AN EFFECTIVE APPROACH TO FLASH VACUUM THERMOLYTIC STUDIES

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ABSTRACT

Flash vacuum thermolysis in combination with field ionization mass spectrometry, supplementary with collision activated spectra of the single field ionized molecules, is shown to be a facile and highly informative method for studying even very complex mixtures of primarily formed products in the gas phase thermolysis of organic molecules. The method allows quantitative detection of substances with half lifes $t_{1/2} > 10^{-3}$ sec. A detailed description of the apparatus, which offers the possibility of studying gas phase thermolyses over a wide range of temperatures (300—1400 K), and the method is given, and possible applications discussed.

INTRODUCTION

In recent years the flash vacuum thermolysis (FVT) technique has become widespread in the study of highly reactive, and rather short-lived intermediates in the gas phase thermolytic decomposition reactions of organic molecules [1—3]. In general, the thermolyses are followed by rapid thermal quenching of the products on a liquid nitrogen cooled cold finger, possibly supplementary with spectroscopic detection systems such as IR [4—6] and/ or UV—VIS spectrophotometers [4,5]. Direct combinations of FVT units and photoelectron spectroscopy (PES) [7], microwave spectroscopy (MWS) [6,8], and electron impact ionization mass spectroscopy (EI-MS) [1,6, 8—10] have been reported. However, these methods all have a somewhat limited applicability, since the spectroscopic assignment may be extremely complicated in cases where the thermolyses lead to a mixture of several, and often unknown, products.

In order to supply the need for an effective method of studying primarily formed products in gas phase thermolytic reactions, not necessarily unstable, we report here a simple FVT technique, which does not suffer from the above-mentioned failing. The method is based on the direct combination of a thermolysis unit and field ionization mass spectrometry (FI-MS) [11,12] complementary with collision activation mass spectrometry (CA-MS) [13] of the single field ionized molecules.

APPARATUS

In contrast to the often rather complicated glassware thermolyzers [2,7,14], we have constructed a simple and effective thermolysis unit as a modification of the Pye Unicam PV4000 pre-column-pyrolysis-system, which is based on the Curie-point pyrolysis technique [15], i.e. the high frequency inductive heating in ferromagnetic materials.

The thermolysis unit (Fig. 1) consists of three main parts: (a) injection block, (b) reactor (hot zone), and (c) line-of-sight inlet system as thermolysis unit—mass spectrometer interface. The injection block (brass) is connected directly to the Curie-point pyrolyzator, the latter being connected to the Varian line-of-sight inlet system by an adapter flange (Fig. 1H). Inside the thermolysis unit a quartz lining tube is placed (Fig. 1E) with an i.d. of 2 mm, which leads the thermolysis products directly into the ion source of a Varian MAT CH5 D instrument (the magnetic sector preceeding the electric sector) equipped with a combined electron impact ionization/field ioniza-tion/field desorption (EI/FI/FD) ion source. The field ion emitter was a 10 μm tungsten wire activated in benzonitrile vapour. The maintenance of the vacuum in the system is based on differential pumping (mercury diffusion pumps) of the ion source, analyzer tube, and the electric sector. Pumping speed was 3×150 l sec^{-1}. The total set-up is shown in Fig. 2.

The internal pressure in the thermolysis unit, especially in the reactor, is of importance for the possible exclusion of bimolecular reactions. In order to estimate the working pressure in the thermolysis unit we studied the pos-sible recombination of *tert*-butoxy radicals to di-*tert*-butyl-peroxide. The radicals are generated thermally by thermolyzing di-*tert*-butyl-peroxide [16] at 1043 K, at which temperature the latter is completely cleaved into *tert*-butoxy radicals. We have not been able to detect the recombination product
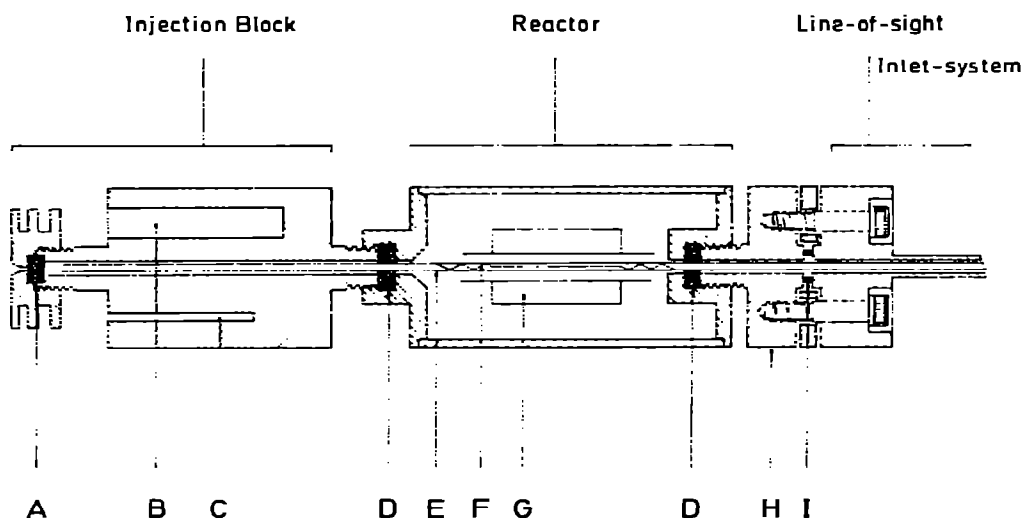

Fig. 1. Thermolysis unit. A, Septum; B, injection block heater; C, thermocouple for tem-perature readout; D, rubber washer; E, quartz lining tube; F, ferromagnetic wire; G, high frequency induction coil; H, adapter flange; I, gold wire sealing.
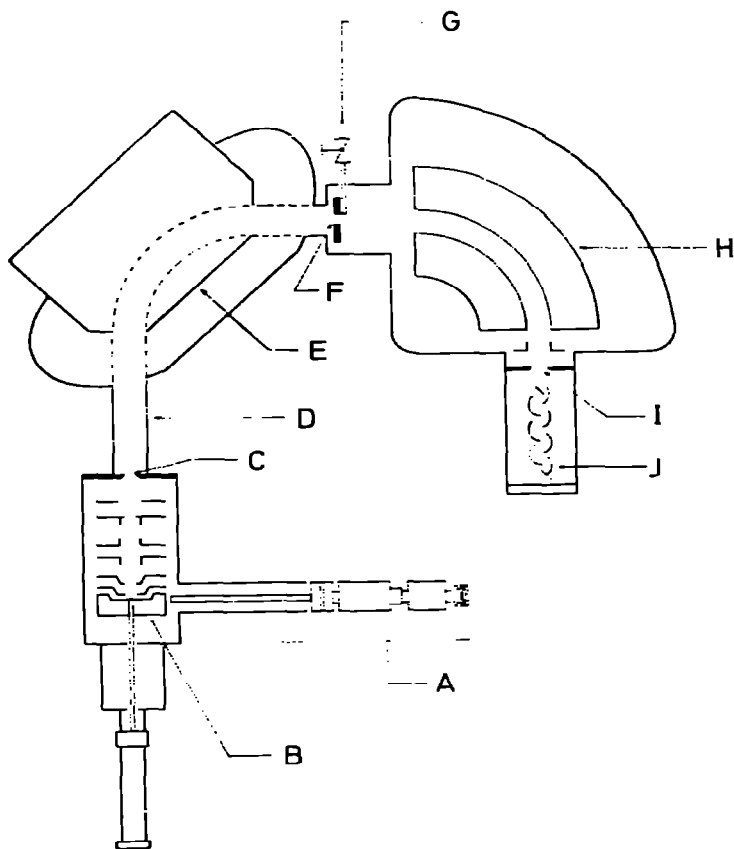
Fig. 2. Thermolysis unit — mass spectrometer set-up. A, Thermolysis unit; B. EI/FI/FD ion source; C, entrance slit; D, analyser tube; E, magnetic sector; F, intermediate focus slit; G, needle valve; H, electric sector; I, collector slit; J, detector (SEM).

by the FI-MS method, which means that it is formed in yields of less than 1%, leading us to the following expression [3,10]

$$\Delta[t\text{-BuO·}]_r = t_{mr}k_r[t\text{-BuO·}] < 0.01 \tag{1}$$

where $\Delta[t\text{-BuO·}]_r$ is the fraction of the radicals which have recombined in the time t_{mr} (mean residence time) with a rate constant k_r; the latter is in the present case reported to be $10^{8.8}$ sec^{-1} [17]. Taking the mean residence time, t_{mr}, arbitrarily to be 10^{-3} sec, it follows from eqn. (1) that $[t\text{-BuO·}] < 10^{-7.8}$, which corresponds to an internal pressure, P_i, less than 5×10^{-4} torr. i.e. the mean free paths for the molecules are larger than the diameter of the reactor, and the intermolecular collision frequency is consequently very low, which means that bimolecular reactions can hardly be expected. Furthermore, based on the above estimate it is seen that the thermolysis unit, and as a part of the latter, the reactor, fulfils the requirements for a Knudsen reactor [3,10,18], i.e. the mean residence time t_{mr} depends only on the actual geometry of the latter (l 40 mm, i.d. 2 mm) and the temperature, and not the internal pressure. The mean residence time in the reactor (contact time in the hot zone) can then be calculated according to the Knudsen

formula [10,18]

$$t_{mr} = 4V/\bar{c}A \text{ sec} \tag{2}$$

with V as the reactor volume and A as the area of the orifice (0.03 cm^2). The mean molecular rate, $\bar{c}$, can be estimated according to the kinetic gas theory

$$\bar{c} = 1.46 \times 10^4 (T/M)^{1/2} \text{ cm sec}^{-1} \tag{3}$$

where T is the reactor temperature and M is the molecular weight of the molecule under investigation, e.g. $T = 800$ K, $M = 200$ gives $\bar{c} = 2.92 \times 10^4$ cm sec^{-1}, and consequently $t_{mr}^r = 5.7 \times 10^{-4}$ sec. A similar estimate for the line-of-sight inlet system (l 25 cm) gives a mean residence time $t_{mr}^i = 3.6 \times 10^{-3}$ sec ($T = 400$ K, $M = 100$).

In spite of the above exclusion of bimolecular reactions, secondary processes, as are consecutive unimolecular decompositions of thermally labile primary formed reaction products, have to be considered. Firstly, a direct rethermolysis in the hot zone (reactor) has to be discussed. The simple first-order rate law $d[A]/dt = k[A]$ can, for small time intervals, be rewritten as

$$\Delta[A]/[A] = k_d \Delta t \tag{4}$$

k_d being the rate constant for the unimolecular decomposition, and $\Delta[A]/[A]$ the fraction of primarily generated A which has decomposed within the time Δt; the latter can, in the present case, be chosen as the mean residence time in the reactor t_{mr}^r. An estimate of the degree of rethermolysis of a compound exhibiting a rate constant k_d can then be directly obtained from eqn. (4), e.g. a degree of rethermolysis less than 1% can be expected for reactions with rate constants, at the appropriate temperature, $k_d < 10^2$ sec^{-1}. Secondly, the possible decomposition in the heated line-of-sight inlet system will be discussed; this is probably the major problem in cases where the primary generated compounds are highly thermally labile, since the mean residence time in this part of the system, t_{mr}^i, is ca. 10 times higher than t_{mr}^r. However, the temperature in the inlet system is in general much lower than the reactor temperature. Under normal conditions it is possible to observe products present in amounts down to 0.1—1.0% relative yield (molar fraction), depending on the FI sensitivities [12] of the compounds under investigation, which means the relation in eqn. (4) becomes

$$\Delta[A]/[A] = k_d t_{mr}^i < 0.99 \tag{5}$$

Using the above conditions for the line-of-sight inlet system ($T = 400$ K, $M = 100$, $t_{mr}^i = 3.6 \times 10^{-3}$ sec) gives $k_d < 2.9 \times 10^2$ sec^{-1}, corresponding to a half life $t_{1/2} > 2.4 \times 10^{-3}$ sec, i.e. labile compounds with half lifes greater than ca. 10^{-3} sec would in general be observable. It is, however, noteworthy that in special cases, compounds with even smaller half lifes may be observed. Thus the unimolecular thermal decomposition of *tert*-butoxy radicals into acetone and methyl radical proceed at 400 K with a rate constant $k_d \cong 10^{4.5}$ sec [19], corresponding to a $t_{1/2} \cong 2 \times 10^{-5}$ sec, and we are able to detect minor amounts of the radicals, approximately 0.2% assuming comparable FI sensitivities of the *tert*-butoxy radicals and acetone.

METHOD

In general, studies of the unimolecular gas phase thermolytic decompositions of organic molecules are carried out in the following way. Samples of ca. 50 μg of the pure compound are introduced (micro-syringes) into the reactor, equipped with the filament with the appropriate Curie temperature, via the heated injection block. To prevent condensation in the latter part of the system, the line-of-sight inlet system, connecting the reactor and the mass spectrometer ion source, is heated.

Owing to the relative fast evaporation of the samples in the injection block (ca. 5—10 sec) the FI-MS spectra must be recorded with a scan rate of 50—100 a.u. sec^{-1} (signal-to-noise > 1000).

Collision activated mass spectra [13] were obtained introducing helium as collision gas via a needle valve (Fig. 2G) into the second field free region of the mass spectrometer. The collision gas is admitted as a molecular gas beam focussed on the ion beam just behind the intermediate focus slit (Fig. 2F). Appropriate adjustment of the magnetic field secures passage of only the desired ion through this slit. The CA-MS spectra of the single ions are obtained by scanning the electrostatic field, and are recorded within 5 sec (signal-to-noise ca. 50).

It can be mentioned that in cases of samples with very low vapour pressures the injection block is disconnected and samples are placed directly onto the ferromagnetic wire by the dip-coating technique [9,15]. However, using this latter method the evidence of pure gas phase thermolysis is lost.
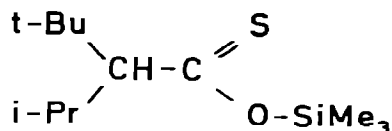
APPLICATIONS AND DISCUSSION

The paramount advantage of the combination of the thermolysis unit with field ionization mass spectrometry (FI-MS) as detection system reported here, is to be sought in the field ionization principle [11,12]. The detection system offers the possibility of analyzing even very complex reaction product mixtures, since FI takes place with no excess energy, excluding polarization by the high electric field, to the neutral molecule [11], i.e. FI gives rise to molecular ions — even of very unstable substances — accompanied only by a very few, if any, fragment ions, generally of low intensity (<1%) [12]. This is in contrast to EI, which may yield complicated electron impact induced fragmentation patterns, which leads to further confusion when they are to be described as superpositions of EI-MS spectra of several, and often unknown, reaction products.

It should in this connection be noted that another soft ionization method chemical ionization (CI) [20] does not reveal the same advantages although the sensitivity of CI-MS is comparable to that of EI-MS, since CI operates at pressures around 1 torr, i.e. bimolecular reactions cannot be excluded. Furthermore, it is to be expected that the bimolecular ionization mechanism [20] will mask the thermal formation of reactive species.

To illustrate the superiority of FI-MS relative to EI-MS as detection system in FVT experiments, we have studied FI-MS, 13 eV EI-MS, and 70 eV

EI-MS spectra following thermolysis of the trimethylsilyl-thionocarboxylate (I) at 1043 K, the thermolysis of I being studied as a part of our current investigations on gas phase thermolytic decompositions of thionocarboxylates [21].

$$
\begin{array}{c}
\text{t-Bu} \\
\quad \diagdown \\
\qquad \text{CH-C} \diagup^{\displaystyle S} \\
\quad \diagup \qquad \diagdown \\
\text{i-Pr} \qquad\qquad \text{O-SiMe}_3
\end{array}
$$

I

We find that I fragments strongly under thermolytic conditions, whereas no FI induced fragmentation is observed. Based on the FI-MS spectrum obtained following thermolysis at 1043 K (Fig. 3a), the overall reaction may be rationalized in the following way
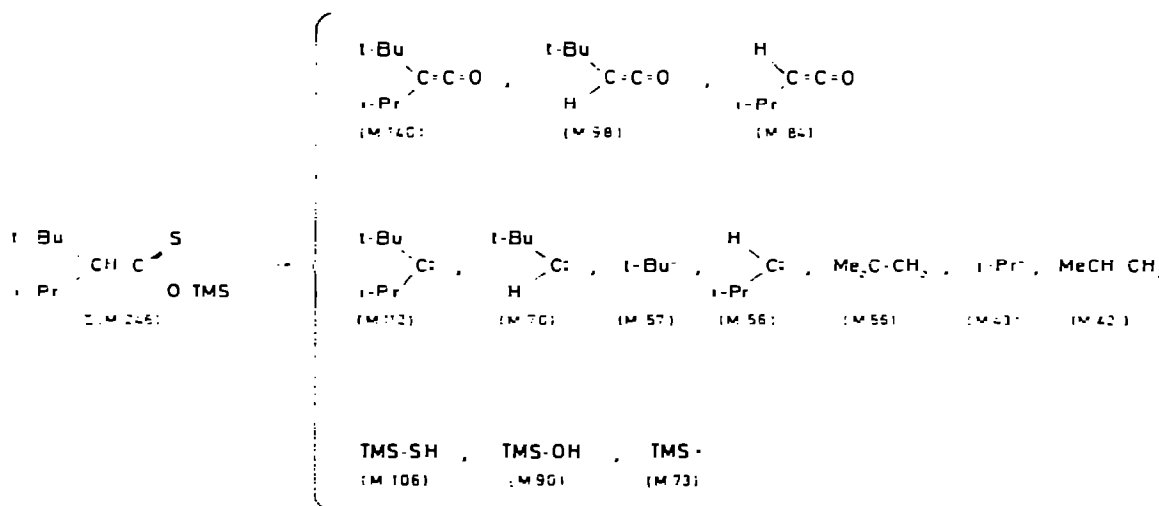

Figure 3b and c, depicting the 13 and 70 eV EI-MS spectra of following thermolysis at 1043 K, clearly illustrates the difficulties of using EI-MS as detection system. Compound I, as well as the reaction products, strongly fragmentate under 70 eV EI-MS conditions, and it is seen that several of the reaction products do not even exhibit molecular ions (Fig. 3c), a fact which is certainly not limited to these special compounds. A rationalization of the above reaction scheme, based on the spectrum shown in Fig. 3c, is obviously extremely difficult, if not impossible; neither does the low voltage 13 eV EI-MS spectrum (Fig. 3b) in the present case clarify the product composition, since decreasing the ionization energy gives rise to molecular ions without sufficient energy to be degraded by multiple pathways leading to fragment ions with lower m/z values. Thus the 13 eV EI-MS spectrum is characterized by more pronounced molecular ions together with fragment ions originating from the more energetically favoured fragmentation pathways. Hence, the latter spectrum is almost to be described as a superposition of the FI-MS and the 70 eV EI-MS spectra, i.e. the electron impact induced fragmentations are
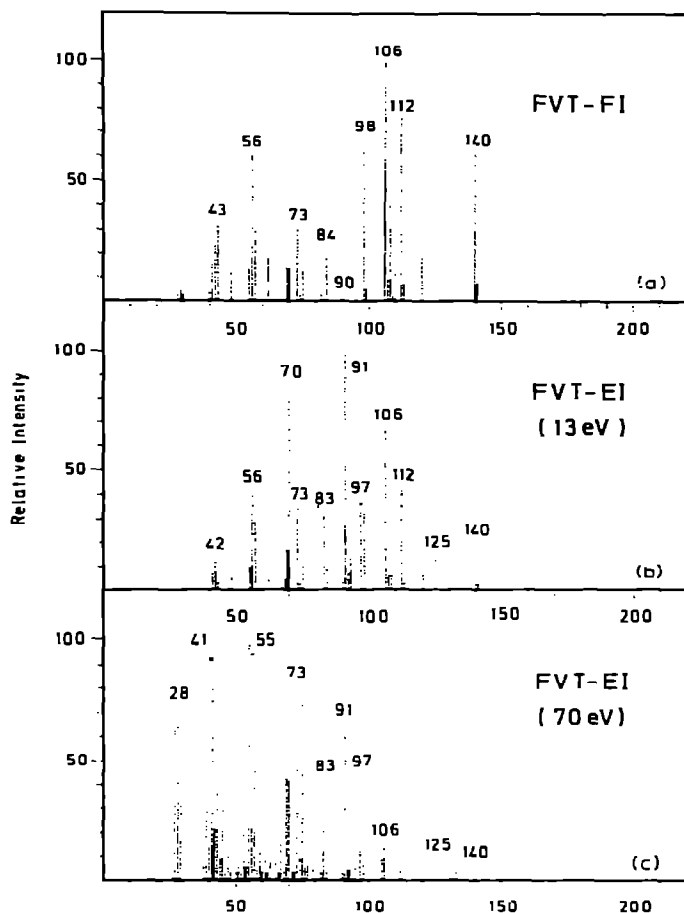
Fig. 3. FI-MS, 13 eV EI-MS, and 70 eV EI-MS spectra obtained following flash vacuum thermolysis of I at 1043 K. Since I is totally degraded at this temperature no molecular ion (M = 246) is observed.

still observed, but simultaneously the molecular ions have grown in.

Additionally it should be mentioned that in cases where the electron impact induced and the thermally induced fragmentations resemble each other, small changes in the spectrum due to the latter may well be drowned in the former. Furthermore, it is obvious in the present case that other conventional detection systems, such as IR-, UV/VIS-, PE-, or MW spectroscopy, would not leave any possibility of rationalizing a reaction scheme as shown above; neither would a simple isolation technique.

The FI-MS detection system enables us to detect all organic reaction products formed in relative yields (molar fractions), generally above 0.01. Small inorganic fragments, however, are not detectable using this technique, as these compounds have very low FI-weight sensitivities. Additionally, the geometry of the ion source of the mass spectrometer used may play an important role [12].

However, although the obtained FI-MS spectra of the thermolysates give extremely valuable primary information about the product compositions, the EI-MS spectra of the single species in the reaction product mixtures

would be rather profitable in the search for further information on the structures, in cases of doubt, of the individual products, since it should be remembered that FI-MS spectra in general do not provide any structural information due to the lack of fragment ions. (Valuable information on the composition of the single compounds can, however, be obtained by intensive studies of the isotopic peaks in the FI-MS spectra.) The additional recording of the CA-MS spectra of the single field ionized molecules [13], however, supplies this want, as the collision of molecular ions of high kinetic energy (≥3 keV) with neutral target atoms of low molecular weight, e.g. helium, is known to give rise to a large variety of fragments. In general, these types of fragments resemble those formed under normal 70 eV electron impact conditions [13]. No interference from even large quantities of other compounds can disturb the CA-MS spectra, as long as they do not have the same molecular weight as the compound under investigation. To illustrate the use of CA-MS, we studied the gas phase thermolysis of 5-phenyl-1,2,3,4-thiatriazole (II) at 1043 K. In Fig. 4 the FI-MS spectra of II without thermolysis and follow-
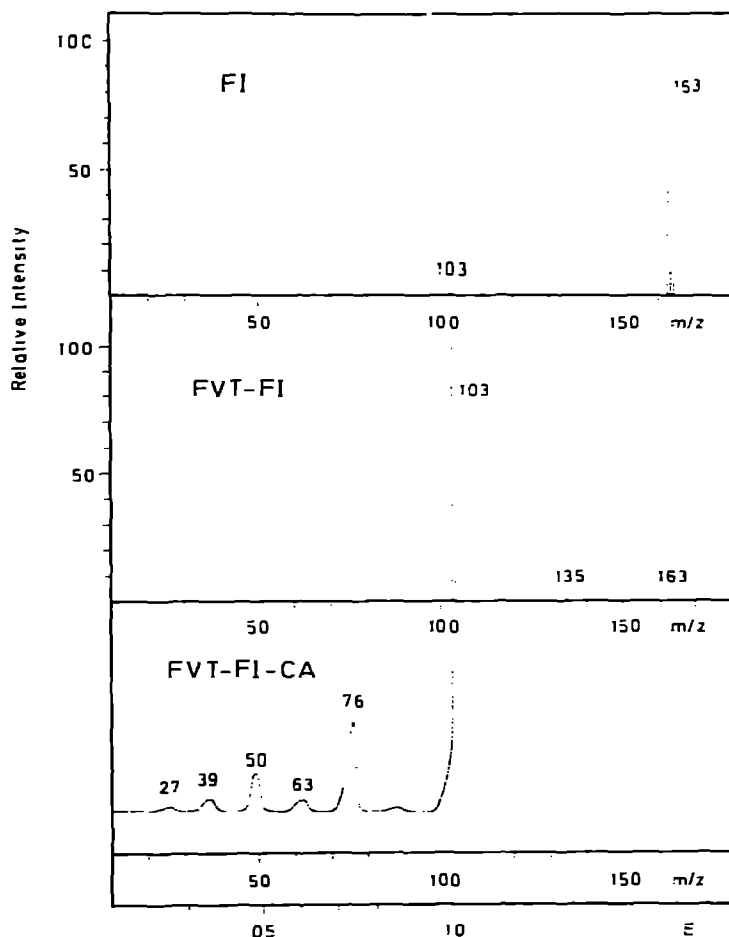

Fig. 4. FI-MS spectra of 5-phenyl-1,2,3,4-thiatriazole (II) without thermolysis [22] and following thermolysis at 1043 K, and CA-MS spectrum of the thermolysate with m/z = 103.

ing thermolysis at 1043 K are depicted together with the CA-MS spectra of the thermolysate with the molecular ion 103; the CA-MS spectrum of the latter is in complete accordance with the previously reported spectrum of benzonitrile [13], in agreement with the known thermal decomposition of II [22].

$$C_6H_5-C \overset{N-N}{\underset{S}{\diagup}} N \longrightarrow C_6H_5CN + C_6H_5NCS + S + N_2$$

II
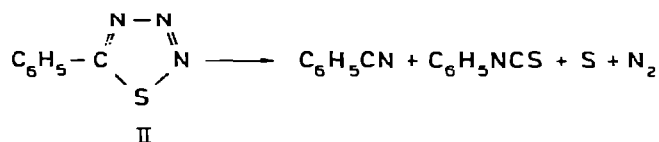
It is noteworthy in this connection that the very simple introduction of the collision gas (Fig. 2) used is profitable since it gives rise to rather intense CA-MS spectra, which enable us to record the complete spectra (0.1—1.0E) within a few sec (see above), i.e. even of rather unstable compounds, in contrast to the much slower recording reported by other authors [23]. (In cases of stable reaction products a direct comparison between the CA-MS spectra with those obtained from authentic samples is expedient.)

The method described here gives the possibility of a wide choice of stabilized, accurately controlled, and reproducible thermolysis temperatures [9,24], as a wide range of ferromagnetic materials with Curie-points from ca. 300—1400 K are readily available. It is obvious that by studying composite reaction mechanisms the mutual product ratios as a function of reaction temperatures may give valuable information on the single involved reactions. Thus, the gas phase thermolysis of 1,1,3,3-tetramethyl-2-thiocarbonyl-cyclo-hexane S-oxide (III) has been rationalized in terms of two concurrent primary reactions that are extrusion of atomic oxygen and formation of the three-membered oxathiirane [25]. At 753 K the two reactions proceed to an almost equal extent *, whereas increasing the thermolysis temperature results in an increase in the thioketene formation, with a simultaneous decrease in
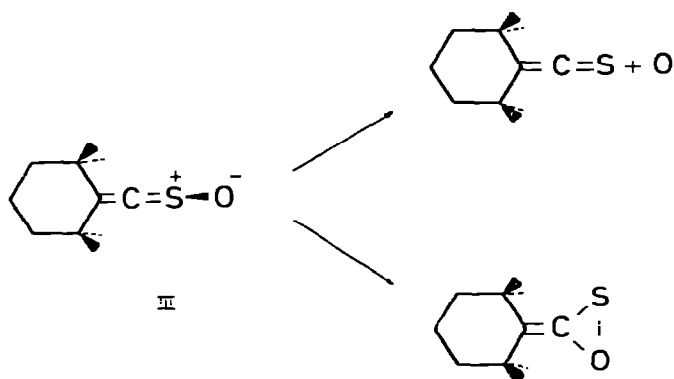

the oxathiirane yield, strongly indicating the thioketene formation to be the

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* It is not possible to calculate the yields of the single species directly from the FI-MS spectra, as the single compounds may exhibit rather different FI-weight-sensitivities [12]. However, introducing mixtures of the available compounds among the reaction products, with varying mutual ratios, the individual relative sensitivities in general can be calculated directly or indirectly [25].

thermodynamically favourable pathway, whereas the electrocyclic ring closure to the oxathiirane is kinetically controlled.

The limiting factors of the present method, as is the case with all FVT studies, are (a) the contact time in the hot zone, and (b) the lower half life limit of the products which secure detection; account of the latter is given in the previous section. The very short contact time, 10^{-4}—10^{-3} sec, is extremely important to avoid secondary thermolytic reactions [3]. However, even using extremely short contact times, it might in several cases be difficult to distinguish between primary and secondary reaction products; e.g., by thermolyzing the thioketene S-oxide (III) at 1043 K, both this and the primary formed thioketene are able to form a vinylidene carbene ($M = 150$) by SO and S extrusions, respectively [25]. In the present case, with both the

(M 198)

(M 150)

(M 182)
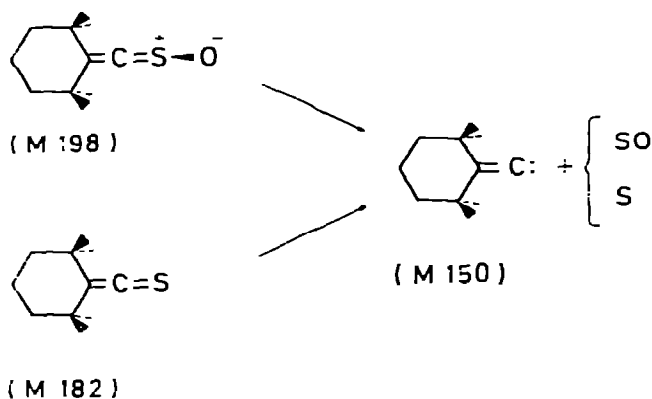
thioketene and the S-oxide as stable compound, it was nevertheless possible to compare directly the two thermally induced fragmentation patterns (Fig. 5), whereby it can be demonstrated that less than 15% of the total amount of thioketene formed by thermolyzing the S-oxide could undergo rethermolysis [25].
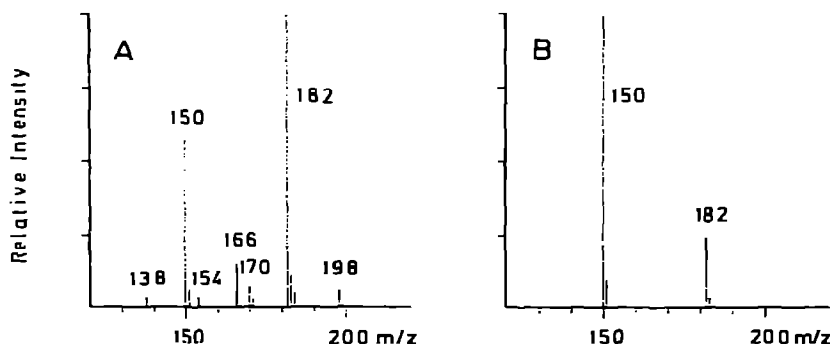

Fig. 5. FI-MS spectra of 1,1,3,3-tetramethyl-2-thiocarbonyl-cyclohexane S-oxide (III) (A) and 1,1,3,3-tetramethyl-2-thiocarbonyl-cyclohexane (B) following flash vacuum thermolysis at 1043 K.

CONCLUSION AND OUTLOOK

The above description of the facile and effective approach to FVT studies has demonstrated that this method, by FI-MS, rapidly gives primary information of even very complex product mixtures originating from gas phase thermolyses of organic molecules, as well as further structural information, by CA-MS, of the individual thermolytically formed species. Furthermore, quantitative information on the product compositions can be obtained by using the relative FI-weight sensitivities (see footnote on p. 55), and finally a mechanistic evaluation is achievable *.

Finally , the advantage of this method as a rapid technique for optimization of the reaction conditions should be remembered, e.g. before turning to more possible further spectroscopical characterization of thermally unstable thermolysates.

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* As with normal mass spectrometric investigations, it should be remembered that isotopic labelling of the starting materials may give important information.

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