It has been found that no matter what the incoming or leaving groups, the difference in the temperature independent factors for two-center and three-center reactions involving carbon is never more than 3%.[38]

From the examples studied here, it appears that a number of S_N2 processes possess a carbon-14 kinetic isotope effect approximately equal in magnitude to that of many reactions involving only bond rupture.[7] It was thought at one time that the magnitude of the kinetic isotope effect could be used to differentiate two-center and three-center processes, such as S_N1 and S_N2 reactions. However, it now appears that only under favorable circumstances can this differentiation be achieved. In cases where the difference in the temperature independent factors for two-center and three-center reactions is of the order of 2 to 3%, it may be possible to utilize kinetic isotope effects to distinguish between S_N1 and S_N2 reactions. For this purpose, measurements of the temperature coefficient would have to be made in order to assign part of the effect to the zero point energy term and the remainder to the temperature independent entropy term.

One factor that seems to have an effect on the magnitude of the kinetic isotope effect is the activation energy of the reaction. It is worthy of note that the largest kinetic isotope effect was observed for the reaction of methyl iodide-C^{14} with pyridine which has the largest activation energy of the reactions considered. It is considered possible that the kinetic isotope effect in the pyridine reaction is higher than the others listed and higher than the calculated value because of the higher activation energy of the pyridine reaction. It is hoped to treat this phenomenon in a quantitative fashion at a later date.

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CHICAGO 16, ILLINOIS

[38] Unpublished results of D. F. Hoeg and G. J. Buist.

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Hexafluorobenzene from the Pyrolysis of Tribromofluoromethane[1,2]

BY M. HELLMANN, E. PETERS, W. J. PUMMER AND L. A. WALL

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The pyrolysis of tribromofluoromethane was studied in graphite, Vycor and platinum tubes at temperatures ranging from 500 to 750°. In all cases hexafluorobenzene was formed. The lowest yields of hexafluorobenzene were obtained in Vycor tubes. Graphite performed nearly as well as platinum tubes under atmospheric pressures. At pressures of 4.5 atmospheres of nitrogen in platinum tubes an optimum net yield slightly over 55% was achieved at 540 to 550°. Side products of the reaction were chiefly bromofluoro derivatives of ethane, propane, benzene and toluene. A mechanism of the reaction is proposed.

Introduction

The synthesis of hexafluorobenzene was first reported by McBee, Lindgren and Ligett.[3] Their method consisted of fluorinating hexachlorobenzene with bromine trifluoride, followed by treatment of the intermediate with antimony pentafluoride, and finally dehalogenation with zinc. This procedure led to the formation of small amounts of hexafluorobenzene together with a variety of other products, mainly perfluorocyclohexenes and cyclohexadienes as well as chlorofluoro compounds.

A more direct method, which also gave higher yields, was described by Desirant.[4] It involved the pyrolysis of tribromofluoromethane in a platinum tube at 630 to 640°. The reported yield of hexafluorobenzene was 45% on the basis of reacted tribromofluoromethane.

Recently another synthesis of hexafluorobenzene was described by Godsell, Stacey and Tatlow.[5] Their paper dealt with the isolation of hexafluorobenzene from a mixture resulting from the treatment of a nonafluorocyclohexane with potassium hydroxide. The desired product was isolated by vapor phase chromatography.

In the light of currently increasing interest in hexafluorobenzene, and perfluoroaromatics in general, it was considered necessary to find a convenient method for synthesizing larger amounts of these compounds. Of the methods described above, the one by Desirant[4] appeared to be the most promising, and consequently a study of this reaction was undertaken for the purpose of determining the effects of variation in tube materials, temperature and pressure on the course of the reaction. The pyrolysis reaction of interest can be represented by this stoichiometric equation

$$6CFBr_3 \xrightarrow[630\text{–}640°]{\Delta} C_6H_6 + 9Br_2$$

The tribromofluoromethane can be prepared from carbon tetrabromide and antimony trifluoride in the presence of a small amount of bromine.

In selecting the tubes for the pyrolysis three dif-

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[1] This paper is based on work sponsored by the Bureau of Aeronautics, Department of the Navy, Washington, D. C.

[2] Presented as part of the Symposium on Fluorine Chemistry, Division of Industrial and Engineering Chemistry, at the 130th Meeting of the American Chemical Society in Atlantic City, N. J., September, 1956.

[3] E. T. McBee, V. V. Lindgren and W. B. Ligett, *Ind. Eng. Chem.*, **39**, 378 (1947).

[4] Y. Desirant, *Bull. Acad. Roy. Belg., Classe Sci.*, [5] **41**, 759 (1955).

[5] J. A. Godsell, M. Stacey and J. C. Tatlow, *Nature*, **178**, 199 (1956).

TABLE I

PYROLYSIS OF TRIBROMOFLUOROMETHANE

Tube material	Temp., °C.	Pressure, atm.	Feed rate, g./min.	Total recovery, %	Bromine liberated, %	Gross yield C_6F_6, %	Recovery $CFBr_3$, %	Net yield C_6F_6, %
Graphite[a]	642–654	1.0	3.5	90	63	24	18	30
[a]	665–675	1.0	3.5	96	85	23	8	25
[a]	690–720	1.0	4.1	93	91	19	1	19
[a]	725–755	1.0	5.4	96	95	21	1	21
	645–652	1.0	3.4	97	72	14	16	17
	750–756	1.0	7.3	95	91	24	8	26
Vycor	640–667	1.0	3.4	88	85	11	1	11
	707–721	1.0	4.5	93	..	10	3	10
	737–762	1.0	5.1	89	..	4	1	4
Platinum	540	1.0	8.3	97	30	14	55	31
	600	1.0	8.2	98	74	30	8	32
	730	1.0	8.9	93	89	18	0	18
	500	4.5	6.5	94	24	12	68	36
	530	4.5	5.1	99	50	29	43	50
	540	4.5	7.0	95	62	38	30	55
	550	4.5	3.5	96	67	40	25	52
	580	4.5	8.8	96	88	34	4	35
	620	4.5	7.8	95	88	31	0	31

[a] These four tubes were packed with charcoal. All others listed were packed with platinum.

ferent materials were chosen; graphite, Vycor glass and platinum. The tubes were packed with platinum gauze, except for several runs in the graphite tubes where coarse cocoanut charcoal was used as packing.

Results

Table I summarizes the results of all runs performed in graphite, Vycor and platinum tubes. The data presented are yields of hexafluorobenzene (gross and net), the recovery of unreacted tribromofluoromethane, and the amount of bromine liberated in the pyrolysis. In graphite tubes with charcoal packing the best yield of hexafluorobenzene was obtained at the lowest temperature, about 650°. This yield was 24%, or 30% based on reacted tribromofluoromethane. Increasing temperatures lowered the yield of hexafluorobenzene, although the amount of bromine liberated was increased. The two runs performed with platinum gauze as packing in graphite tubes show a reverse trend inasmuch as the better yield is obtained at the higher temperature (about 750°). A possible explanation of this may be that the tighter charcoal packing allowed for more contact time, which favored better reactions at lower temperatures, while at higher temperatures this may have given rise to more side reactions.

The results of the pyrolyses in Vycor glass tubes show considerably lower yields of hexafluorobenzene, as well as poor recovery of tribromofluoromethane. Increasing temperatures again produce lower yields. As one might expect, the interaction of fluorine-containing materials with glass results in the removal of fluorine atoms and consequently poorer yields of fluoro compounds.

Finally, a number of runs were performed in platinum tubes. The first three runs listed were done under nitrogen pressure of 1 atmosphere in an attempt to duplicate the results of Desirant.[4] The optimum yield obtained was 30% gross, or 32% net, at 600°. However, a noticeable improvement in the yield was achieved by performing the pyrolyses under nitrogen pressure of 4.5 atmospheres. Under these conditions the efficiency of the reaction was improved, as is evidenced by a lowered optimum temperature. The highest yield of hexafluorobenzene was obtained at 540 to 550° with the net yield reaching about 55%.

Tentative identification of some of the by-products was made by combining the high boiling fractions from all pyrolyses performed in graphite tubes and refractionating them under reduced pressure. Samples of individual cuts were analyzed by a mass spectrometer. A number of compounds were tentatively identified. Some of these compounds, in order of their decreasing abundance, are listed below

$C_2F_2Br_4$, $C_6F_4Br_2$, C_6F_5Br, $C_7F_6Br_2$, C_7F_7Br
$C_2F_2Br_2$, C_7F_8, $C_3F_4Br_2$, $C_3F_6Br_2$, $C_2F_4Br_2$

It appears that most of the by-products were bromofluoro derivatives of ethane and propane as well as benzene and toluene. The presence of the latter seems to indicate that occasionally fluorine was removed instead of bromine.

Discussion

In the light of the foregoing evidence, a mechanism of the reaction is postulated, which consists of the following four steps

$$2CFBr_3 \longrightarrow CFBr_2CFBr_2 + Br_2 \quad (1)$$

$$CFBrCFBr_2 \longrightarrow CFBr{=}CFBr + Br_2 \quad (2)$$

$$3CFBr{=}CFBr \longrightarrow C_6F_6Br_6 \quad (3)$$

$$C_6F_6Br_6 \longrightarrow C_6F_6 + 3Br_2 \quad (4)$$

Steps 1 and 2 should proceed rapidly at the temperature of the reaction. Increased pressure should have no effect on step 1 and a relatively minor effect on step 2. Step 3 would be the rate-determining step which should be strongly pressure dependent. The postulated intermediate $C_6F_6Br_6$, however, would be expected to be very unstable and decompose rapidly with the loss of bromine. One of the possible products of this decomposition should be hexafluorobenzene. The effect of pressure would be to drive the reaction to the left but again the rapidity of the bromine removal could be expected to overcome the opposing effect of pressure.

The residues (b.p. > 115°) of all the pressure runs in the platinum tube were combined and subjected to a steam distillation. The volatile fraction (79%) was dried and pyrolyzed again under the optimum conditions listed above. The material recovery was essentially quantitative. The weight of bromine removed amounted to 34% by weight of the recovered products. A partial analysis of the remaining fraction was as follows: 4.6% by weight hexafluorobenzene, 15.5% bromopentafluorobenzene, and small amounts of some C_7F_7Br product.

From these results it is quite evident, then, that the residues obtained from the initial pyrolysis of $CFBr_3$ still contain intermediates, such as $CFBr{=}CFBr$ and $CFBr_2{-}CFBr_2$, which are capable of producing more hexafluorobenzene by further concentration and pyrolysis. This, however, improves the net yield of C_6F_6 by only a few per cent.

Experimental

Tribromofluoromethane.—This compound was prepared essentially by the method of Rathsburg[6] using stoichiometric amounts of tetrabromomethane and antimony trifluoride in the presence of a small amount of bromine. Standard glass equipment was used. By refluxing for 4–6 hours from a bath kept at 120 to 140° and subsequent distillation, yields of 60 to 70% were obtained, which contribute a substantial improvement over the 19% yield reported by Rathsburg. The product was purified by washing with sodium bisulfite and sodium hydroxide. After drying over calcium chloride the product was fractionated in a four-foot column. Some of the tribromofluoromethane used in subsequent experiments was obtained from the Columbia Chemical Company, Columbia, South Carolina.

Hexafluorobenzene.—Pyrolysis of tribromofluoromethane was performed in a platinum tube 80 cm. long, 1 cm. wide and about 1 mm. thick. An electrically heated furnace was wound around this tube and the temperature of this furnace was controlled by an automatic relay. The entrance and exit of the tube were cooled by water-cooled brass condensers. Tribromofluoromethane was introduced from a reservoir by means of a solenoid pump. The outlet of the pyrolysis tube was connected to an ice-cooled trap followed by Dry Ice traps. For the runs performed at higher pressures a capillary tube was inserted between the traps. This proved to be adequate for keeping the system under pressure and ensure a slow and even flow rate. In a typical run tribromofluoromethane was introduced into the reservoir, and a slow stream of dry nitrogen was passed through the system while the furnace was brought to the desired temperature. The relay controlling the addition of tribromofluoromethane was then activated and the reagent added at a constant rate. After completion of the addition the product in the receiver and traps was carefully washed with sodium bisulfite and dilute sodium hydroxide. The loss of bromine was determined by weighing the product before and after washing. After drying, the washed product was fractionated to recover hexafluorobenzene (b.p. 79 to 81°) and unreacted tribromofluoromethane (b.p. 106 to 108°). The residues were saved for further purification.

The experiments in graphite and Vycor tubes were performed in a similar but cruder apparatus. The tubes were inserted vertically into a ceramic furnace with the inlet and outlet cooled by brass condensers. The dimensions of the tubes were 86 cm. long, 1.3 cm. wide and 2 mm. thick. The heated length of the tubes was 60 cm. The graphite tube was inserted into a tight fitting iron tube to ensure even heating and to protect the tube from breaking. At the top of the tube a dropping funnel with a bypass tube was inserted by means of a rubber stopper. The outlet of the pyrolysis tube was connected to two traps, one cooled in ice, the other in Dry Ice. Again dry nitrogen was passed through the system during the run. The rate of addition was controlled by setting the stopcock of the dropping funnel. The product was worked up as described above, with the additional step of combining all residues and fractionating them under reduced pressure to obtain samples for mass spectrometer analysis.

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WASHINGTON 25, D. C.

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[6] M. Rathsburg, *Ber.*, **51**, 669 (1918).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

Solvolysis of Alkyl Borates. Catalysis by Amines and Phenols[1]

BY CLINTON L. DENSON AND THOMAS I. CROWELL

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The ethanolysis of *sec*-butyl borate is subject to general catalysis by amines and phenols. The catalytic constants of the amines obey the Brönsted catalysis law except for negative deviations ascribed to steric effects.

The ethanolysis of *sec*-butyl borate, an ester interchange producing ethyl borate, recently was found to be subject to general acid and base catalysis.[2] The catalytic constants obtained, together with the existence of a solvent-catalyzed reaction, indicated that the solvolysis rate was only moderately sensitive to the acid or base strength of the catalyst, so that the effect of structure on reactivity of a greater variety of catalysts might easily be determined. We have now extended our previous results to include two phenols and a series of amines covering a fairly wide range of basicity and steric requirements.

Experimental

Materials.—*sec*-Butyl borate and dry ethanol were prepared as before.[2] Reagent grade pyridine was used. Other liquid amines were redistilled; aniline was distilled from zinc dust. Solid amines and *p*-nitrophenol were recrystallized from methanol–water and dried in a vacuum desiccator. Phenol was recrystallized from petroleum ether.

Procedure.—Solvolysis rates were determined dilatometrically in ethanol, at 25°, as previously described except that the time intervals were adapted to the method of Guggenheim and the data plotted accordingly, to give the first-order rate constants.[3]

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[1] From the M.S. thesis of Clinton L. Denson, University of Virginia, 1957.

[2] G. T. Perkins and T. I. Crowell, THIS JOURNAL, **78**, 6013 (1956).

[3] E. A. Guggenheim, *Phil. Mag.*, **1**, 538 (1926).