

Mass Spectrometric Techniques Applied to the Investigation
of the Thermal Degradation of Polymers

by

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Abstract

The problems of analyzing mixtures of fluorocarbons by mass spectral techniques are discussed. The effects of temperature and of the energy of the ionizing electrons on mass spectra are illustrated. The application of the linear, pulsed time-of-flight mass spectrometer to the study of reacting fluorocarbon systems is discussed and the experimental program based on this application is outlined.

Introduction.

The mass spectrometric research program at the National Bureau of Standards applied to the problem of thermal degradation of polymers has been primarily occupied with completing the instrumentation necessary for investigation of fast reactions and the analysis of fluorocarbon mixtures. The laboratory now has two instruments available for these studies. They are a modified Consolidated Electrodynamics Corporation Model 21-102, 5-inch radius of curvature, 180° magnetic deflection mass spectrometer and a Bendix Corporation Model 14 time-of-flight mass spectrometer.

The mass spectral analysis of fluorocarbon systems is quite difficult due to the similarity of the mass spectra of the fluorocarbons and the lack of high mass ions. In order to analyze the products of the reactions of fluorocarbon radicals to be studied with the Bendix instrument it is necessary to have a fairly complete understanding of the ionization-dissociation processes of the fluorocarbons involved and to know the effect of temperature on these processes.

The Consolidated Electrodynamics Corporation 21-102 Mass Spectrometer and its Applications.

1. Description

The CEC instrument has been rebuilt to provide better sensitivity and stability. A heated inlet system has been added to permit examination of liquid and solid materials. The instrument now consists of a heated inlet oven with a stainless steel inlet block, high resolution analyzer and associated electronics. The valves and expansion volume of the inlet system are stainless steel with teflon seats and gaskets. This system can be maintained at 200°C or raised to over 250° for several hours at a time. A new high resolution analyzer is used with a four coil, high temperature magnet which has had the pole faces cut to accomodate this analyzer.

To improve the stability of the instrument the following changes have been made:

a. The instrument power is supplied by a 3 kva constant voltage transformer having low harmonic output. This transformer receives its input power from one isolated output of a 7.5 kva isolation transformer. A second output from an isolation transformer supplies power for the mechanical requirements of the instrument. A single ground return point is provided for the entire instrument.

b. The regulation circuit of the magnet power supply has been changed so that it now acts as a constant current supply rather than a constant voltage supply thus correcting for the temperature variation of the magnet coil resistance.

c. The high voltage supply and regulation circuit have been replaced with a commercial 6000v 20ma supply having greater stability.

d. The r-c controlled sweep circuit has been replaced by an electromechanical sweep which is quite stable and very easily controlled.

e. The dc amplifier has been replaced by a vibrating reed electrometer which drives a pen recorder. This change reduced the noise level significantly thereby increasing the sensitivity of the instrument.

f. Some slight modifications were made in the filament emission control circuits which give greater stability of operation when using low energy electrons to produce ionization.

The instrument is capable of remaining on a mass peak for many hours, and has sensitivity and noise level equivalent to currently available commercial instruments. The 180° mass spectrometer is suited to several studies applicable to the better understanding of the mechanism of thermal degradation of polymers.

2. Applications.

Utilizing the heated inlet system it is possible to examine material not volatile at room temperatures. After analytical schemes are devised this may give some information as to the nature of some of the waxy products and residues formed in thermal degradation experiments.

Investigations of the ionization-dissociation processes occurring in the "low molecular weight polymers" such as the straight chained hydrocarbons and fluorocarbons can also be carried out with this mass spectrometer. The resulting information coupled with knowledge of radical ionization potentials may permit estimation of bond strengths and heats of formations. There are many problems involved in obtaining good values for these quantities from the interpretation of experimental ionization efficiency curves ^{1,2}. These problems are both theoretical and experimental, arising primarily from the lack of knowledge of the exact processes involved in the dissociation, from the experimental difficulties in completely accounting for all the energy involved in these processes, and from the distortion of the ionization efficiency curves produced by the instrument itself. The ionization efficiency curves of the radicals being studied would also lead to a means of identifying the radicals in reacting systems.

The information on the ionization efficiencies of the various ions in the mass spectra of such homologous series also provides the basis for analysis of mixtures of these materials. The low voltage mass spectra can be used to help identify the species present in a gaseous mixture since the number of dissociation processes can be greatly reduced when ionization is produced by low energy electrons thereby simplifying the mass spectra. In the fluorocarbon systems being investigated this reduction of the mass spectral data produced by ionizing with low energy electrons will simplify the analytical problem. However, the similarity of the cracking patterns of the fluorocarbons will still make the analysis of such reacting systems difficult. This will be further complicated by the variation of the mass spectra with temperature.

The difficulty in analyzing a mixture of fluorocarbons solely on the basis of the information obtained from the 70 volt mass spectra can be seen by referring to Table I. This table presents the 70 volt mass spectrum for some saturated fluorocarbons and for C_2F_4 ^{2/}. The saturated fluorocarbons are seen to have their major mass peak at $m/e = 69$, the CF_3^+ ion, with generally no parent molecular ion $[C_nF_{2n+2}]^+$. Mixtures of certain of these components could easily be analyzed, e.g. CF_4 , C_2F_4 , and C_2F_6 or C_3F_8 , since the mass spectral contribution due to C_2F_4 can be based upon the C_2F_4 ($m/e = 100$) peak; the contribution due to C_2F_6 or C_3F_8 can be based upon the C_2F_5 ($m/e = 119$) or C_3F_7 ($m/e = 169$) peaks respectively with the remaining portion of the mixture mass spectrum due to CF_4 , which could be checked by comparison with its mass spectrum. This analysis along with the knowledge of the relative ionization cross sections for these compounds with 70 volt electrons would yield the partial pressure of each component in the original gaseous mixture. However, if the mixture contains several saturated fluorocarbons then the analysis becomes difficult and ambiguous when based solely on the 70 volt electron mass spectra. This is a result of the similarity of the mass spectra of the saturated fluorocarbons and the relatively small contribution of the high mass ions to the mass spectra of these compounds. A quantitative analysis is difficult if it has to be based upon a minor mass peak which would be the case if the mixture contained a heavier fluorocarbon, e.g. perfluorobutane, C_4F_{10} , in which the highest mass peak $m/e = 219$, $C_4F_9^+$ ion, is 2.6% of the major peak CF_3^+ or less than 0.7% of the contribution of C_4F_{10} to the total mass spectrum of the mixture. The 70 volt mass spectra of higher members of the perfluoroalkane series are even more similar and contain less information on which an analysis can be based.

The dependence of these mass spectra on temperature is also necessary information. If there is a significant temperature dependence then a quantitative determination will be impossible for a reaction performed and analyzed at a temperature other than that at which the comparison cracking pattern was obtained.

3. Experimental.

Using a modification of the technique of Reese et al ^{4/} the dependence of the cracking pattern of C_3F_8 on temperature was studied. The temperature of the ion source was adjusted in the range of 150°C to 300°C by varying the power to the auxiliary source heater of the isatron on the CEC 21-102 mass spectrometer. When the temperature stabilized, the cracking pattern of the perfluoropropane was obtained. The experimental parameters of interest during this procedure were as follows:

- a) pressure against the mass spectrometer leak was approximately 50 microns of C_3F_8 ;
- b) time delay between admitting the sample and obtaining the mass spectrum was 2 minutes;
- c) 70 volt ionizing electrons at a collector current of 10 microamperes were used;
- d) the magnet current was 0.81 amperes. This value gave ample coverage of the mass range studied.

The cracking pattern was obtained by scanning (electrostatically) from high mass to low mass and back again. To remove the effect of the decrease in pressure against the leak with time the two values for each mass peak were averaged for each determination. The results of these studies on C_3F_8 are given in Table II. The pattern coefficients, percent change per degree centigrade, in Table II, are calculated at $250^\circ C$ and are expressed relative to the CF_3^+ peak. The absolute temperature coefficient and sensitivity can be obtained from this data if the variation in equilibrium source pressure with temperature is known. This information was obtained by studying the temperature effect on the mass spectral sensitivity of a rare gas, argon. The results of this study are found in Table III. The variations in equilibrium ion source pressure with temperature, as studied with argon, were performed by recording the ion current of Ar^+ ($m/e = 40$) with the same experimental parameters listed. In this case the temperature was varied by removing the power to the isatron heater and allowing the ion source to cool. The variations of temperature with time and of inlet pressure with time are found in Table IV. With this information the variation in source equilibrium pressure can be obtained by correcting the experimental data in Table III for inlet pressure variation, this data being found in the column headed corrected peak height.

4. Discussion.

It is seen in Table II that there is a small but significant temperature dependence for all the ions even for the small range of temperatures studied. To correct these temperature coefficients for the variation in equilibrium source pressure with temperature and obtain the absolute temperature coefficients requires interpretation of the data found in Table III. For this purpose it is convenient to assume that the mass spectrometer system is composed of three regions as follows:

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- a) the inlet system to the gold leak,
- b) the inlet tube from the gold leak to the mass spectrometer and the ion source,
- c) the mass spectrometer analyzer and pumping system.

From Table IV the pressure in the inlet system can be corrected for the loss of molecules through the gold leak and therefore the inlet system can be considered as an infinite supply of gas molecules for the mass spectrometer. The number of molecules entering the ion source through the gold leak must be equal to the number leaving the ion source through the ion exit slit, electron beam slit and any other openings in the source. This number per unit time becomes a constant, n , after the inlet pressure variation with time is corrected as discussed above. The number of molecules leaving the ion source per unit time is now dependent upon the number of molecules present in the source, n_0 , and the mean velocity of these molecules, since the mean lifetime of a molecule in the source will depend only on its mean velocity for a fixed source geometry, i.e.

$$N = kn_0\bar{c} \quad (1)$$

where k is the geometry factor. The mean velocity is given by

$$\bar{c} = \sqrt{\frac{8RT}{\pi M}} \quad (2)$$

and therefore the number of molecules in the source at any time is

$$n_0 = \frac{n}{k} \sqrt{\frac{\pi M}{8RT}} \quad (3)$$

The data in Table III when plotted as sensitivity vs $(T)^{-1/2}$ is a straight line whose slope at 250° gives a temperature coefficient for argon of -0.17% per $^\circ\text{C}$. Since the ionization cross section for argon is independent of temperature in this range, the pattern coefficients for C_3F_8 can be corrected for this variation in n_0 . This results in the corrected pattern coefficients in Table V.

The studies of the ionization-dissociation processes, of both the positive and negative ion mass spectra and the temperature dependence of the mass spectra of the perfluoroalkanes and selected other perfluoro compounds are being continued.

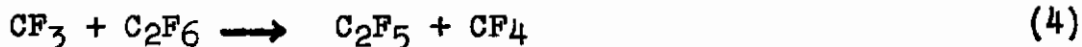
The Bendix Corporation Model 14 Mass Spectrometer and its Applications.

1. Description.

This instrument is capable of obtaining a positive ion or negative ion mass spectrum produced by pulsed (10 kc rate) or continuous ionization. The mass spectrum can be displayed on an oscilloscope, from which the individual mass spectra (obtained every 100 μ sec) can be recorded by a revolving drum camera. Alternately, a slower recording camera can integrate these mass spectra optically at shutter speeds from 1/10 sec to 1/100 sec. The output of the ion multiplier can be monitored by means of six gating-electrometer circuits so that the variation with time of six different mass peaks can be recorded simultaneously (at a frequency response of 150 cycles for maximum fidelity). The mass spectrum can be obtained by time scanning with the gating circuits. Thus, this instrument has the capability of recording rapid changes in dynamic reactions or the variation of steady state reactions (e.g. in flow reactors) with experimental parameters, i.e. concentration, temperature, time. These features together with the physical construction and geometry of its ion source make the Bendix instrument highly suited for the study of reactive species. These studies to be performed in flow systems are directed towards the evaluation of rate constants and energetics for radical recombination, abstraction and disproportionation reactions.

2. Discussion.

In the system chosen to begin the study of fluorocarbon reactions with the Bendix mass spectrometer, $\text{CF}_3 + \text{C}_2\text{F}_6$, the following fluorocarbon molecules and radicals can be expected: CF_3 , C_2F_5 , C_2F_4 , C_2F_6 , C_3F_8 , C_4F_{10} . These would be produced from the following probable reactions:



To understand the proposed reaction, the CF_3 radical concentration and the concentrations of the stable products C_3F_8 , C_4F_{10} , C_2F_4 have to be known as functions of temperature, time and initial concentration of C_2F_6 . There are many analytical problems which must be solved before this can be done.

A group of ions can be selected on the basis of the information in Table I which will permit the analysis of this system provided that the concentration of CF_3 radicals can be determined and that the mass spectra of the products are a known function of temperature. The low voltage mass spectra will permit the determination of the CF_3 radical since its ionization potential is 10.1 ev $\frac{2}{\text{}}$ while the appearance potential of the mass 69 peak from the fluorocarbons is about 15 ev (15.4 from CF_4 , 14.3 from C_2F_5 , 14.4 from C_3F_8 $\frac{3}{\text{}}$ etc.) Thus if the mass spectra of these compounds produced by low energy electrons (suitable values to be experimentally determined to give maximum analytical information) are known then the composition of the reacting system can be determined.

It is also necessary to know the effect of temperature on the mass spectra since the open ion source of the Bendix mass spectrometer (which makes it a good instrument for studying reactive species) minimizes collisions of the gases with the ion source walls. Therefore, the temperature of the gases being ionized is essentially that of the reacting system. Thus the mass spectra obtained with this instrument is influenced much more by the sample temperature than in the CEC instrument where the molecules come into thermal equilibrium with the ion source walls before ionization. $\frac{7}{\text{}}$

Conclusion.

This research involves closely interrelated experimental programs on these two mass spectrometers which will add to the small but growing compilation of data available on the thermochemistry of fluorocarbons. This data along with the mass spectrometric analytical schemes being developed in these studies will help provide the basis for analyzing and understanding fluorocarbon polymers systems at elevated temperatures.

Table I

Mass Spectra of some Fluorocarbons at 270°C

<u>Ion</u>	<u>CF₄</u>	<u>C₂F₆</u>	<u>C₃F₈</u>	<u>C₄F₁₀</u>	<u>C₂F₄</u>	<u>m/e</u>
C	7.8	1.49	2.4	0.19	12.6	12
F	6.7	1.22	0.98	.14	2.77	19
CF	4.9	18.3	28.8	12.2	100.	31
CF ₂	11.8	10.1	9.3	4.16	29.5	50
CF ₃	100	100	100	100	2.83	69
CF ₄	0	-	-	-	-	88
C ₂	-	-	-	-	3.03	24
C ₂ F	-	-	-	-	1.44	43
C ₂ F ₂	-	-	-	-	0.99	62
C ₂ F ₃	-	-	-	-	63.1	81
C ₂ F ₄	-	0.55	6.55	8.40	33.8	100
C ₂ F ₅	-	41.3	9.0	18.3	-	119
C ₂ F ₆	-	0.15	-	-	-	138
C ₃ F ₃	-	-	0.55	1.20	-	93
C ₃ F ₅	-	-	.23	8.37	-	131
C ₃ F ₆	-	-	.05	2.55	-	150
C ₃ F ₇	-	-	24.6	2.14	-	169
C ₃ F ₈	-	-	0	-	-	188
C ₄ F ₇	-	-	-	0.03	-	181
C ₄ F ₉	-	-	-	2.57	-	219
C ₄ F ₁₀	-	-	-	0	-	238

Table II

Variation of the Mass Spectra of C₃F₈ with Temperature

<u>m/e</u>	<u>Ion</u>	<u>Temperature °Centigrade</u>					<u>Pat- tern** Coeffi- cients</u>
		<u>210</u>	<u>236</u>	<u>258</u>	<u>279</u>	<u>291</u>	
		<u>Relative Abundance*</u>					
31	CF ⁺	24.0 ₀	24.1 ₈	23.7 ₂	24.1 ₁	23.6 ₄	-0.04
50	CF ₂ ⁺	7.6 ₇	7.5 ₆	7.5 ₉	7.6 ₇	7.6 ₈	+0.02
69	CF ₃ ⁺	100	100	100	100	100	-
100	C ₂ F ₄ ⁺	6.1 ₀	5.8 ₃	5.6 ₂	5.7 ₆	5.8 ₄	-0.07
119	C ₂ F ₅ ⁺	9.1 ₉	9.3 ₀	9.4 ₃	9.5 ₀	9.4 ₁	+0.06
169	C ₃ F ₇ ⁺	22.2 ₄	20.9 ₈	19.9 ₆	19.0 ₇	18.9 ₆	-0.22

*Relative abundance of the ions compared to the largest peak CF₃⁺, m/e 69.

**Percent change in relative abundance at 250°C per degree centigrade.

Table III

Mass Spectrometric Sensitivity for Argon as
a Function of Temperature

<u>Time</u>	<u>Ar⁺ peak height</u>		<u>Sensitivity^a</u>			
	<u>Uncorrected</u>	<u>Corrected</u>	<u>mv/u</u>	<u>T</u>	<u>$\frac{1}{T} \times 10^4$</u>	<u>$\sqrt{\frac{1}{T} \times 10^2}$</u>
0 ^b	4705	4705	72.74	574	17.42	4.17
1	4700	4716	72.91	574	17.42	4.17
2 ^c	4685	4717	72.93	574	17.42	4.17
3	4700	4748	73.40	563	17.76	4.22
4	4705	4769	73.73	555	18.01	4.24
5	4705	4785	73.98	548	18.24	4.27
6	4710	4806	74.30	542	18.45	4.30
7	4720	4832	74.70	535	18.69	4.32
8	4725	4853	75.03	530	18.86	4.34
9	4750	4894	75.66	527	18.97	4.35
10	4755	4915	75.99	522	19.15	4.38
11	4760	4936	76.31	518	19.30	4.39
12	4770	4962	76.71	515	19.41	4.40
13	4780	4988	77.11	513	19.49	4.41
17	4798	5070	78.38	501	19.96	4.47
22	4795	5147	79.57	488	20.49	4.52
27	4790	5222	80.73	480	20.83	4.56
32	4765	5277	81.58	475	21.05	4.59
42	4690	5362	82.90	463	21.59	4.64

- a) Input resistance to electrometer was $10^{11} \Omega$. ✓
 b) Inlet system opened to mass spectrometer.
 c) Power to isatron heater shut off.

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Table IV

Variation of Inlet Pressure and Isatron Temperature with Time

<u>Time (Minutes)</u>	<u>Temp. °C</u>	<u>Pressure Microns</u>
0	301	55.97
1	290	-
2	284	55.68
3	275	-
4	269	55.39
5	262	-
6	257	54.96
7	254	-
8	249	54.60
9	245	-
10	242	54.24
12	-	53.96
15	228	53.24
17	-	52.88
20	215	-
21	-	52.16
23	-	51.73
25	207	51.37
27	-	51.09
29	-	50.66
30	202	-
31	-	50.30
35	195	-
40	190	-

Table V

Pattern Coefficients* for C₃F₈ Corrected for Change in

Source Gas Density with Temperature

<u>m/e</u>	<u>31</u>	<u>50</u>	<u>69</u>	<u>100</u>	<u>119</u>	<u>169</u>
ion	CF ⁺	CF ₂ ⁺	CF ₃ ⁺	C ₂ F ₄ ⁺	C ₂ F ₅ ⁺	C ₃ F ₇ ⁺
Pattern Coefficient	+0.13	+0.17	-	+0.10	+0.23	-0.05

*Pattern Coefficient is given in terms of the percent change in the relative abundance of the ion per degree centigrade at 250°C.

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