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IDENTIFICATION OF TELLURIUM-CONTAINING COMPOUNDS BY MEANS OF MASS SPECTROMETRY

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Summary

A general mass spectrophotometric method for the identification of tellurium-containing compounds is described. The method is based on the analysis of the typical pattern of cluster peaks containing tellurium due to $-Te-$, $-Te_2-$ or $>TeX_2$ ($X = Cl, Br$). A comparison of the computer calculated and experimental mass spectra of some of the compounds containing tellurium is given.

Introduction

A difficulty in organotellurium chemistry is the identification of the various tellurium compounds formed in the reaction of organic substrates with Te^{IV} compounds such as TeX_4 (where X is a halogen), R_nTeX_{4-n} (R = organic residue, $n = 1,2$) or with Te^{II} compounds, such as TeX_2 and RTeX.

Although the mass spectra of several organotellurium compounds are reported in the literature [1-5] the data are often presented with inadequate detail. In our work on the reactions between TeX_4 ($X = Cl, Br$), R_nTeX_{4-n} (R = phenyl, *p*-anisyl) and anthracene, Ph_3P and various olefins [6] it was found that a detailed mass spectra cluster peak analysis based on the functional groups $-Te-$, $-TeTe-$, $>TeX_2$ and TeX_3 (X = halogen) can serve as a general fingerprint for the identification and characterization of organic and inorganic tellurium compounds.

Results and discussion

The mass spectra of tellurium compounds are characterized mainly by the relative intensities of the eight naturally occurring isotopes of tellurium [7]. The intensity of a spectral line in the spectrum is the sum of the probabilities of all combinations of the different isotopes having the same *m/e* value. For example for the group TeX_n ($X = Cl, Br$) the probability of the i^{th} combination is $p_i = (n/m)a^m b^{n-m} q_i$ (q_i = abundance of the Te^i isotope, a = of the X^k and b = of the X^{k+2} isotope).

TABLE 1

CALCULATED PEAK INTENSITIES OF THE VARIOUS ISOTOPIC COMPOSITIONS OF Te, Te_2, $TeBr_2$, $TeCl_2$, $TeCl_3$, TeBr AND TeCl

Spectral line[a]	Peak intensities (%)						
	Te	Te_2	$TeBr_2$	$TeCl_2$	$TeCl_3$	TeBr	TeCl
M	0.09	≈0	0.02	≈0	1.04	0.05	≈0
$M + 1$					0.37		
$M + 2$	2.47	≈0	0.66	1.7	2.98	1.28	1.8
$M + 3$	0.89	≈0	0.22	0.05	3.32	0.45	0.7
$M + 4$	4.74	0.07	2.44	3.5	10.18	3.6	3.9
$M + 5$	7.03	0.056	2.20	4.3	3.07	3.96	5.25
$M + 6$	18.72	0.3	7.67	12.5	21.99	11.73	18.1
$M + 7$		0.43	3.74	2.7	1.00	3.51	1.7
$M + 8$	31.75	1.33	18.48	25.3	30.66	25.24	28.7
$M + 9$		≈1	1.76	0.04	0.11		
$M + 10$	34.27	3.9	29.12	32.6	19.31	33.01	35.8
$M + 11$		3.2					
$M + 12$		8.2	15.3	14.9	5.34	17.13	8.6
$M + 13$		5.1					
$M + 14$		15.14	8.7	2.2	0.54		
$M + 15$		4.82					
$M + 16$		22.91					
$M + 17$							
$M + 18$		22.05					
$M + 19$							
$M + 20$		11.74					

[a] $M = {}^{120}\mathrm{Te}^{k}\mathrm{X}_n$ (^{k}Cl = 35, ^{k}Br = 79).

The calculated data for Te, Te_2, TeBr, $TeBr_2$, TeCl, $TeCl_2$ and $TeCl_3$, are given in Table 1 and Fig. 1. The experimental spectra for comparison are given in Fig. 2. (For the calculation we used a computerized program (APL) based on the above probability equation, and the published values for isotopic composi-

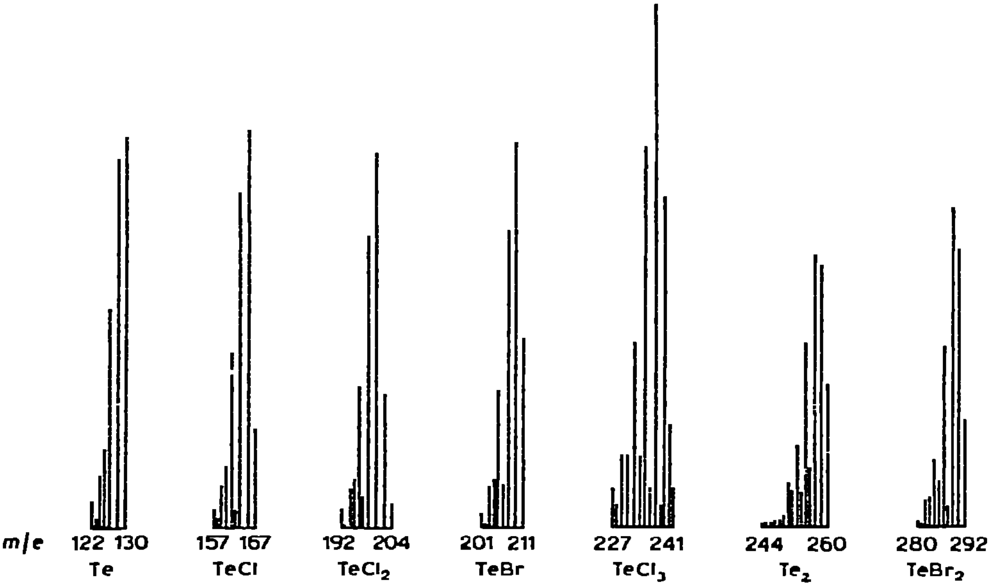


Fig. 1. Calculated mass spectra of Te, Te_2, TeBr, TeCl, $TeBr_2$, $TeCl_2$ and $TeCl_3$.

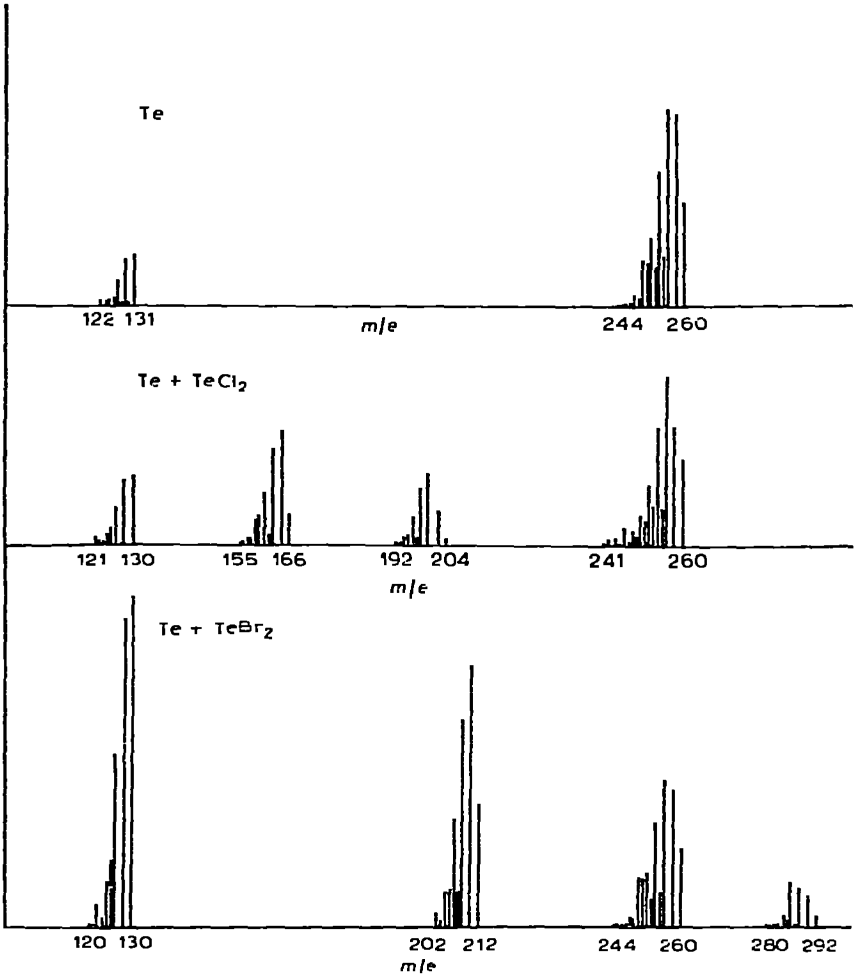


Fig. 2. Experimental mass spectra of Te, Te + $TeCl_2$ and Te + $TeBr_2$.

tion of tellurium and the halogens.) As can be seen from Table 1 and Figs. 1 and 2 each tellurium functional group mentioned above has its characteristic pattern of spectral lines which can serve as a fingerprint for its identification.

Te. The mass spectrum of elemental tellurium (Fig. 2) is composed of two main zones, m/e 120-130 (Te^{+}) and 244-260 (Te_2^{+}). Peaks at 61.5, 62.5, 63.5, 124.5, 125.5, 126.5 and 127.5 due to m/2e of low intensity are typical for the spectrum. There is good agreement between the calculated and the experimentally found intensities of the peaks.

TeX_2 + Te. It was found [6] that the "tarry products", which are formed in most reactions between TeX_4 and olefins [8-11] and which were never completely analyzed, are composed of TeX_2 and Te, in various proportions. The spectra obtained are shown in Fig. 2, and it can be seen that the cluster peaks are as follows: Te_2 (*m/e* 244-260), Te (*m/e* 120-130), TeX (for Cl: *m/e* 157-167; Br: *m/e* 201-211), TeX_2 (for Cl: *m/e* 192-204; Br: *m/e* 280-292).

From a comparison of the relative abundance of the peaks at 244-260 and

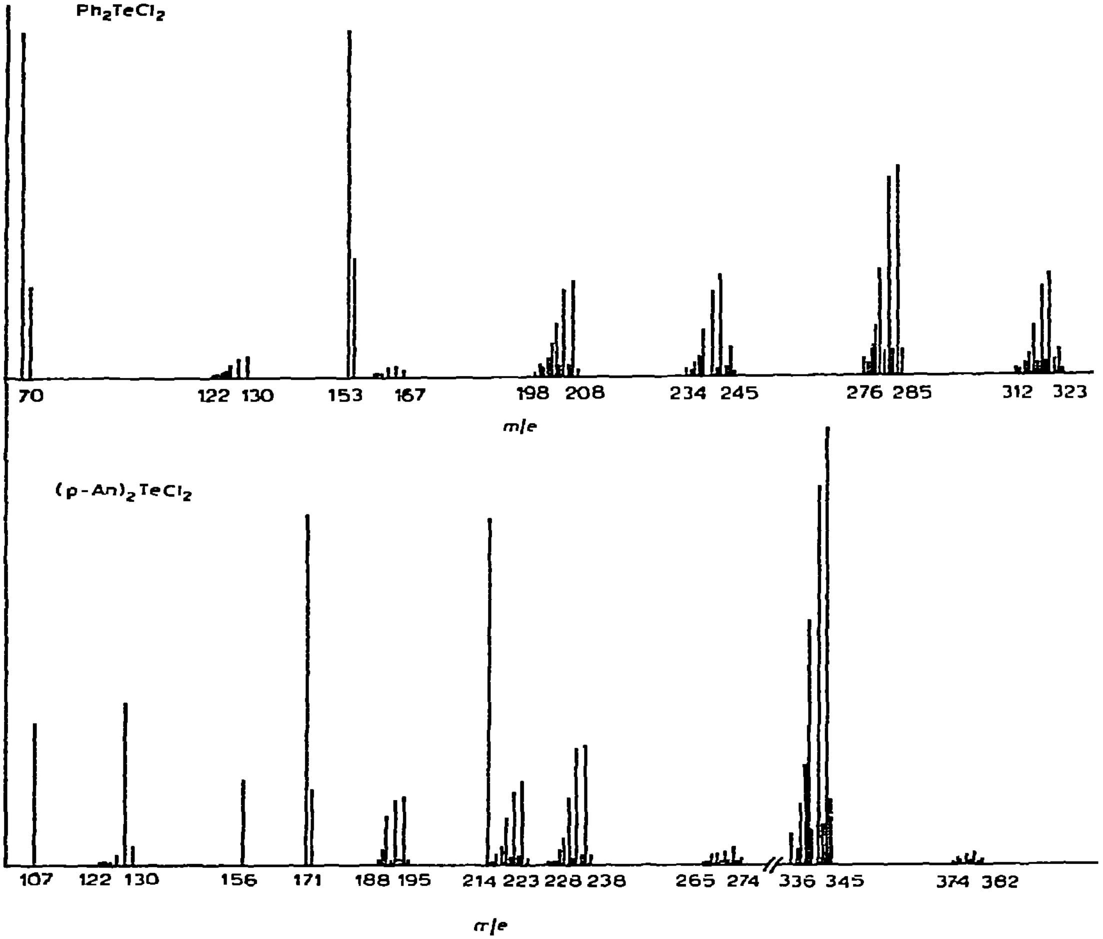
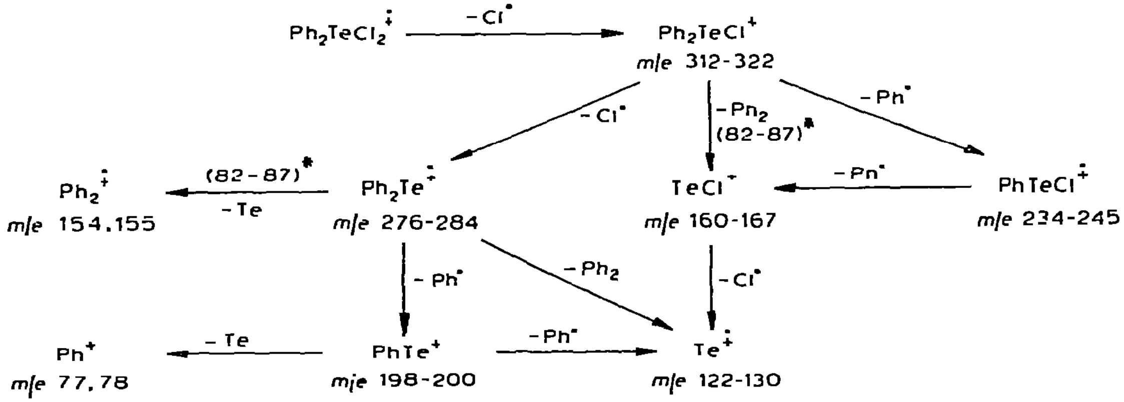


Fig. 3. Mass spectra of Ar_2TeCl_2 (Ar = phenyl, *p*-anisyl).

SCHEME 1. FRAGMENTATION OF Ph_2TeCl_2



122-130 in the spectrum of TeX_2 with the spectrum of elemental tellurium it appears that the fragment $Te^{+\cdot}$ is derived from both $TeX_2^{+\cdot}$ and $Te_2^{+\cdot}$ (Te_2 is the main constituent of free tellurium in the gas phase [12]). The secondary spectrum (*m/2e*) characteristic of TeX_2 is present. In the case of Te + $TeCl_2$, only tellurium contributes to the secondary spectrum (see above on Te), whereas in the case of the $TeBr_2$ + Te the $TeBr_2$ is also a contributor. For $TeBr_2$ + Te additional secondary peaks appear at *m/2e*: 100.5, 101.5, 102.5, 103.5, 104.5 and 105.5, which are at relative intensities corresponding to $TeBr^{2+\cdot}$, and at 141.5, 142.5, 143.5 due to $TeBr_2^{2+}$.

Replacement of X by an organic residue, e.g. in Ph_2TeCl_2, *p*-An_2TeCl_2 (*p*-An = *p*-Anisyl), Ph_2Te and *p*-An_2Te, does not change the general pattern of the cluster peaks from the various functional tellurium groups present in the molecule. The naturally occurring ^{13}C of the organic residue does not change the typical tellurium pattern, although it changes the relative peak intensities (Table 1) and introduces some more lines between those from the tellurium. Examples of mass spectra of some organotellurium compounds are given in Fig. 3.

Ar_2TeX_2 (Ar = phenyl, *p*-Anisyl). The fragmentation pattern of the Ar_2TeX_2 on electronic impact is expected to be the sum of the patterns from the TeX_2 and Ar_2Te components. The fragmentation schemes for Ph_2TeCl_2 and *p*-An_2TeCl_2 are given in Schemes 1 and 2 respectively. In both Ph_2TeCl_2 and *p*-An_2TeCl_2 the molecular peaks are absent and the highest *m/e* observed is due to *M* — Cl. Tellurides such as Ph_2Te and *p*-An_2Te have fragmentation patterns like those of the corresponding Ar_2TeX_2, including metastable peaks, but without the halide-containing peaks. As can be seen from the examples given above of the many organotellurium compounds analyzed by us, the presence of tellurium-containing groups can be detected in all cases.

Experimental

Instrumention

Mass spectra were recorded on a Hitachi—Perkin—Elmer RMU-6 spectrometer at 70 eV.

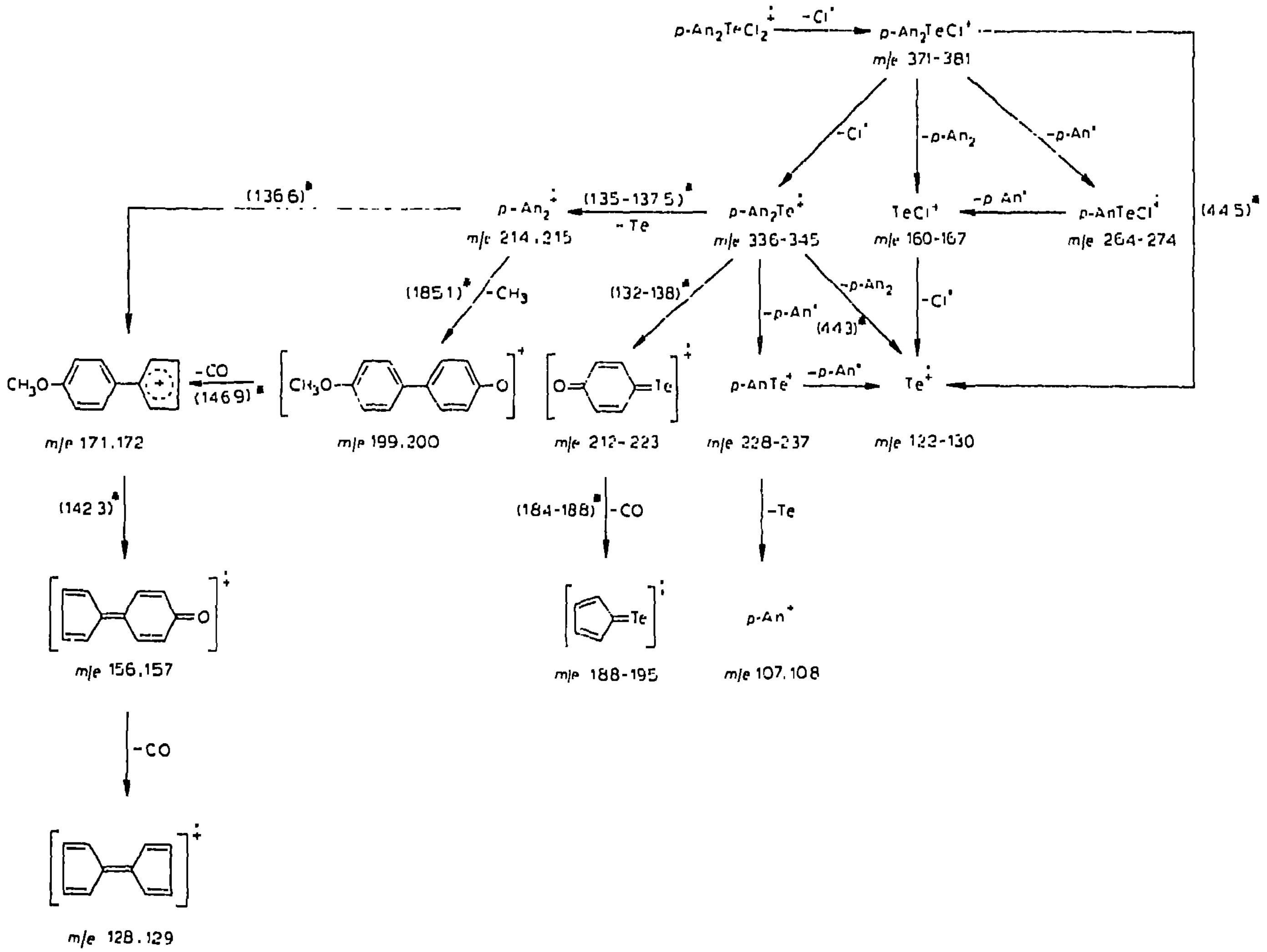
Materials

Te + TeX_2 (X = Cl, Br) were obtained from the tarry residue of the reaction reported in ref. 6 by a CCl_4 solvent Soxhlet extraction of the organic materials. The inorganic residue was dried in vacuum. The $TeCl_2$ was identified by its disproportionation to $TeCl_4$ + Te on refluxing in ether [13]. The disproportionation product was identified as its pyridine complex [14]. Elemental analysis showed only tellurium and chlorine or bromine to be present. Mass spectra of $TeCl_2$ + Te were recorded at a probe temperature of 220° and sample tempararture of 220-240°, while for $TeBr_2$ + Te the probe and sample temperatures were 190°.

p-An_2TeCl_2 and p-An_2Te were synthesized as described by Bergman [15]. Mass spectra of *p*-An_2TeCl_2 were taken at a probe and sample temperature of 200° and that of *p*-An_2Te at a probe and sample temperature of 110°.

Ph_2TeCl_2 was made from PhHgCl and $TeCl_4$ in dioxane [15]. Mass spectra were taken at a probe and sample temperature of 250°.

SCHEME 2. FRAGMENTATION OF p-An_2TeCl_2



Te was of 99.99% purity (Merck, Darmstadt). Mass spectra were taken at a sample and probe temperature of 250°.

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