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SIMULTANEOUS THERMAL ANALYSIS–MASS SPECTROMETRY ON LUBRICANT SYSTEMS AND ADDITIVES *

K.-H. OHRBACH [1], G. MATUSCHEK [2], A. KETTRUP [1,2] and A. JOACHIM [1]

[1] *University GH Paderborn, FB 13, Applied Chemistry, P.O. Box 1621,*
D-4790 Paderborn (F.R.G.)
[2] *Gesellschaft für Strahlen- und Umweltforschung mbH München,*
Institut für Ökologische Chemie, Ingolstädter Landstrasse 1, D-8042 Neuherberg (F.R.G.)

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ABSTRACT

In order to determine characteristic thermal analysis data of lubricant systems and additives, simultaneous thermal analysis–mass spectrometry was applied in air and argon atmospheres. In addition, investigations by means of differential scanning calorimetry and thermogravimetry were carried out in air and nitrogen flows. The thermobalance was coupled with a sampling device for the collection of the released volatiles and further gas chromatographic analysis.

INTRODUCTION

The continuously increasing development of high-performance engines leads to stringent requirements as to the lubricant systems applied, which can not be fulfilled by using different mixtures of basic oils or basic types of greases. With respect to reducing the friction and to improving the anti-wear as well as the anti-oxidative properties, the lubricants are added together with a large number of different types of substances. In addition to the well established standard testing methods, applications of thermal analysis such as thermal analysis–mass spectrometry (TA–MS) differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetry (TG) are promising tools for determining particular characteristics of such lubricant systems.

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EXPERIMENTAL

TA–MS Equipment and measuring conditions

The TA–MS analysis system consists of a Netzsch STA 429 thermal analyzer and a Balzers QMG 511 quadrupole mass spectrometer. Two specially arranged ceramic tubes were used to produce the pressure drop from ambient pressure up to 10^{-3} Pa, to permit the simultaneous recording of the mass spectra. The heating rate applied was 10 K min^{-1} in argon and air atmospheres. The MS data were processed by a Digital Equipment PDP 11/23 + microcomputer. The operating system was RT 11 and the programming language Fortran IV. The software was self-developed.

TG and DSC equipment and measuring conditions

The TG and DSC measurements were performed using a Perkin–Elmer TGA 7 thermogravimetric analyzer and a DSC 7 differential scanning calorimeter in air and nitrogen atmospheres. The TGA 7 instrument was directly coupled with an adsorption device. As an adsorbent we used NIOSH charcoal tubes, and for the desorption acetone.

GC equipment

The desorption solutions were injected into a DANI 3900 capillary gas chromatograph equipped with a flame ionization detector and a 50 (25 m) OV 101 fused silica column.

Greases

Different high-temperature greases having an application range up to 1600 K, and an assembly paste containing molybdenum sulphide were used.

Additives

Zinc dialkyldithiophosphate (ZnDDP), zinc dialkylcarbamate (ZNDC), zinc naphthenate (ZNNP), lead naphthenate (LNNP) and poly(methylmethacrylate) (PMMA) were used.

Lubricating oil

High-performance API-CD diesel engine oil SAE 10 W 40 containing an unknown concentration of ZnDDP, the sample N with an increased concentration of 20% ZnDDP by weight, and the sample N with a decreased concentration of 20% ZnDDP by weight.

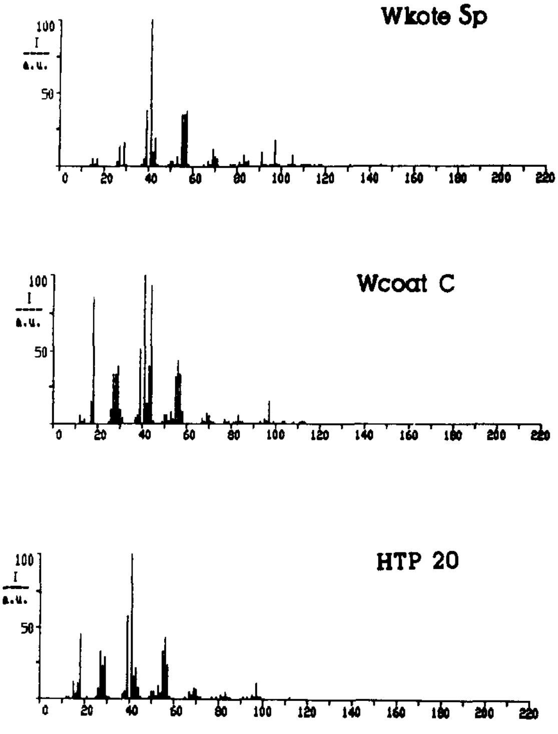
RESULTS AND DISCUSSION

The aim of these investigations was to examine the thermal and, if possible, the oxidation stability of high temperature stable greases, antioxidative agents and a diesel engine oil to which was added different concentrations of ZnDDP. In addition, the degradation behaviour of ZnDDP in air and in inert gas was investigated and is discussed in this paper by way of an example.

Greases

All lubricant systems investigated were commercial products. The given specifications are abbreviations of trade names. They all consist of an unknown type of synthetic oil and different amounts of solid greases such as molybdenum sulphide and graphite. The oil content differs from approximately 50% for Wkote Sp up to 99% for HTP 20. The synthetic oils appear to be very similar in all cases, as a comparison of the spectra in Fig. 1 shows.

The mass spectra for these three different lubricant systems can be regarded as a fingerprint. The position of the characteristic peaks is identical, representing typical hydrocarbons with mass-to-charge ratios of 41, 55,


Wkote Sp

Wcoat C

HTP 20

Fig. 1. Mass spectra of Wkote Sp, Wcoat C and HTP 20.

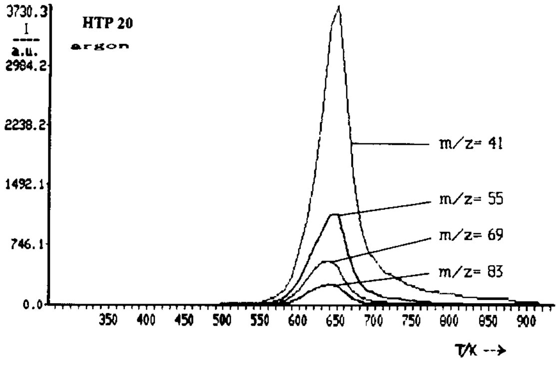


Fig. 2. Ion current of HTP 20.

69, 83 and 97. The mass spectral data were recorded at the temperature of the corresponding DTG maximum. All spectra are background- or memory-free because the residual gas and any contaminants in the recipient are automatically subtracted from all MS data.

The temperature-dependence of the intensity of a typical hydrocarbon evolution for the lubricant system HTP 20 is shown in Fig. 2. A special software option permits representation and evaluation of each fragment detected.

The results of the TG adsorption investigations followed by flame ionization GC separation were not significant for one of the lubricant systems. For this reason the gas chromatogram of HTP 20 is shown in Fig. 3 as an example.

The shapes of the DSC curves for the lubricant systems are also quite similar. Figure 4 shows the exothermic oxidative decomposition of Wkote in air and the evaporation of the volatile compounds in a nitrogen atmosphere. Table 1 gives a summary of the DSC data for the lubricant systems.

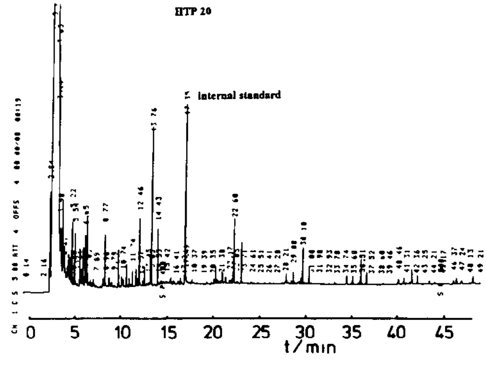


Fig. 3. Chromatogram of HTP 20.

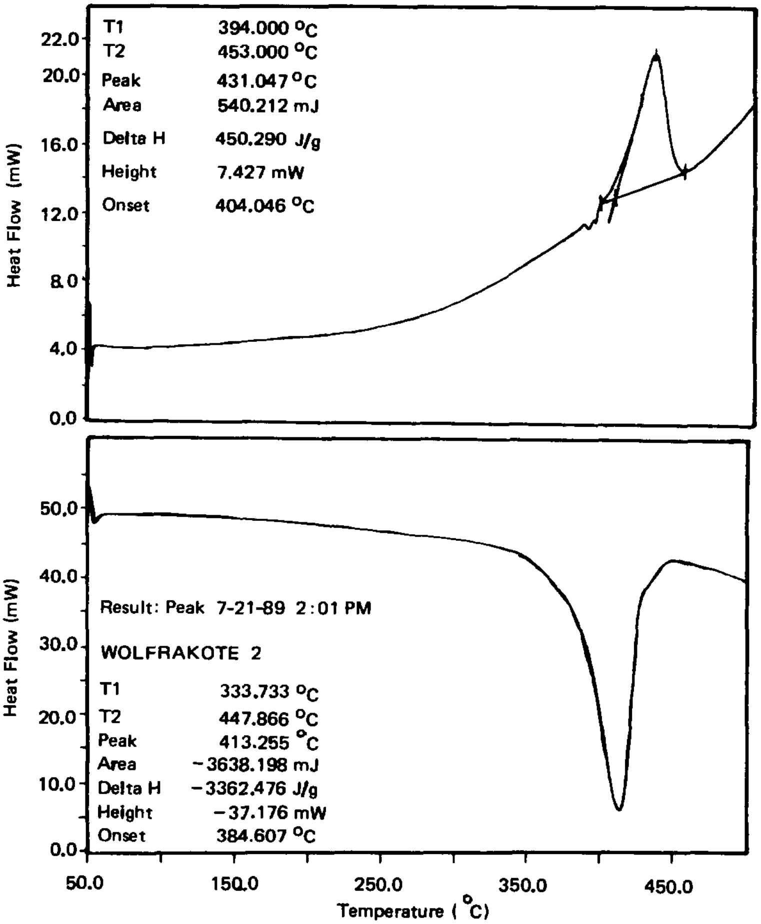


Fig. 4. DSC curves for Wkote Sp.

TABLE 1

DSC data for Wkote Sp, Wcoat C and HTP 20

	Sample		
	Wkote Sp	Wcoat C	HTP 20
Air			
T_{onset} (K)	677	668	643
T_{peak} (K)	704	704	681
ΔH (J g^{-1})	450.3	436.9	1638.8
Nitrogen			
T_{onset} (K)	658	661	641
T_{peak} (K)	686	676	668
ΔH (J g^{-1})	−3362.5	−2730.6	−10952

All in all, it seems to be obvious that the methods described were not suitable for distinguishing between different lubricating systems or for performing a kind of a screening test for quality or purity control. This is the same problem as occurs in polymer analytics. With individual compounds of high purity, all statistical evaluations are satisfactory and all data are significant. In the case of mixtures, however, a single compound added in small amounts may be the reason for reducing the total number of reproducible thermal analysis parameters to only one, the onset temperature in a pure oxygen atmosphere.

Additives

The characterization of additives is much easier. The additives investigated belong to the group of anti-oxidative, anti-wear, anti-corrosive and detergent additives. Poly(methylmethacrylate) is used to improve the viscosity index of a lubricant system.

Zinc dithiophosphates

Figure 5 shows the general structure of the Zn-dialkyl or-aryl dithiophosphates and the substituents R. Further information was not available. The alkyl substituents are labelled C_{10}, C_4 and iso-C_6, aryl and aromatic.

Determination of the initial temperatures T_1 of the mass loss experiments has shown that the aryl ZnDDPs are less reactive than the alkylated compounds. The thermal stability of the additives increases from long chain alkylated to aromatic zinc dithiophosphates (see Fig. 6).

The mass spectra recorded at the temperatures of the DTG peak maxima of the same TA–MS runs are shown in Fig. 7. A comparison shows that the spectra of the alkylated samples 1–3 are quite similar, as are those of products 4 and 5.

The mass fragments detected correspond with alkylated thio-compounds which may be formed by inter- and intramolecular rearrangements during

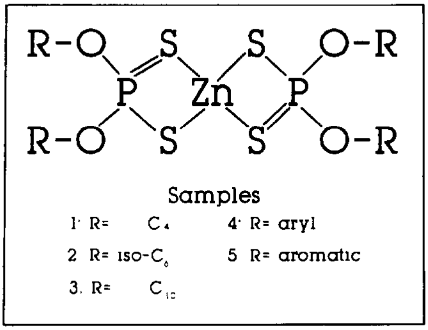
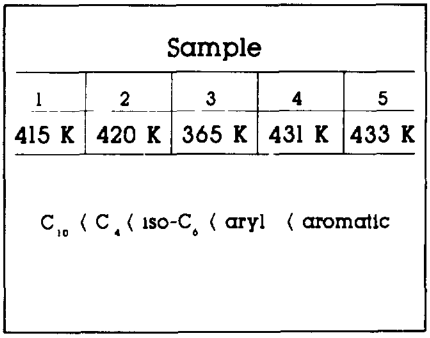


Fig. 5. Structure of ZnDDP.



Sample

1	2	3	4	5
415 K	420 K	365 K	431 K	433 K

C_{10} < C_4 < iso-C_6 < aryl < aromatic

Fig. 6. Stability of ZnDDP.

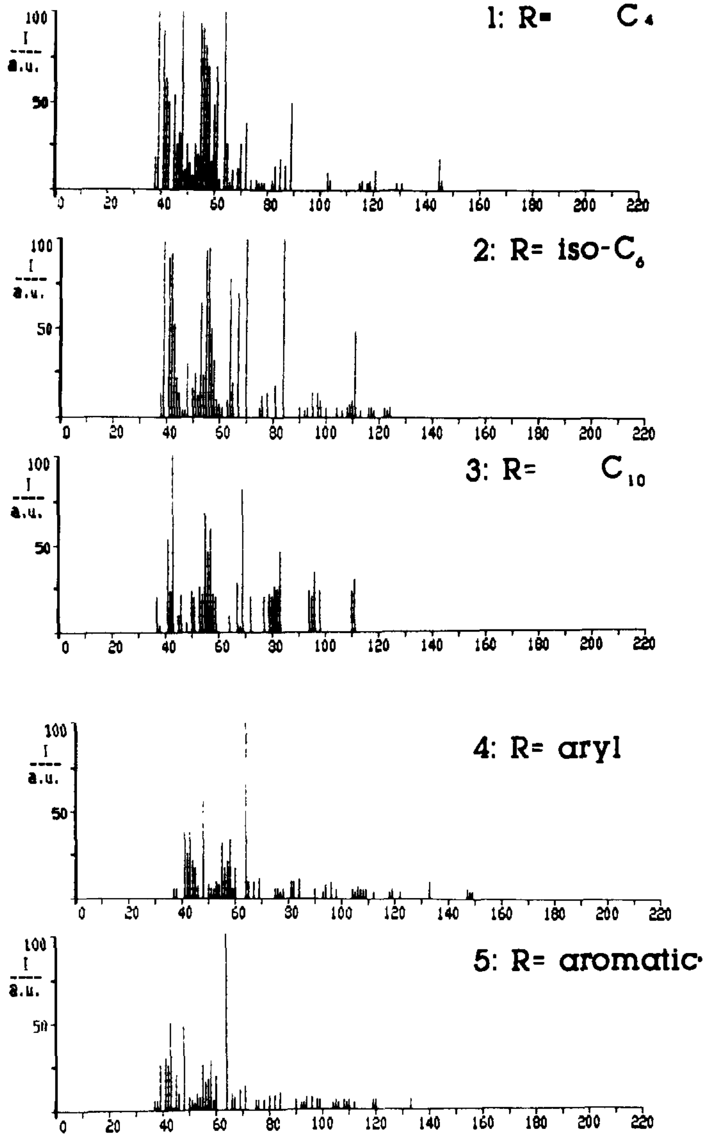


Fig. 7. Mass spectra of ZnDDP.

FRAGMENTS
ZnDDP

open chain	cyclic
146: C_4H_9-S-C_4H_9	111: C_5H_3OS
122: $C_4H_9S_2$	97: C_5H_5S
103: C_4H_9-S-CH_3	95: $C_5H_3O_2$
89: C_4H_9S	83: C_5H_7O
	81: C_5H_5O

Fig. 8. Fragments of ZnDDP.

thermal treatment. The products identified are mainly open-chain compounds. They are typical fragmentation products for substituted ZnDDP additives, especially for short-chain compounds. The formation of cyclic

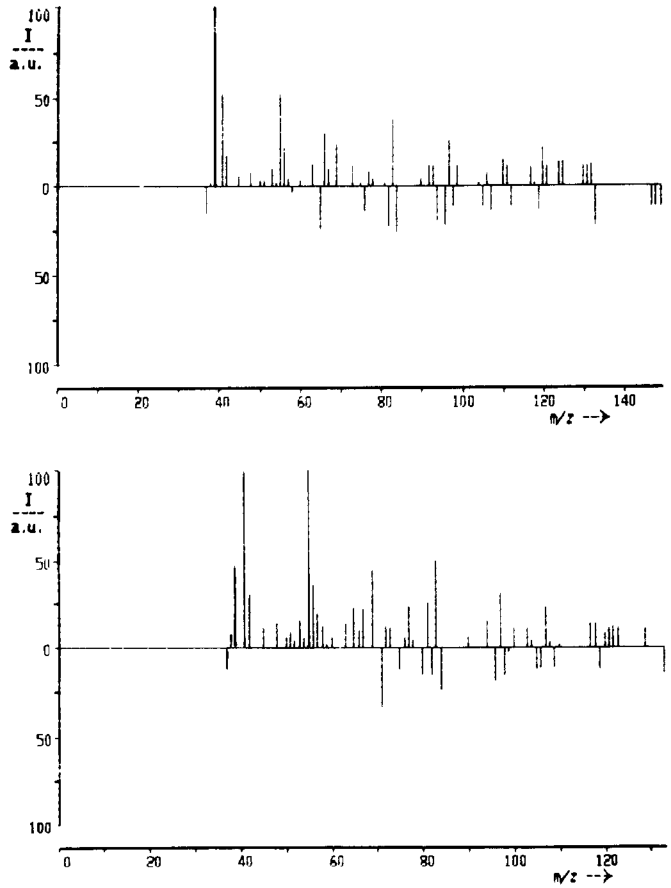


Fig. 9. Difference spectra of ZnDDP samples 4 and 5.

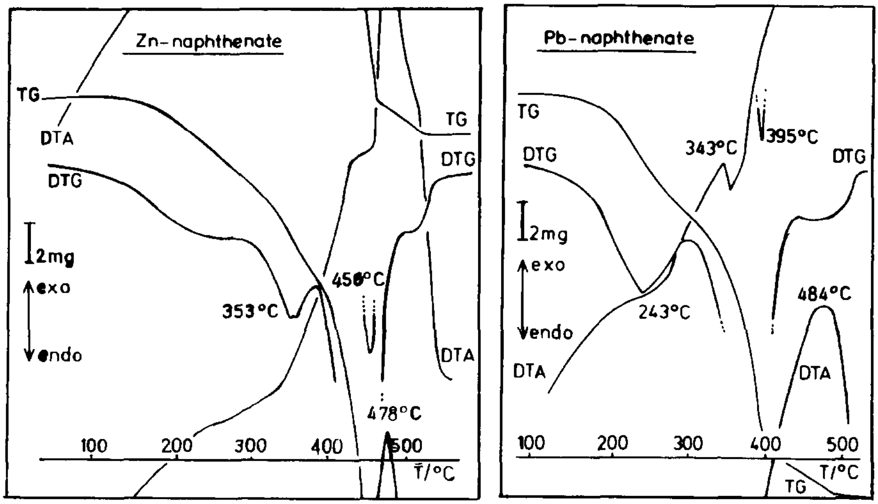


Fig. 10. Thermal analysis curves for the two naphthenates in air.

hydrocarbons was observed for additives having a chain length longer than four carbon atoms (see Fig. 8).

The decomposition of the aryl and aromatic ZnDDPs is based on a two-stage degradation mechanism. The difference spectra in Fig. 9 support this TG result.

The difference spectra were obtained by subtracting the MS data for the ZnDDP samples 4 and 5 in the first DTG maximum from those in the second DTG maximum. By using this software option in addition to the TG/DTG data it is possible to distinguish between alkylated and aromatic additives.

Naphthenates

The shapes of the thermal analysis curves of zinc naphthenate and lead naphthenate is quite similar (see Fig. 10). The initial temperatures and the total weight loss are in the same range. The mass spectra of both additives are nearly identical. The TA values are summarized in Table 2.

TABLE 2

TA values for the naphthenates

	Sample	
	Zn-naphthenate	Pb-naphthenate
T_i (K)	337	379
Δm (%)	83	81
DTG_{max} (K)	626, 729	516, 668
DTA_{max} (K)	757	616, 757

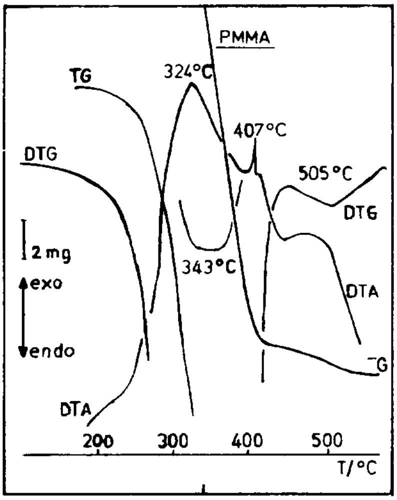


Fig. 11. Thermal analysis curves for PMMA in air.

Poly(methylmethacrylate)

Studies of the decomposition behaviour of polymethylmethacrylate have shown that it will depolymerize up to 90% to the monomer. Owing to the high oxygen content of PMMA, it burns completely in the gas phase. The mass loss of PMMA in an air atmosphere amounts to 98%. The decomposition occurs in two steps with the DTG maximum temperatures at 597 K and 778 K (324 °C and 505 °C). The DTA curve also shows two sharp maxima at 483 K and 683 K (210 °C and 410 °C, see Fig. 11). From the simultaneously recorded mass spectra we know that the decomposition products of PMMA in air are nearly 100% water and carbon dioxide.

Investigations in an argon atmosphere have yielded the same products (see Fig. 12). In an argon atmosphere, however, peaks of the series of typical chain fragments appear at differences of 14 a.m.u. The spectrum was recorded at about 623 K (350 °C).

The main MS peaks of PMMA detected in an argon atmosphere are summarized in Fig. 13. From a chain length of three carbon atoms the differences between the masses of the structural elements is 14 a.m.u. The

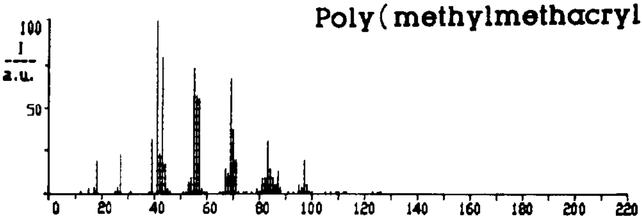


Fig. 12. Mass spectrum of PMMA in Ar.

FRAGMENTS
PMMA

m/z 27: C_2H_3
m/z 39: C_3H_3
m/z 41: C_3H_5
m/z 55: C_4H_7
m/z 69: C_5H_9
m/z 83: C_6H_{11}
m/z 97: C_7H_{13}

Fig. 13. Fragments of PMMA.

masses 27 and 39 are typical fragments which always occur as carbonization or char products.

Lubricating oil

To determine the influence of ZnDDP with $R = C_{10}$, the lubricating oil samples (see Experimental section) were heated in air from ambient temperature up to 800 K at a heating rate of 10 K min^{-1}. Although the shapes of the TG (three stages), DTG and exothermal DTA curves obtained for the three samples is nearly identical, they show significant shifts of the characteristic data owing to the different ZnDDP concentrations. With increasing concentrations of ZnDDP increasing values were observed for the initial temperature of the mass loss, the amount of the first mass loss, the standardized DTG peak heights and the maximum temperature of the total ion current intensities taken from the simultaneously recorded mass spectra.

From these results the conclusion may be drawn that the selected TA/MS data are a measure for the anti-oxidative efficiency of the added ZnDDP. A decrease in the ZnDDP content causes a lowering of the oxidation stability of the diesel engine oil.

The TG, DTG, and DTA curves of ZnDDP ($R = C_{10}$) recorded in an air flow are shown in Fig. 14. The shape of the DTA curve is exothermic with a shoulder in the region of 503 K (230 °C) and two exothermic peaks having a maximum at 572 K and 710 K (599 °C and 437 °C), respectively. The mass loss occurs in two stages with maximum reaction rates at 457 K and 553 K (184 °C and 280 °C), respectively. This is in agreement with the MS data taken from the plot of the total ion current intensities (Fig. 15), with maximum temperatures at 453 K and 553 K (180 °C and 280 °C). Small amounts of ZnDDP containing low boiling components are vaporized at 413 K (140 °C) and above.

In the case of the experiments in an argon flow, the characteristic temperatures are shifted to higher values by about 30 K. This results from

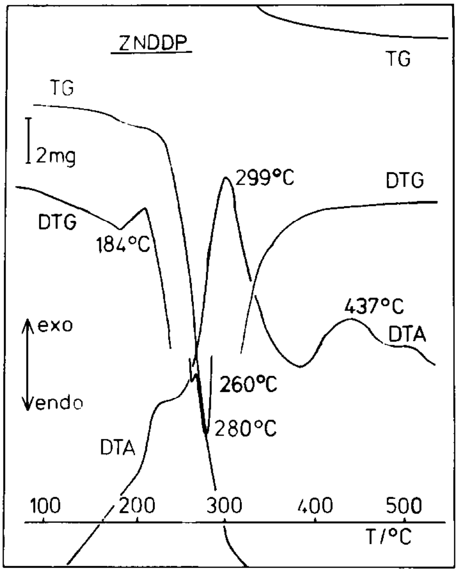


Fig. 14. Thermal analysis curves for zinc dialkyldithiophosphate (R = C_{10}).

protection of the sample against the oxidative effects, caused by the absence of oxygen.

Interpretation of the mass spectra of all these materials, as mentioned in the Experimental section, is very difficult because the products were only available in technical grade. An assignment of structural elements to registered peaks is only possible for a small number of permanent gases of for the typical degradation of the aliphatic homologeous series from C1 up to C10 (see Fig. 16). The peak at 141 a.m.u. corresponds with the cleavage of complete aliphatic chain $C_{10}H_{21}$.

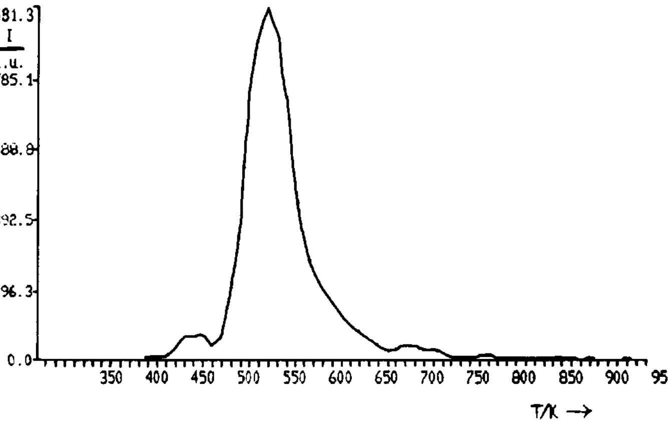


Fig. 15. Total ion current intensity of zinc dialkyldithiophosphate (R = C_{10}).

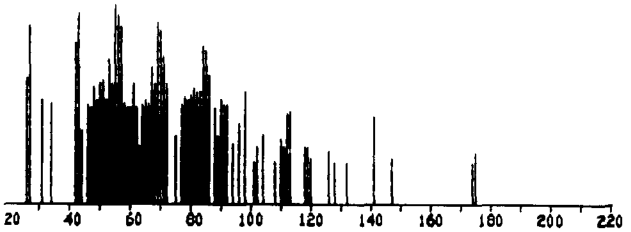


Fig. 16. Mass spectrum of ZnDDP at a temperature at 523 K (250 °C) in an argon atmosphere.

Investigation of lubricating systems and additives by means of thermal analysis is very difficult. The difficulties exist with regard to reproducibility and significance of the data. Combined methods such as TA–MS or modified techniques such as on-line TG adsorption followed by gas chromatographic analysis may become more important in the future.

Different applications of the TA–MS method have been described elsewhere [1–5].

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