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THERMOGRAVIMETRY COMBINED WITH CHEMICAL IONIZATION MASS SPECTROMETRY A NEW TECHNIQUE IN THERMAL ANALYSIS*

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ABSTRACT

Detailed accounts are given on the simultaneous application of a thermobalance and a quadrupole mass spectrometer with chemical ionization (CI), investigating thermal decomposition reactions under normal pressure most efficiently.

In the combined dynamic system the purge gas of the thermoanalyzer is simultaneously used as reaction gas in the chemical ionization source. The use of CI, a type of high pressure mass spectrometry, has the advantage of avoiding all interface problems and of restricting the fragmentation of released volatile compounds. Therefore, this technique allows the identification of volatiles and the determination of their sequence of release even in complex decomposition reactions.

The capability of the tandem system is demonstrated by the thermal decomposition of some selected compounds.

INTRODUCTION

Quite a lot has been written about the mass spectrometric identification of volatile decomposition products in thermogravimetric analysis[1–6]. In combination with a thermobalance a mass spectrometer with rapid scan capability represents the most powerful analytical tool for indentifying volatiles, released during thermal decomposition reactions. Formerly time-of-flight mass spectrometers were used being nowadays replaced by quadrupole mass spectrometers.

Instrumental problems, which are reported, lie mainly in the interface-systems, caused by the difference in the working pressure of the two apparatus. In recent papers two ways are suggested for solving these interface problems.

(1) Systems in which the mass spectrometer is included in the high vacuum-sytem of the thermobalance[3–6]. This method has the disadvantage that thermolysis can only be carried out in vacuum.

(2) Systems in which the thermobalance works under normal pressure, using complicated pressure reducing systems (seperators, capillary) between the thermoanalyzer and the mass spectrometer in order not to exceed the maximal working pressure of the latter instrument[1,2].

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The aim of this paper is to present a combined TG–MS system, in which the thermobalance works under normal pressure, connected to the mass spectrometer in a very simple manner by using a chemical ionization (CIMS) source, working at elevated pressure. The TG–CIMS system offers the great advantage in using the purge gas of the thermobalance as reaction gas in the chemical ionization source, in addition to the dual function of controlling the atmosphere in the furnace cell and of sweeping the volatiles into the mass spectrometer. In CIMS, a type of high pressure mass spectrometry[7], the ion source can be charged with a pressure up to 1 Torr. A complicated pressure reduction system between thermobalance and mass spectrometer is therefore avoided. The purge gas flow from the thermobalance is simply split by a three-way metering valve.

According to the reaction gas used a suitable working pressure between 0.4 and 1 Torr can be established in the ion source. Up to a flow-rate of 20 ml min^{-1} the purge gas, i.e. reaction gas may be injected directly into the ion source without any pressure reduction.

The ionization of the volatiles by CI results in ion–molecule reactions, which occur between the ionized reaction gas molecules and the sample molecules. The amount of energy involved in these reactions tends to be low, therefore, fragmentation of sample molecules is greatly reduced.

Chemical ionization offers the advantage of simpler cracking patterns, intense molecular ions (or quasimolecular ions in case of hydrocarbons used as reaction gas) and therefore easy-to-interpret spectra, especially useful in the analysis of mixtures, which often occur in the course of thermal decomposition.

TG–CIMS should be performed, whenever one is interested in a detailed simultaneous analysis of the complex mixture of volatiles, evolved during thermal degradation reactions. The combined use of TG and CIMS promises to be a powerful analytical tool. Not only can we expect higher system sensitivity but we can also get additional information, not obtainable by use of a mass spectrometer in EI mode.

The application of TG–CIMS is only limited by the sensitivity of both instruments. The mutual adjustment of the sensitivities of both apparatus in the tandem system is easily performed.

In this paper the use of TG–CIMS is demonstrated by the investigation of the well-known thermal decomposition of calcium oxalate hydrate and copper tetrammine sulphate hydrate. The thermal decomposition of potassium trifluoroacetate is chosen as an example for demonstrating the special advantages of TG–CIMS.

EXPERIMENTAL

Instrumentation

Figure 1 shows the schematic diagram of the used tandem instrument, which consists of a Mettler thermoanalyzer TA 2, coupled to a Finnigan Quadrupole mass-spectrometer 3200, with a combined EI–CI source.

The line from the thermobalance to the mass spectrometer is 1/8 in. o.d. stainless-steel tubing. The quartz furnace is connected to the coupling line by means of

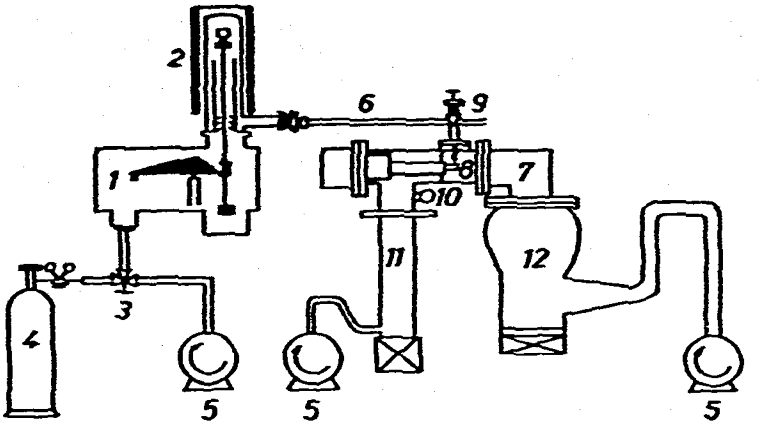

Fig. 1. Schematic diagram of the combined system TA–QMS with Chemical Ionization. 1 = Thermobalance; 2 = furnace; 3 = 3-way valve; 4 = reaction gas cylinder; 5 = rotary pumps; 6 = coupling line; 7 = quadrupole mass spectrometer; 8 = CI-ion source; 9 = metering valve; 10 = ionization gauge; 11 = analyzer diffusion pump; 12 = CI diffusion pump.

a glass connection, NS 14, which extends into a 1/4 in. glass tube. This glass tube is joined to the coupling line by a 1/4 in. Swagelock nut with a reducing (1/4–1/8 in.) port connector. In case of condensable gases the coupling line can be baked by heating tapes.

The distance between the outlet from the quartz furnace and the mass spectrometer inlet is about 60 cm. This is the minimum distance between the two apparatus. Close to the mass spectrometer inlet a three-way metering valve (Nupro cross pattern series S model with vernier handle) is used for adjusting the reaction gas pressure in the ion source. This pressure lies between 0,4 and 1 Torr and depends on the gas used.

The best CI-reagent gas for the problem being studied is selected as purge gas for the thermoanalyzer. Besides the rare gases, such as helium and argon, also nitrogen and methane were tested in our investigations. The applicability of methane is limited by the fact, that it may react with the examined substances especially at higher temperatures. The flow-rate of the purge gas lies between 60 and 80 ml min^{-1}. This rate has no influence on the stability of the thermobalance and enables the response time of the mass spectrometer to be less than 1 sec. For the investigation of special problems purge gas with a flow-rate of up to 20 ml min^{-1} can be introduced into the mass spectrometer without splitting.

Procedure

The crucible with the sample is put on the sample holder of the TA. According to the special characteristic of the TG–CIMS system, the sample size is independent of the rate of gas evolution and is only limited by the instrumental sensitivities. In our investigations sample weights between 20 and 40 mg were used. After the thermobalance system is closed, it is evacuated by a mechanical pump. The whole system is filled with the reagent gas, whereafter the flow-rate is adjusted by a flow meter. The connection tubing between the thermobalance and the mass spectrometer is attached to the outlet of the quartz furnace. Now the pressure of the reagent gas in the ion source is adjusted by the metering valve.

The thermoanalyzer was programmed for a heating rate of 4°C min^{-1} and the DTG-sensitivity was adjusted to 5 mg min^{-1}. After the QMS was programmed for the desired mass range, the ionization energy for chemical ionization was adjusted to 100 eV.

The mass spectra were recorded at regular temperature intervals or alternately a single mass of interest was monitored continuously by an external strip chart recorder. After completion of the analysis, a plot of the gas evolution as a function of temperature was made for the volatiles of interest.

RESULTS AND DISCUSSION

The decomposition of calcium oxalate has been extensively investigated and was considered suitable to test the effectiveness of the TG–CIMS system. The TG- and DTG-curves as well as the gas release patterns of a 38.2 mg sample of calcium oxalate hydrate are shown as a function of temperature in Fig. 2. Helium was used as reaction gas. The optimal ion source pressure was 0.4 Torr.

Comparing the curves in Fig. 2 an extremely short response time of the QMS is observed. This is due to the high sensitivity of the QMS on the one hand and on the other to the laminar gas flow through the connection line, which enables a rapid transport of the volatile decomposition products from the thermobalance to the mass spectrometer. The slope of the DTG curve and the gas release patterns show an almost identical increase up to the top, which is a result of the optimal adjustment of the sensitivities of both apparatus. A slight tailing, which is observed in the gas release patterns, depends on the actual dead volume within the furnace and the interface system.

As is known, in the first step of the decomposition of calcium oxalate hydrate the water is released. During the next step the formation of CO corresponds to the transformation of the oxalate to carbonate. The simultaneous appearance of minimal quantities of CO_2 is explained by a partial oxidation of CO caused by traces of oxygen, still present within the system. This phenomenon was also observed by the thermal decomposition of strontium oxalate[8]. In the last decomposition stage the formation of CO_2 illustrates the conversion of carbonate to oxide.

The results of the thermolysis of copper-tetrammine sulphate hydrate (29.7mg) and the mass spectrometric investigations of the released volatiles are shown in Fig. 3. The thermal decomposition of this compound was selected to demonstrate the applicability of the combined system introduced in this paper. A lot of experiments, carried out with different apparatus, are reported about the thermal decomposition of copper tetrammine sulphate[9–13]. These investigations led to different results, particularly, regarding the decomposition of the anhydrous copper sulphate, as an intermediate compound in the formation of copper oxide.

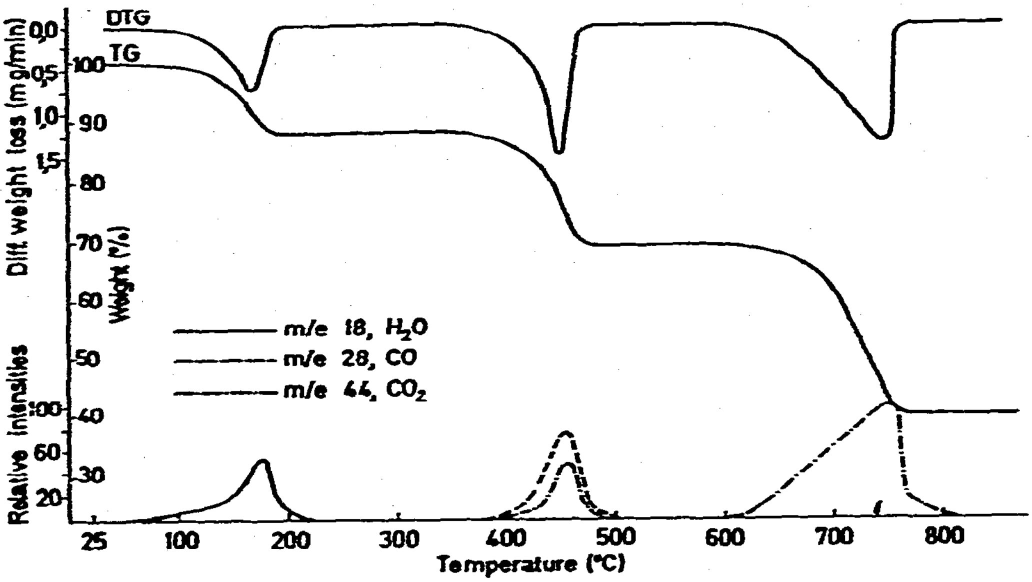

Fig. 2. TG/DTG curves and MS-profile of calcium oxalate hydrate, 38.2 mg sample.

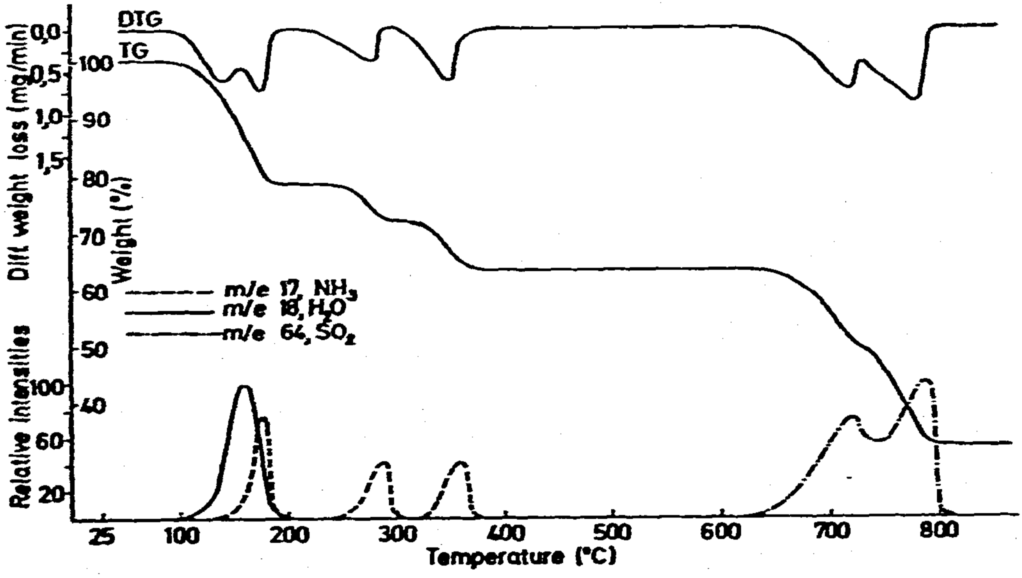

Fig. 3. TG/DTG curves and MS-profile of copper tetrammine sulphate hydrate, 29.7 mg sample.

Argon was selected as CI-reaction gas with an ion source pressure of 0.5 Torr. The first decomposition stage starts at 108 °C with the loss of water, whereafter at 152 °C water and ammonia are evolved simultaneously.

The use of chemical ionization restricts the fragmentation of the molecules in general. Thus, the registration of the molecular ion peak of ammonia, *m/e* 17 is not disturbed by the occurrence of the OH^+-fragment of water. In spite of the low resolution of the quadrupole mass filter, the simultaneous release of water and ammonia can be pursued with exactness. At this stage besides the water two of the four ammonia molecules in the complex are volatilized, as confirmed by calculating the TG-curve.

Two remaining ammonia molecules are released in the second and third decomposition stage, beginning at a temperature of 240 and 326 °C, respectively. Thereafter copper sulphate remains in the crucible and is stable up to 626 °C. Above this temperature it gradually begins to decompose. As shown in Fig. 3 the decomposition of copper sulphate occurs in a two-stage process, which according to Borchard and Daniels[14] takes its course via the thermal unstable basic copper sulphate $CuO \cdot CuSO_4$. The residue of the thermolysis is pure copper oxide in correspondence to the calculation on the weightloss curve.

By the use of TG–CIMS it was attempted to prove, whether SO_2 or SO_3 is to be considered as the primary decomposition product of anhydrous copper sulphate. In this investigation nitrogen was used as purge and reaction gas in the CI-source. Argon could not be used according to the appearance of the Ar_2^+-peak at *m/e* 80, which is in coincidence with the molecular ion peak of SO_3.

Mass spectra of the volatiles were recorded at intervals of 10 °C between 600 and 830 °C.

The plot of the intensities of *m/e* 64 and *m/e* 80 against temperature is illustrated in Fig. 4 and shows the simultaneous appearance of SO_2 and SO_3. According to the

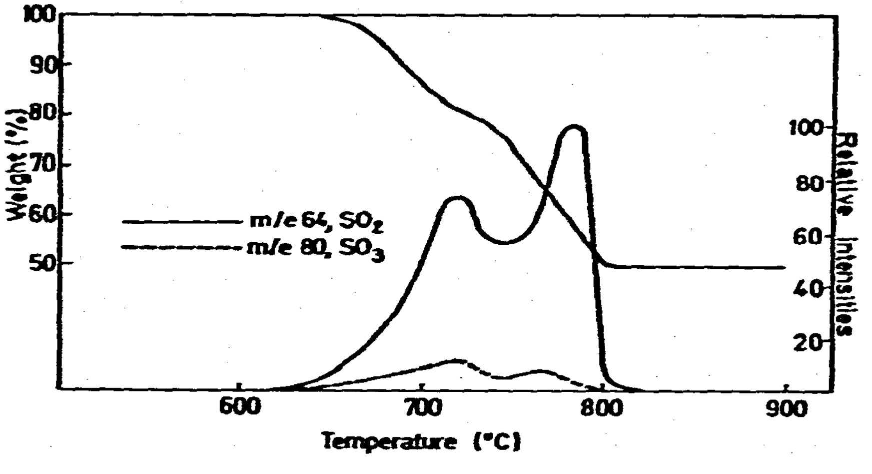

Fig. 4. TG curve and MS profile of *m/e* 64 SO_2 and *m/e* 80 SO_3 during the last decomposition step of copper tetrammine sulphate hydrate.

thermodynamic data[15] for the exothermic gas reaction

$$SO_2+1/2O_2 \rightleftharpoons SO_3+91.7\ \text{kJ} \qquad (1)$$

the results prove that during the thermal decomposition of copper sulphate SO_2 and SO_3 must occur simultaneously in a ratio corresponding to the state of equilibrium at any given temperature.

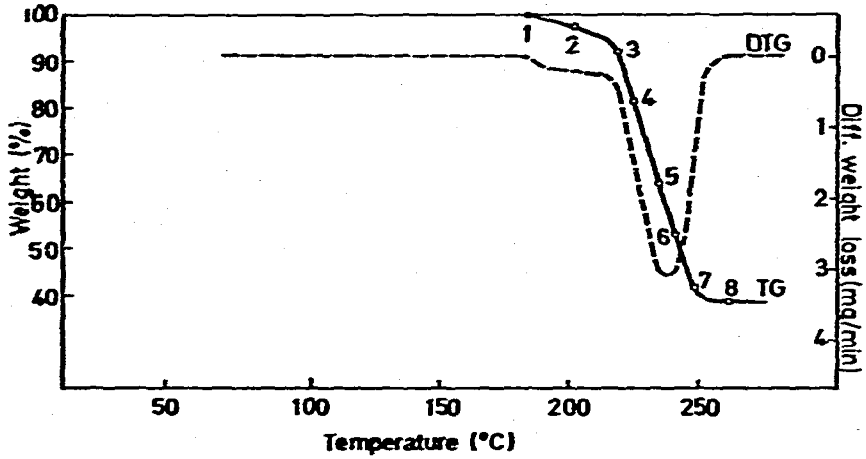

Fig. 5. TG/DTG curves of 34.2 mg potassium trifluoroacetate.

Figure 5 shows the thermogravimetric curve of a 34.2 mg sample of potassium trifluoroacetate. During the complex decomposition a large number of reaction products occur. Therefore mass spectra were performed in a mass range of *m/e* 40–400 at characteristic temperatures shown on the TG-curve. The most interesting mass spectra of this series are given in Fig. 6.

As a result of the high inductive effect of fluorine, the mass spectra of fluorinated organic compounds show extended fragmentation. In order to keep this fragmentation as low as possible, methane was used as the CI-reaction gas. The ion source pressure was adjusted at 1 Torr.

The great difference in the use between noble gases and hydrocarbons, such as methane, as a reaction gas for CI lies in the ionization mode. While the sample molecules using a noble gas were ionized by charge exchange reactions,

$$A+e^- \rightarrow A^+ +2e^- \qquad (2)$$

$$A^+ +S \rightarrow A+S^+ \qquad (2a)$$

Ar = noble gas atom;
S = sample molecule;

the ionization in the case of methane is performed by proton transfer (or in special cases by hydride abstraction). This leads to a lowering in the energy evolved for ionization of the sample molecules, so that fragmentation is greatly restricted. These

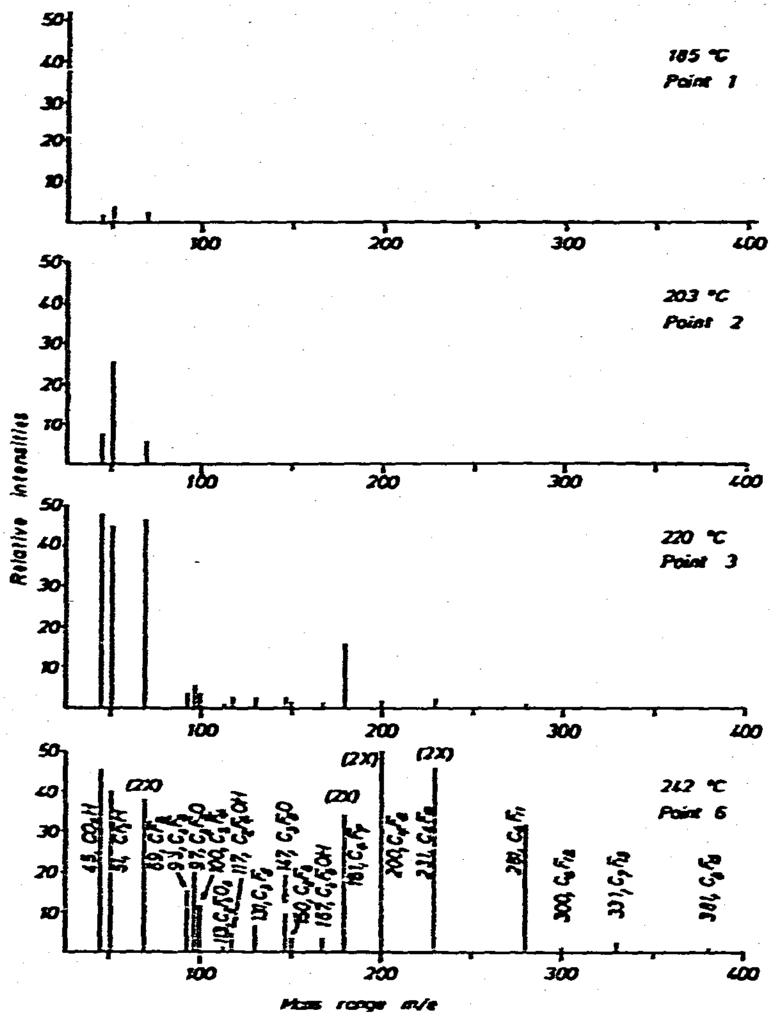

Fig. 6. Mass spectra at selected temperatures during the thermal analysis of potassium trifluoroacetate

reactions may be written as follows: Primary EI-reaction:

$$CH_4 + e^- \rightarrow CH_4^+, CH_3^+, CH_2^+, CH^+ + 2e^-$$

All of the primary ions of methane react rapidly with methane to give product ions which are either non-reactive or only slightly reactive with the reaction gas itself, but which can react with the sample molecules:

Secondary ion–molecule reactions:

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3 \quad (4)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2 \quad (5)$$

$$CH_2^+ + CH_4 \rightarrow C_2H_3^+ + H_2 + H \quad (6)$$

CH_5^+ and $C_2H_5^+$ are the major secondary ions, which comprise about 90% of the total ionization, ionizing sample molecules by proton transfer reactions:

$$CH_5^+ + S \rightarrow CH_4 + SH^+ \tag{7}$$

$$C_2H_5^+ + S \rightarrow C_2H_4 + SH^+ \tag{8}$$

As can be seen in eqns (7) and (8) the ionization of the sample molecules by CI with methane leads to quasimolecular ions at *m/e* $(M+1)^+$.

In former investigations on the thermal decomposition of trifluoroacetates[16,17] the attempt was made to identify the released volatiles by IR-analysis. But only the major decomposition compounds were identified and no data could be given about the sequence of appearance and disappearance of each major and minor component. TG–CIMS enables the identification of the total number of the released volatiles, gaining a complete insight in the decomposition reaction of the compound under investigation.

The decomposition starts at 185°C and is complete at 254°C, leaving potassium fluoride as a residue. Although the TG and DTG curves show a one-step process, no simultaneous evolution of every volatile was confirmed by the mass spectrometric investigations. Between 185 and 220°C only *m/e* 45 CO_2H and the fragments *m/e* 51 CF_2H and *m/e* 69 CF_3 occurred with increasing intensity.

At 220°C peaks at *m/e* 167 and *m/e* 117 indicate the occurrence of hexafluoroacetone and trifluoroacetyl fluoride as quasi-molecular peaks, respectively. It should be said, that by use of argon as reaction gas, peaks of the molecular ions of the above-named molecules did not occur in the spectra.

According to the beginning decomposition of trifluoroacetic anhydride at 216°C, yielding CF_3–COF, CO_2 and CO[18], only the small peak at *m/e* 113 CF_3–CO_2^+ indicates the presence of an insignificant amount of trifluoroacetic anhydride in our spectra. Above 220°C a series of homologous fluorinated olefines and their fragments, starting with tetrafluoroethylene are identified in the mass spectra. At 242°C the decomposition reaches its maximum. At this temperature *m/e* 331 C_7F_{13} and *m/e* 381 C_8F_1[8] are recognized as fragments with the highest molecular weight. Up till now only in the thermolysis of salts of long-chain perfluorocarboxylic acids fluorinated olefines have been obtained as decomposition products[19].

In our opinion, secondary reactions of the high reactive carbon-fluorine fragments, especially the diradical CF_2 account for the occurrence of the large number of fluorinated olefines as well as the oxygen containing decomposition compounds.

Further investigations on the thermal degradation of trifluoroacetates, especially with regard to primary and secondary reactions during this complex decomposition process will be carried out in the future.

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