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COMPUTER-AIDED MS ANALYSIS OF THE FIRST DECOMPOSITION STEP OF 2,5-DIARYL-2H-TETRAZOLES

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The product mixtures formed during the first step of thermal decomposition of some 2,5-diaryl-2H-tetrazoles were investigated by MS analysis after quenching of the mixtures to room temperature and dissolution in methylene chloride. The multivariate evaluation program SEKOS was used. This is based on the computer-aided analysis of intensity *vs.* time curves of multicomponent mixtures in a mass-spectrometer. The working principles and the advantages of the evaluation program are discussed.

The first thermal decomposition step of some 2,5-diaryl-2H-tetrazoles has been investigated by direct product analysis with the multivariate evaluation program SEKOS [1] which is based on the computer-aided analysis of intensity *vs.* time curves (ITC) of multicomponent mixtures in a mass-spectrometer. The working principles and the advantages of the program are discussed in this paper.

5-(4-Cyanophenyl)-2-phenyl-2H-tetrazole decomposes on melting, in a strongly exothermic reaction accompanied by a mass loss of 11.15% (Fig. 1). The mass loss coincides exactly with the value calculated for 1 N_2, and therefore seems to correspond to the well-known fact that 2H-tetrazoles eliminate nitrogen on thermal treatment [2]. Accordingly, after the first decomposition step one might expect compound *3* as a dimerization product of the intermediate diaryl nitrileimine (Fig. 2).

However, the UV spectroscopic, HPL chromatographic and MS analyses led to the conclusion that in fact a product mixture is formed: 35% tetrazine *3*, 41% 1,2,4-tetrazole *4* and at least three further products could be detected. Therefore, the mass loss found in the described case randomly corresponds to the value of 1 N_2; for some other 2,5-diaryl-2H-tetrazoles, considerably greater mass losses were found.

The reaction mechanism of the first decomposition step is more complicated, because the diaryl nitrileimine *2* can also decompose into aryl nitrene Y-PhN and aryl nitrile X-Ph-CN. The latter can react with residual diaryl nitrileimine to give the triazole *4*, while the volatile Y-PhN causes a further mass loss [3].

The spectroscopic and chromatographic analyses are time-consuming and must be supplemented by MS or other structural data, and the synthesis of

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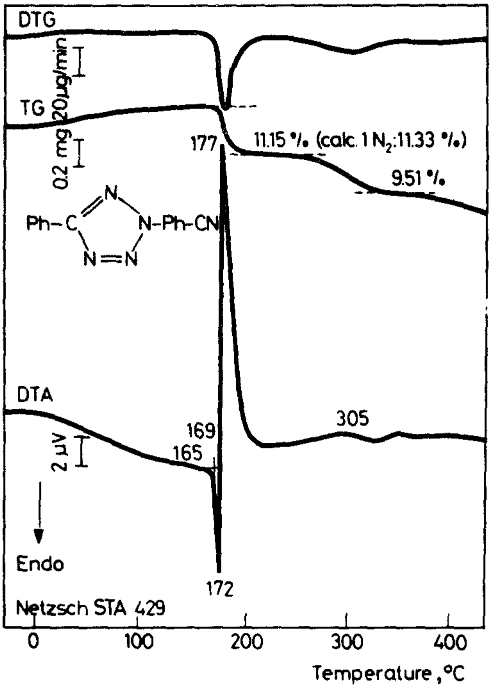

Fig. 1 TG, DTG and DTA curves of 5-(4-cyanophenyl)-2-phenyl-2-H-tetrazole; m = 3.05 mg, heating rate 5 deg min^{-1}, 70 ml N$_2$/min, Pt-mini crucible.

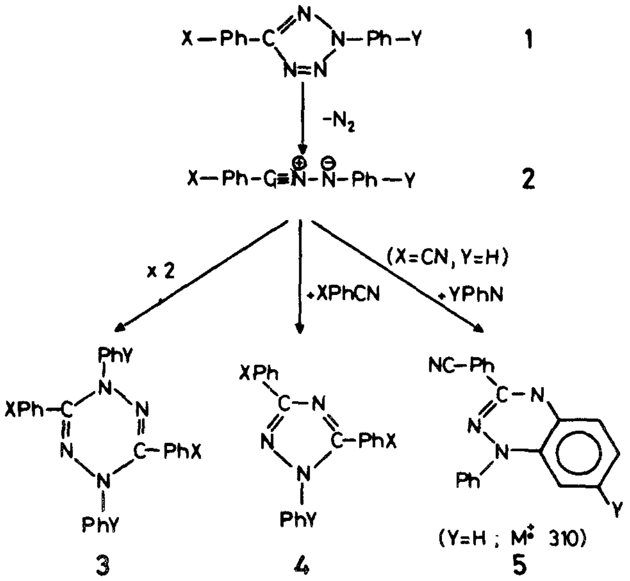

Fig. 2 Thermal degradation reactions of substituted 2,5-diaryl-2H-tetrazoles from the melt

reference substances is often necessary. Therefore, we attempted to analyze the product mixture after the first TG step, directly after quenching the sample to room temperature and dissolving it in methylene chloride. 3 μl of the product mixture solution (ca. 1 μg/μl) was introduced into the MS inlet and, after removal of the solvent in vacuo, the sample was completely evaporated (40–50 deg $\min^{-1}$) in a computer-aided mass-spectrometer (HP 5995 A). During the evaporation, about 100 mass-spectra are recorded at constant intervals. Their addition yields the sum spectrum of the mixture, yielding a survey of all fragment ions formed and their intensities (Fig. 3).

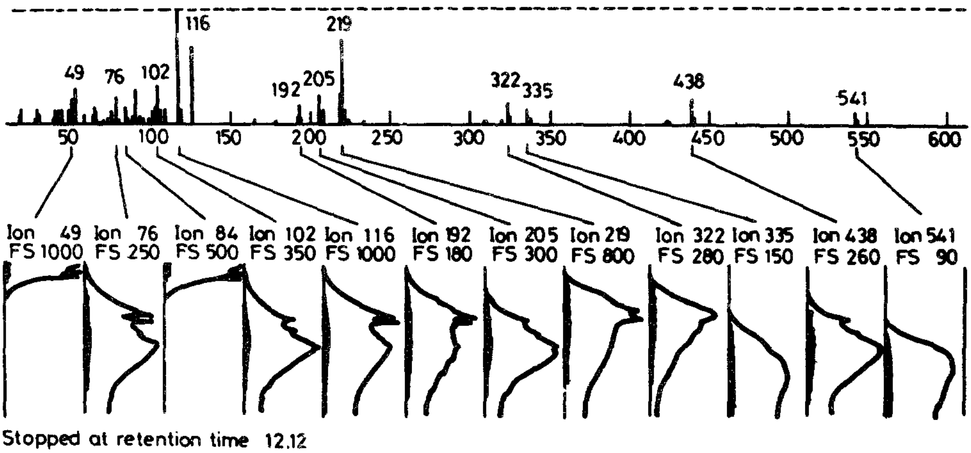

Fig. 3 Mixture's sum spectrum and intensity-time curves (ITC) of the most intensive fragment ions

If the components exhibit sufficiently different evaporations, analysis of the individual fragment ion intensities as a function of time during the evaporation run allows the ssignment of these fragments to definite compounds; this means that the ITC overlapping least of all (i.e. linearly independent) are selected (Fig. 4).

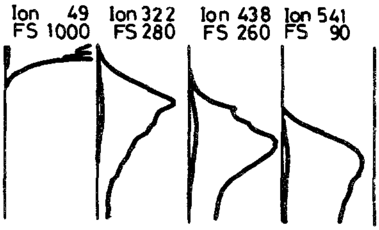

Fig. 4 ITC of the "real masses"

On the assumption that the linearly independent ITC correspond to the partial pressure *vs* time dependence of the individual components of the mixture in the MS, the measured fragment ion intensities are classified by a correlation calculation. In this way one obtains the spectra of the individual components of the mixture (Fig. 5).

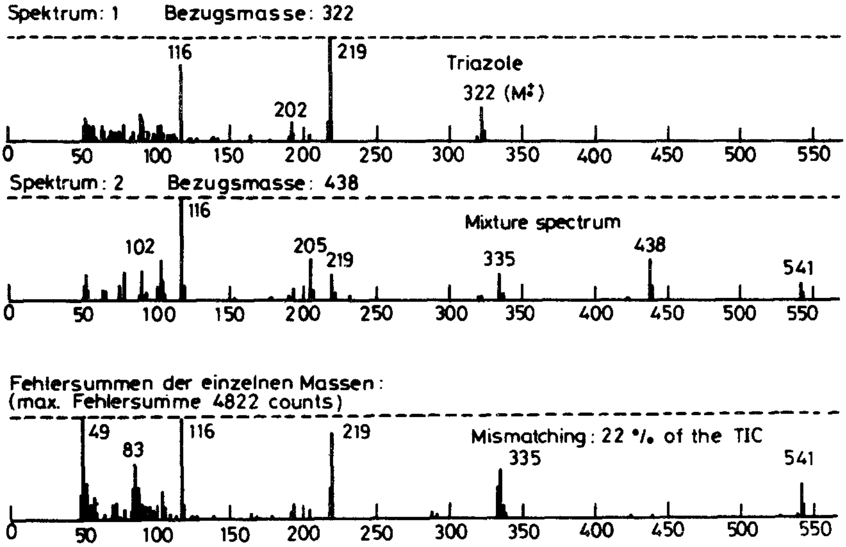

Fig. 5 Calculated component's spectra together with error spectrum

The correlation test has to be repeated with a varying number of components (i.e. the number of linearly independent ITC) until the measured data set (i.e. the sum of the spectra for the mixture) can be reproduced in a sufficiently correct way by using the chosen ITC and component spectra (Fig. 6). The usual deviation amounts to 5–20% of the whole total ion current (TIC).

After determination of the number of main components and their spectra in the described manner, the absolute fragment ion intensities per spectrum are added. In this way, one finds the TIC of every component. This is determined more by the number of evaporated molecules than by other effects, e.g. the ionization section of the molecules. Therefore, the contribution of a component TIC to the whole TIC of the sum spectrum corresponds to the percentage of the component in the mixture. The values coincide satisfactorily with the concentrations determined chromatographically [3]. The application of the SEKOS program rapidly (about 2h) yields results

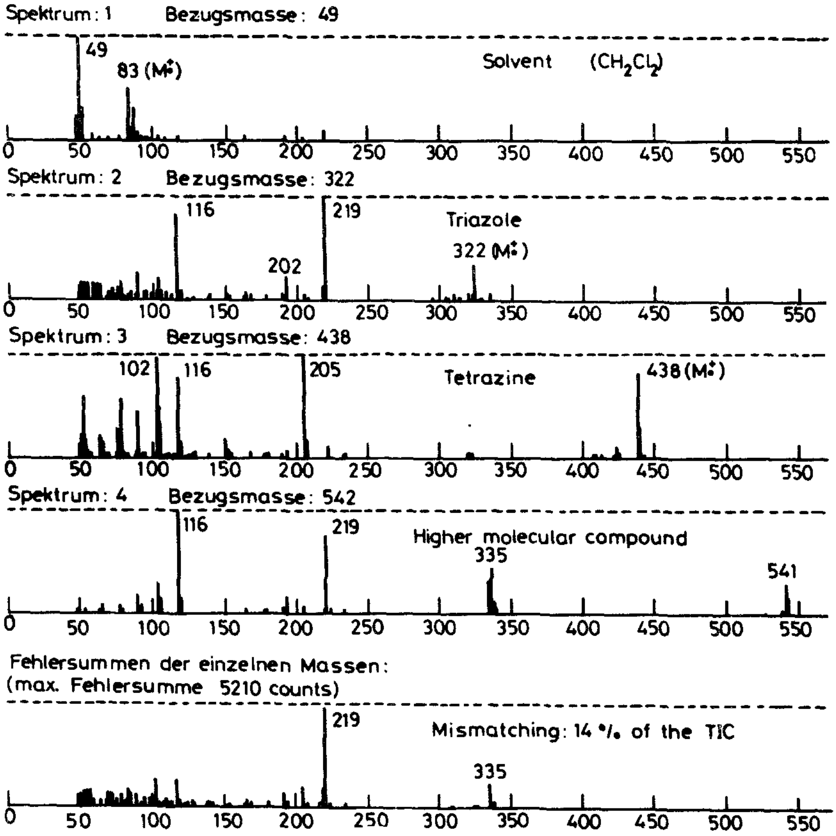

Fig. 6 Component's spectra calculated with a greater (i.e. more correct) number of components

with better structural information than other methods, e.g. it allows the detection of higher molecular or more polar compunds, which can often not be observed with chromatographic methods.

The suitability of the program is well illustrated by the detection of product 5, formed in a third possible reaction of the diaryl nitrileimine (see Fig. 2).

The disadvantages are that only 10 components can be followed up, and that the boiling or sublimation temperatures of the compunds in vacuo must not exceed 300°.

References

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Zusammenfassung – Das bei der thermischen Zersetzung von 2,5-Diaryl-2H-tetrazolen im ersten Schritt gebildete Produktengemisch wurde nach Abschrecken auf Zimmertemperatur und Auflösen in Dichlormethan massenspektrometrisch untersucht. Dazu wurde das multivariate Auswertungsprogramm SEKOS benutzt, das auf einer Computer-gestützten Analyse von Intensität-Zeit-Kurven mehrkomponentiger Mischungen im Massenspektrometer beruht. Das Arbeitsprinzip und die Vorteile des Auswerteprogramms werden erklärt.

РЕЗЮМЕ — Масс-спектрометрически исследована смесь продуктов, образующихся на первой стадии термического разложения некоторых 2,5-диарил-2Н-тетразолов, после их охлаждения до комнатной температуры и последующего растворения в метиленхлориде. Была использована SEKOS программа оценки со многими переменными, являющаяся основой компьютерного анализа кривых интенсивность — время многокомпонентных смесей в масс-спектрометре. Объяснены принципы работы и преимущества такой программы.