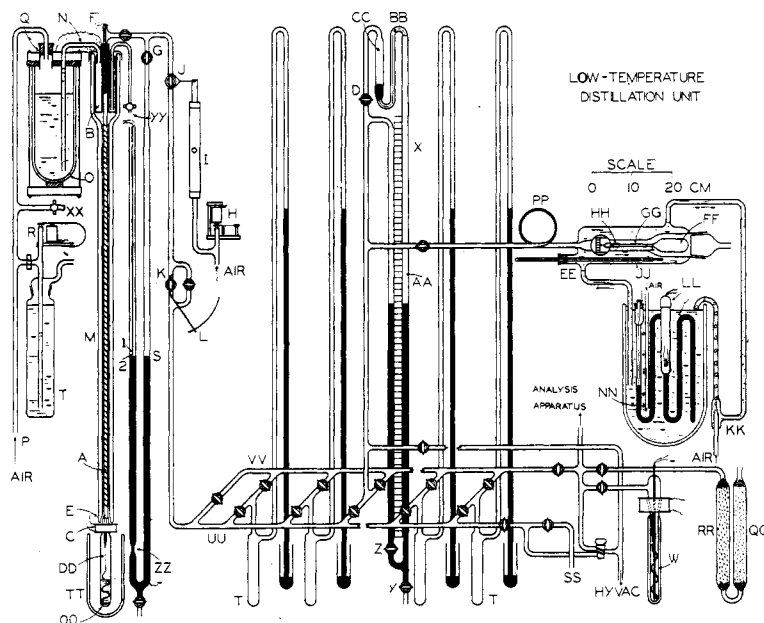

Fig. 1.

extreme case. When the fluorine to ethane ratio of 6:1 was used, free fluorine appeared in the condensate, giving it an orange color. It was necessary to remove this halogen before rectification, by repeated melting, freezing and exhausting the product, which may have affected somewhat the values observed in this case.

The trend of the results was quite clear, however. As the proportion of fluorine in the reaction mixture increased, the quantities of carbon tetrafluoride and hexafluoroethane increased, while the amount of ethane recovered decreased, as would be expected. Also azeotrope B was formed in maximum quantity under conditions when both of its components would be expected to be present in considerable proportions at the same time. The results also compare favorably with the preliminary observations reported earlier,[2] if the marked improvements in technique developed since then are considered. On the whole, it appears that direct fluorination is more similar to chlorination than has been supposed hitherto. A study of the influence upon this reaction of diluting the fluorine with nitrogen is now in progress.

Summary

Ethane has been fluorinated in the vapor phase, using progressively changing proportions of the reacting gases.

The more important products have been identified, and the approximate proportions in which they were formed have been determined.

DURHAM, NORTH CAROLINA   RECEIVED JULY 21, 1939

Studies on Proteins in Liquid Ammonia. V. Reaction of Sodium in Liquid Ammonia with Peptones and Related Substances[1]

BY CLEMMY O. MILLER AND RICHARD G. ROBERTS

From previous work[2,3] reported in this series, it is known that certain amino acids, peptides, proteins and related substances are acidic in liquid ammonia. A preliminary report[4] on peptones studied under similar conditions has been made. In this paper we have compared the reactions of Armour's Meat Peptone, Merck's Meat Peptone and Witte's Peptone when metallic sodium is added to them in liquid ammonia by determining the hydrogen evolved from them, and correlating it with their nitrogen content. This method is also used to follow the course of an acid digestion of silk fibroin through several of its peptones, since it reveals the presence of certain compounds and reactive groups that do not affect a Sörensen formol titration or a Van Slyke amino nitrogen determination greatly. It has been noted by others[5] that certain procedures carried out in non-aqueous solvents can reveal groups that do not ordinarily dissociate in aqueous solutions.

Experimental

Method.—The manner of drying the liquid ammonia over sodium and of drying the peptones and related substances has been described previously, as has also been the apparatus for collecting and analyzing the hydrogen.[2,3] The silk peptones were prepared by treating silk fibroin with 70% sulfuric acid at room temperature for one, two, three, four and ten days according to the method described by Morrow[6] for the preparation of four day silk peptones. The synthetic silk peptone was simply a mixture of glycine, alanine and tyrosine made up in the proportions found in silk fibroin.

(1) Some of the data presented here were collected in the laboratories of the Northwestern University Medical School.

(2) C. O. Miller and R. G. Roberts, THIS JOURNAL, **56**, 935 (1934).

(3) R. G. Roberts and C. O. Miller, ibid., **58**, 309 (1936).

(4) R. G. Roberts and C. O. Miller, Proc. Soc. Exptl. Biol. Med., **30**, 821 (1933).

(5) E. J. Cohn, Ann. Rev. Biochem., **4**, 141 (1935).

(6) C. A. Morrow, "Biochemical Laboratory Methods," John Wiley and Sons, Inc., New York, N. Y., 1927.

Discussion

Our work on amino acids showed that a linear curve rising at a forty-five degree angle was obtained when the varying amounts of sodium added were plotted against the hydrogen evolved for one nitrogen equivalent of the substances used. With dipeptides such as glycylglycine or glycyl-dl-alanine the curve is linear, but the slope is less than for the amino acids. The curve with proteins can be divided into three segments, one and three roughly paralleling the base line, while segment two roughly parallels the rising curve of the amino acids. Protein curves in general resemble a one-day digestion silk peptone (Fig. 1, curve III). Diketopiperazine gives a curve similar to the proteins except that segment two rises only about 50% as high on the average as the latter. In general the curves of peptones resemble the curve of diketopiperazine. As shown in Fig. 1 Armour's peptone (curve I) gives a smooth curve, while Witte's peptone (curve II) gives sharp segments as if a definite amount of sodium or hydrogen had to be absorbed before a definite quantity of acidic hydrogen could be liberated. For one to one ratios of sodium to nitrogen, Merck peptone is relatively more acidic than either Armour or Witte peptone. Curve III of the one-day digestion silk peptone resembles the curve of silk fibroin; it is still acting like a protein. By the second day, however, the acidity has dropped to that which is characteristic of peptones and the three-day digestion gives a typical peptone curve (IV). By the fourth day the digest has become increasingly acidic again, about equal to that of the one-day digest. The ten-day digest is more acidic than the four-day digest, and gives a curve characteristic of amino acids (V). The ten-day digest seems to be the limit of acidity for a silk fibroin hydrolyzed by sulfuric acid, since a mixture (glycine 53.3%, alanine 31.1% and tyrosine 15.6%), the proportions found in silk fibroin, and