perturbating effect does not exist, the PbFCl structure was obtained for the whole series of the rare earth and yttrium oxybromides.

Acknowledgment.—The authors wish to thank the American Society for Testing Materials for the grant which made this work possible.

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Mass Spectrometric Studies of the Thermal Decomposition of Poly(carbon monofluoride)

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Received May 7, 1965

Poly(carbon monofluoride) was decomposed under a high vacuum at 420–580°, and the products were analyzed in a Bendix time-of-flight mass spectrometer. From mass spectra obtained at ionizing energies of 70, 25, and 16 e.v., it was found that the products consisted of perfluoroparaffins, tetrafluoroethylene, and two series of polyunsaturated compounds with general formulas C_nF_{n+4} and C_nF_{n+3}, where $n \geq 3$, for even and odd numbers of C atoms present in the molecule, respectively. Polyolefinic fluorocarbons with 22 or more C atoms were detected in the mixture.

The formation of poly(carbon monofluoride) (C_nF_n) from graphite and fluorine is now well known[1-7] and the structure and properties of this compound have been described by Rüdorff.[2,5] It has been found that when rapidly heated, poly(carbon monofluoride) deflagrates with production of a flame giving finely divided soot together with carbon tetrafluoride and higher fluorocarbons.[5] Attempts to analyze the various thermal decomposition products by mass spectrometry are discussed in this paper.

Experimental

Poly(carbon monofluoride) was prepared in the form of a fine gray powder by allowing spectroscopically pure graphite to react with 99.8% pure fluorine in a nickel reaction vessel at 450°.

Approximately 1 g. of the compound was placed in a Vycor glass tube of $^3/_8$-in. o.d. and 6-in. length closed at one end. A glass-wool plug was placed above the material and a constriction (about 0.5 mm.) was made on the tube at about 3 in. from the closed end. The open end was then attached to the inlet of the ion source of a Bendix Model 14-206A time-of-flight mass spectrometer through a Swagelok fitting using Teflon ferrules. After evacuation, the poly(carbon monofluoride) was slowly heated using a small electric furnace with the temperature monitored by a thermocouple. The mass spectra were scanned using the pulsed operation at various temperatures and under various electronic energies while the pressure in the ion source was maintained between 10^{-5} and 10^{-6} torr. To a first approximation, the thermal decomposition products pass through the ionization chamber without collision. There are, however, a few collisions and some grids, and plates in the region might be as hot as ~800°. Such collisions are believed to have little effect on the mass spectra since the species being observed were themselves generated at 400–600°.

In an attempt to simplify the identification of the decomposition products of C_nF_n, the compound was decomposed outside the mass spectrometer in a vacuum system and the products were collected into three fractions in traps respectively cooled in ice, Dry Ice–acetone, and liquid nitrogen. These fractions were then analyzed separately in the mass spectrometer.

Results

Total Decomposition of C_nF_n in the Mass Spectrometer.—On slow heating the poly(carbon monofluoride) started decomposing at about 420° with production of fluorocarbons with up to about six carbon atoms. The biggest peak observed at an ionizing energy of 70 e.v. was CF_3^+ followed by $C_3F_5^+$ and $C_2F_4^+$, at a temperature of 465°. As the temperature was further increased, the number of fluorocarbon peaks also increased enormously and at 580° ions with mass numbers even greater than 1000 were obtained. Mass assignments were made by considering the common mass differences of 12 (C), 19 (F), 31 (CF), 50 (CF_2), etc., in various combinations from definitely known lower mass peaks. The mass spectra were very complex at an ionizing energy of 70 e.v., but at 25 e.v. they were less complicated and at 16 e.v. they were fairly simple, because of the decrease in fragmentation. In Table I are listed the predominant ionic species observed at corrected electron energies of 70, 25, and 16 e.v., respectively. The reproducibility of the spectra was satisfactory.

Analysis of Fractionated Products.—Simple fractionation of the C_nF_n pyrolysis products yielded solid, liquid, and gaseous fractions at room temperature, and these were individually analyzed in the mass spectrometer. The mass spectra obtained were analogous to those obtained in the total decomposition of the C_nF_n in the mass spectrometer except that there was a progressive increase in the number of carbon atoms from gas to the solid. The gaseous sample showed fluorocarbons with up to about 8 C atoms, the liquid fraction showed up to about 14 C atoms, and the solid up to 22 or more C atoms.

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TABLE I

MASS SPECTRA OF THE THERMAL DECOMPOSITION PRODUCTS OF POLY(CARBON MONOFLUORIDE) AT 580°

Positive Ion	m/e	% Total Ion Current at 70 eV	25 eV	16 eV	Positive Ion	m/e	% Total Ion Current at 70 eV	25 eV	16 eV
CF	31	12.66	2.73	---	$C_{10}F_{12}$	348	0.04	0.55	0.51
CF_2	50	10.24	4.24	1.52	$C_{10}F_{13}$	367	0.06	0.49	---
CF_3	69	19.68	6.79	19.70	$C_{10}F_{14}$	386	0.03	0.79	1.01
C_2F	43	0.28	---	---	$C_{10}F_{15}$	405	0.06	0.36	---
C_2F_2	62	0.33	---	---	$C_{10}F_{16}$	424	0.03	0.49	---
C_2F_3	81	7.11	4.24	---	$C_{11}F_{12}$	360	---	0.18	---
C_2F_4	100	7.54	7.28	42.93	$C_{11}F_{13}$	379	0.04	0.24	---
C_2F_5	119	10.24	6.31	0.51	$C_{11}F_{14}$	398	0.03	0.73	1.01
C_3F	55	0.26	---	---	$C_{11}F_{15}$	417	0.06	0.67	---
C_3F_2	74	0.57	---	---	$C_{11}F_{16}$	436	0.04	0.67	1.01
C_3F_3	93	7.96	0.42	---	$C_{11}F_{17}$	455	---	0.18	---
C_3F_4	112	0.41	0.36	---	$C_{11}F_{18}$	474	---	0.18	---
C_3F_5	131	7.25	5.09	0.51	$C_{12}F_{13}$	391	0.04	0.18	---
C_3F_6	150	0.85	6.55	17.68	$C_{12}F_{14}$	410	---	0.30	---
C_3F_7	169	0.92	2.00	---	$C_{12}F_{15}$	429	---	0.12	---
C_4F_2	86	4.27	---	---	$C_{12}F_{16}$	448	0.03	0.30	0.51
C_4F_4	124	0.44	---	---	$C_{12}F_{17}$	467	0.01	0.24	---
C_4F_5	143	0.74	0.55	---	$C_{12}F_{18}$	486	0.03	0.18	---
C_4F_6	162	0.57	3.64	0.51	$C_{13}F_{15}$	441	---	0.30	---
C_4F_7	181	0.74	2.49	---	$C_{13}F_{16}$	460	0.03	0.91	1.01
C_4F_8	200	0.11	1.82	2.02	$C_{13}F_{17}$	479	---	0.12	---
C_4F_9	219	0.28	0.48	---	$C_{13}F_{18}$	498	---	0.24	---
C_5F_3	117	0.44	---	---	$C_{13}F_{19}$	517	---	0.12	---
C_5F_4	136	0.07	---	---	$C_{13}F_{20}$	536	---	0.24	---
C_5F_5	155	0.43	---	---	$C_{13}F_{21}$	555	---	0.12	---
C_5F_6	174	0.07	0.12	---	$C_{14}F_{15}$	453	---	0.12	---
C_5F_7	193	0.51	1.33	---	$C_{14}F_{16}$	472	0.01	0.24	---
C_5F_8	212	1.07	6.31	2.02	$C_{14}F_{17}$	491	---	0.24	---
C_5F_9	231	0.07	0.30	---	$C_{14}F_{18}$	510	0.01	0.85	1.01
C_5F_{10}	250	0.06	---	---	$C_{14}F_{19}$	529	---	0.12	---
C_6F_4	148	0.06	---	---	$C_{14}F_{20}$	548	0.01	0.18	---
C_6F_5	167	0.07	---	---	$C_{14}F_{21}$	567	---	0.12	---
C_6F_6	186	0.10	---	---	$C_{15}F_{17}$	503	0.01	0.12	---
C_6F_7	205	0.28	0.49	---	$C_{15}F_{18}$	522	0.01	0.30	0.51
C_6F_8	224	0.07	0.36	---	$C_{15}F_{19}$	541	---	0.18	---
C_6F_9	243	0.92	4.00	0.51	$C_{15}F_{20}$	560	---	0.36	---
C_6F_{10}	262	---	4.24	3.03	$C_{16}F_{18}$	534	0.01	0.24	---
C_7F_5	179	0.09	---	---	$C_{16}F_{20}$	572	0.01	0.67	---
C_7F_7	217	0.14	---	---	$C_{16}F_{21}$	591	---	0.12	---
C_7F_8	236	0.09	0.18	---	$C_{16}F_{22}$	610	---	0.42	---
C_7F_9	255	0.17	0.61	---	$C_{17}F_{20}$	584	---	0.42	---
C_7F_{10}	274	0.10	1.33	1.01	$C_{17}F_{21}$	603	---	0.06	---
C_7F_{11}	293	0.40	1.94	---	$C_{17}F_{22}$	622	---	0.24	---
C_7F_{12}	312	0.04	0.91	---	$C_{17}F_{23}$	641	---	0.06	---
C_8F_9	267	---	0.30	---	$C_{17}F_{24}$	660	---	0.12	---
C_8F_{10}	286	0.04	0.30	---	$C_{17}F_{25}$	679	---	0.12	---
C_8F_{11}	305	0.11	0.85	---	$C_{18}F_{20}$	596	---	0.12	---
C_8F_{12}	324	0.07	1.21	1.01	$C_{18}F_{21}$	615	---	0.12	---
C_8F_{13}	343	0.10	0.49	---	$C_{18}F_{22}$	634	---	0.30	---
C_8F_{14}	362	---	0.18	---	$C_{18}F_{23}$	653	---	0.06	---
C_9F_{10}	298	0.07	0.24	---	$C_{19}F_{20}$	608	---	0.36	---
C_9F_{11}	317	0.07	0.42	---	$C_{19}F_{22}$	646	---	0.24	---
C_9F_{12}	336	0.04	0.67	0.51	$C_{20}F_{22}$	658	---	0.18	---
C_9F_{13}	355	0.04	0.36	---	$C_{20}F_{24}$	696	---	0.85	---
C_9F_{14}	374	0.03	0.55	---	$C_{21}F_{24}$	708	---	0.18	---
$C_{10}F_{11}$	329	0.06	0.24	---	$C_{22}F_{26}$	758	---	0.36	---

Discussion

At first sight, the mass spectra of the total decomposition products look extremely complicated, especially at an ionizing energy of 70 e.v. Since poly(carbon monofluoride) contains only carbon and fluorine, the possible products are only perfluorocarbons—aliphatic and/or aromatic. However, a cursory glance at Table I shows that aromatic perfluoro compounds are not present to any measurable extent because of the absence of the ion $C_6F_6^+$. Perfluorobenzene is known to give a large parent ion,[8] but perfluoroalkanes, both normal and branched chain, give rather complicated mass spectra.[9] The largest peak is usually CF_3^+ with appreciable amounts of alkyl ions of the type $C_nF_{2n+1}^+$ formed by fragmentation. The parent ions in these cases are always negligible. From the abundance of the relatively low molecular weight ions such as CF_2^+, CF_3^+, $C_2F_5^+$, $C_3F_5^+$, $C_3F_7^+$, etc., it is evident that perfluoroparaffins are present in the decomposition products of poly(carbon monofluoride), although it is impossible to identify them individually by simple mass spectrometry.

The interesting thing about these mass spectra comes from the fact that perfluoroolefins in general give both a large parent ion peak and an ion peak with one F atom less, together with lower fragments. The parent ions are observable because of their resonance stabilization, resulting in reduced ionization potentials of the double bond (π) electrons.[10]

It may be clearly seen from Table I that tetrafluoroethylene is the most abundant olefin in the series. The fact that its abundance remains a maximum even at the lowest ionizing energy of 16 e.v. proves that it is not a fragment of higher members in the mass spectrometer. It is also interesting that for compounds with three or more C atoms there are two series of predominant ion peaks. For ions with an even number of C atoms the general formula is C_nF_{n+4} and for those with an odd number it is C_nF_{n+3}. There are also two other series of peaks corresponding to C_nF_{n+3} and C_nF_{n+2}, respectively, for ions with even and odd numbers of C atoms. There is no doubt that the two latter series arise out of the removal of a fluorine atom from the two former series, since at increasing ionizing voltages the intensities of C_nF_{n+4} and C_nF_{n+3} decrease with a corresponding increase in the C_nF_{n+3} and C_nF_{n+2}, peaks, respectively. Thus, it is reasonable to believe that the two series C_nF_{n+4} for even and C_nF_{n+3} for odd number of C atoms in the molecules consist of parent ions which are highly unsaturated olefins. As a matter of fact at 16 e.v. only the assumed parent ion peaks are present to any measurable extent, although they become very weak with increasing mass numbers, which confirms the presence of the two series of poly unsaturated fluorocarbons in the mixture. Even-C ions of formula C_nF_{n+6} and odd-C ions of formula C_nF_{n+5} and C_nF_{n+7} are also observed at low ionizing voltages.

Considering the structure of poly(carbon monofluoride) as proposed by Rüdorff,[2] it is probable that these two types of unsaturated compounds are unbranched. Thus, the difference in these types is that for molecules with an even number of C atoms the ends are two CF_3 groups while for those with an odd number they consist of a CF_2 and a CF_3 group. Structural differences cannot be unequivocally detected in a complex mixture of this type by simple mass spectrometry and it is possible

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that compounds with branched chains are also present along with the linear fluorocarbons. Nevertheless, with an ionizing energy of 16 e.v., ions of the type C_nF_{n+2} which have to have two CF_2 end groups are not observed in abundance, with the exception of tetrafluoroethylene and perfluorobutadiene, indicating that branched-chain fluorocarbons are not present in the mixture to any appreciable extent. Perfluorocycloparaffins and perfluorocycloolefins both seem to be absent since ions of the type C_nF_{2n} and C_nF_n are not observed at low ionizing voltages. Thus the mass spectra for the decomposition products from poly(carbon monofluoride) apparently arise from perfluoroparaffins of formula C_nF_{2n+2} which give rise to low molecular weight fragments, tetrafluoroethylene, and the various types of polyunsaturated compounds containing three or more C atoms with the formulas C_nF_{n+4} and C_nF_{n+6}, etc., for even-C molecules and C_nF_{n+3}, C_nF_{n+5}, C_nF_{n+7}, etc., for odd-C molecules.

On structural grounds [$(CF)_n$] and by analogy to the thermal depolymerization of Teflon[11,12] [$(CF_2)_n$], one might expect the formation of difluoroacetylene ($CF \equiv CF$), in the thermal decomposition of poly(carbon monofluoride). Although a small ion peak for C_2F_2 at an ionizing energy of 70 e.v. is observed, it must be attributed to fragmentation of higher molecular weight compounds, since it disappears at the lower energies of 25 and 15 e.v.

Acknowledgments.—This research was performed under United States Air Force Contract No. AF 33(615)-1138, through funds administered by Wright-Patterson Air Force Base. The authors are pleased to acknowledge the aid of Dr. T. C. Ehlert in initial stages of this work and helpful conversations with Drs. R. A. Kent and P. L. Timms.

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The Fluorosulfuric Acid Solvent System. II.[1] Solutions of Antimony Pentafluoride, Antimony Tetrafluoride Monofluorosulfate, and Antimony Pentafluoride–Sulfur Trioxide Mixtures

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Received April 2, 1965

Conductometric, cryoscopic, and nuclear magnetic resonance studies on solutions of SbF_5, SbF_4SO_3F, and SbF_5–SO_3 mixtures in fluorosulfuric acid show that there exists a series of acids with the general formula $H[SbF_{5-n}(SO_3F)_{1+n}]$ where n = 0, 1, 2, and 3 which increase in strength with increasing values of n. The acid $H[SbF_2(SO_3F)_4]$ is a strong acid of the fluorosulfuric acid solvent system. Dimeric and probably higher polymeric forms of these acids are also present in the solutions and n.m.r. studies show that polymerization occurs through fluorosulfate bridges. The fluorosulfuric acidium ion, $H_2SO_3F^+$, has been shown to have an abnormally high conductivity in this solvent and it is concluded that it conducts by proton transfer.

Introduction

Woolf[2] found that antimony pentafluoride gives conducting solutions in fluorosulfuric acid which can be titrated with the strong base potassium fluorosulfate, indicating that SbF_5 behaves as an acid; however, he determined neither the mode nor the degree of ionization. This paper describes conductometric, cryoscopic, and nuclear magnetic resonance studies on solutions of SbF_5, $SbF_4(SO_3F)$, and SbF_5–SO_3 mixtures in fluorosulfuric acid.

Experimental

Electrical Conductivity Measurements.—The apparatus used for the conductivity measurements has been described previously.[1] Additions of antimony pentafluoride and sulfur trioxide were made to the conductivity cell in the form of concentrated solutions in fluorosulfuric acid. All the measurements were made at 25°.

^{19}F Nuclear Magnetic Resonance.—The n.m.r. measurements were made with a Varian Associates HR 60 spectrometer operating at 56.4 Mc./sec. and equipped with a variable temperature accessory. Temperatures were measured with a copper–constantan thermocouple and a Leeds and Northrup temperature potentiometer. The spectra were calibrated by the side-band technique using a Muirhead-Wigan D-890-A decade oscillator. Solutions were prepared in tubes made from selected 5-mm. glass tubing. The components were introduced by means of capillary droppers, and the tubes then were sealed off.

Cryoscopic Measurements.—The apparatus and experimental technique are described in part III.[3]

Materials.—Fluorosulfuric acid and potassium fluorosulfate were purified as described previously.[1] Commercial antimony pentafluoride was triple distilled in an all-glass apparatus in an atmosphere of dry air (b.p. 142–143°). Sulfur trioxide was distilled from 30 or 65% oleum to which potassium persulfate had

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