

IKE AND METASTABLE ION EVIDENCE FOR FRAGMENTATION PATHWAYS IN THE MASS SPECTRA OF ORGANOLEAD SUBSTITUTED NITROGEN HETEROCYCLES*

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ABSTRACT

Spectra-structure correlations are made of methylplumbyl substituted heterocyclic compounds consisting of nitrogen containing condensed five and six membered rings. Fragmentation behavior under electron impact is elucidated by means of IKE and metastable ion spectra, and the relationships to structure are discussed. The molecular ion decomposition pathways and the formation of rearrangement ions are described. A comparison of ion abundance distributions is given for lead containing, and non-lead containing ions.

INTRODUCTION

A limited number of heterocyclic-organolead compounds have been synthesized [1]. Only about a dozen representatives of this class are reported in the literature, but an active synthetic program is now in progress in certain laboratories, and an increasing number of these compounds is now being prepared [2-7]. Structural information, especially electron impact fragmentation data, is lacking. In this work the mass spectra of some trimethyl and triphenyl lead complexes of pyrole, indole and carbazole have been studied.

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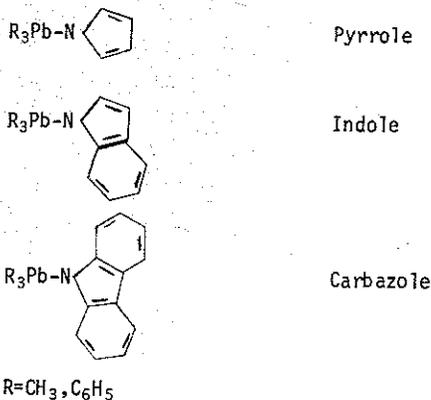
EXPERIMENTAL

The mass spectra of the compounds studied were determined using a CEC 21-110B instrument, operating at 70 eV with an ion source temperature of 200 °C. Samples were admitted via a direct insertion probe. A constant reading was maintained on the beam monitor throughout each scan.

Two decoupling methods of observing reaction paths for "metastable" processes were used: Ion kinetic energy (IKE) spectra were obtained by varying the electric sector voltage [8, 9], and metastable ion spectra were obtained using a variable accelerator voltage [10-12]. The IKE and metastable ion spectra were displayed using an *x-y* recorder to plot the output of the ion current amplifier versus the accelerator, or electric sector voltage. A digital voltmeter was used to read the voltages instantaneously.

RESULTS AND DISCUSSION

The generalized formulae for the lead-heterocyclic compounds that were analyzed are as follows:



The corresponding spectra are shown in Fig. 1. Lead ion (m/e 208) is the most abundant ion in the spectra of the triphenyllead substituted compounds and is formed by ion decomposition through several pathways. The principal precursor ions for lead ion are seen in the variable ion accelerator voltage scan of triphenylleadpyrrole shown in Fig. 2. The lead daughter ion is seen at the left hand side of the figure and the three major, and two minor, precursor ions are seen to the right. The three largest peaks at masses 285, 362 and 439 correspond to phenyl, diphenyl, and triphenyl-lead ions respectively; the two other less abundant ions at masses 274 and 351, leadpyrrole ion and phenylleadpyrrole ion.

RELATIVE INTENSITY

Fig. 1

ION ABUNDANCE
10

Fig. 2

IKE
observed
involved
losses
mono
three

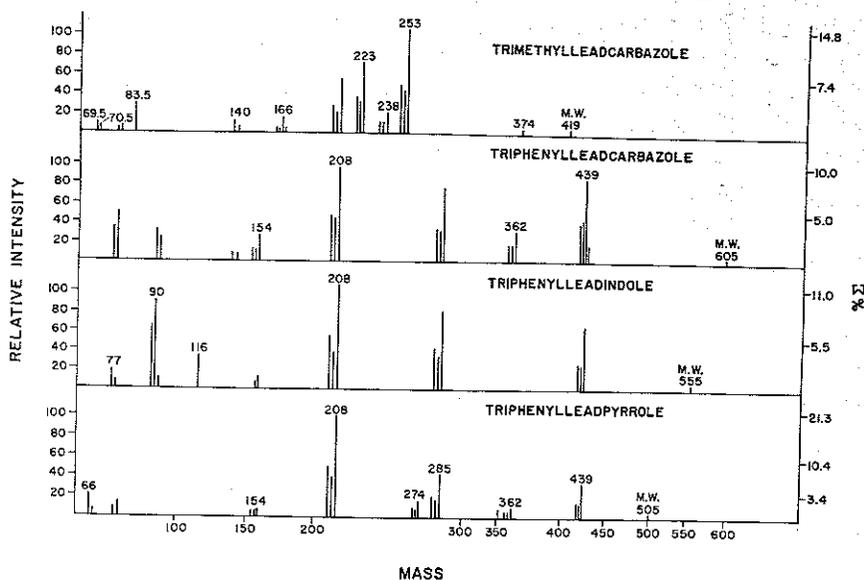


Fig. 1. Mass spectra of certain organolead substituted nitrogen heterocycles.

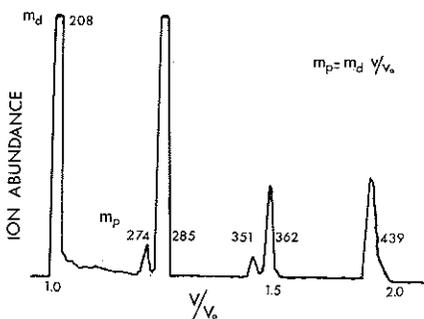


Fig. 2. Precursor ions for lead ions in triphenylleadpyrrole.

Figure 3 shows the ion kinetic energy spectrum of triphenylleadpyrrole. The IKE method is used mainly as a means of surveying the major metastable processes observed in the spectrum. The ion fragments depicted and the decay process involved are listed in Table I.

The three metastable processes illustrated here correspond to the fragment losses giving rise to the triphenyllead ion at mass 439, the lead ion at mass 208, and monophenyllead at mass 285, and agree completely with the appearance of the three most abundant ions in the conventional mass spectrum (see Figs. 1 and 4).

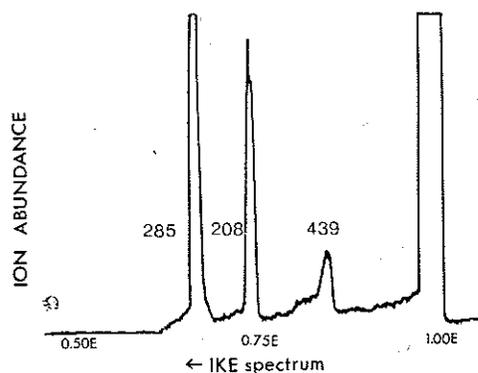


Fig. 3. Ion kinetic energy spectrum of triphenylleadpyrrole.

TABLE 1

SUMMARY OF DECAY PROCESSES DEPICTED IN FIG. 3

V_2/V_1	M_1	M_2	Decay process
0.871	505	439	$\phi_3\text{PbPy}^+ \rightarrow \phi_3\text{Pb}^+ + \text{Py}^-$
0.734	285	208	$\phi\text{Pb}^+ \rightarrow \text{Pb}^+ + \phi^-$
0.656	439	285	$\phi_3\text{Pb}^+ \rightarrow \phi\text{Pb}^+ + \phi_2^-$

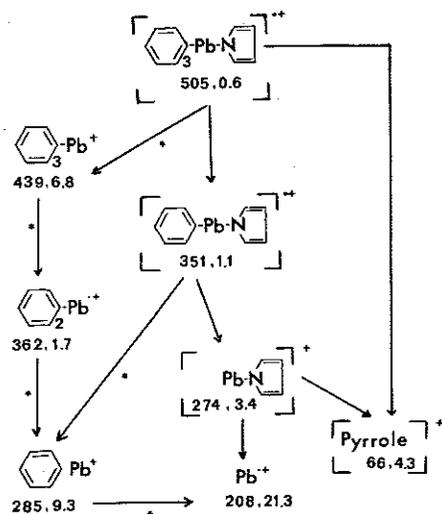


Fig. 4. Fragmentation pathway diagram for triphenylleadpyrrole.

Tabulation of the conventional spectrum, in combination with the metastable ion data obtained as in the examples given in Figs. 2 and 3, provides the information necessary for constructing fragmentation pathway diagrams.

The fragmentation pathway diagram for triphenylleadpyrrole is seen in Fig. 4. The mass of the principal ion fragments observed in the spectrum, and the ion abundance, are indicated by the numbers shown below the structural representation of each ion. Ion abundance is expressed as the percentage of total ionization. The molecular ion decomposition paths are indicated with arrows. When the pathway is supported by the appearance of a metastable ion an asterisk is shown besides the arrow. The molecular ion for triphenylleadpyrrole is observed at mass 505. It is of low intensity; only 0.6% of total ionization. Fragmentation of the rather weak lead-nitrogen bond provides the phenyllead ion series which finally terminates with the most intense ion in the spectrum, the lead ion itself. Loss of phenyl groups from the molecular ion produces an ion of low intensity at mass 351. This ion then loses another phenyl group and forms the moderately intense leadpyrrole ion at mass 274. Breaking the weak leadpyrrole bond provides another path for the formation of the lead ion. When the charge resides on the pyrrole this cleavage provides an alternate path, in addition to direct cleavage from the molecular ion for the formation of the pyrrole ion.

The origin of unusual ions in a mass spectrum may be traced by a kinetic energy spectrum as in Fig. 5. This shows an ion kinetic energy spectrum of triphenylleadindole. The intense ion beam for the parent ion is seen on the right,

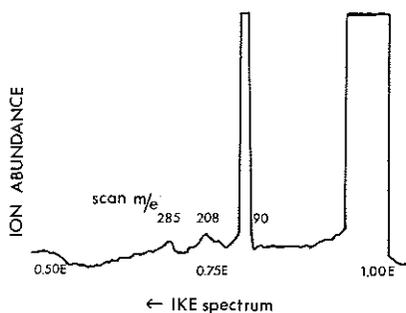


Fig. 5. Ion kinetic energy spectrum of triphenylleadindole.

and the remainder of the spectrum shows the relative abundances of the ions corresponding to the metastable transitions. These are rather weak except for the peak at mass 90. When the search is made for the precursor ions forming mass 90, by varying the ion accelerating voltage, a very large precursor ion is found 26 mass units higher at mass 116. The transition thus corresponds to the loss of acetylene to form mass 90. The transitions corresponding to the peaks in the IKE spectrum are seen in Table 2.

Figure 6 shows the fragmentation scheme for triphenylleadindole. The molecular ion at mass 555 has low intensity. As with the triphenylleadpyrrole complex described previously, rupture of the lead-indole bond gives rise to the phenyllead ion series. The fragments leading to the indole ion are likewise analogous.

TABLE 2

SUMMARY OF DECAY PROCESSES DEPICTED IN FIG. 5

M_1	M_2	Decay Process
$116^+ \rightarrow 90^+ + 26$		$C_8H_5N^+ \rightarrow C_6HN^+ + C_2H_2$
$285^+ \rightarrow 208^+ + 77$		$\phi Pb^+ \rightarrow Pb^+ + \phi$
$439^+ \rightarrow 285^+ + 154$		$\phi_3 Pb^+ \rightarrow \phi Pb^+ + \phi_2$

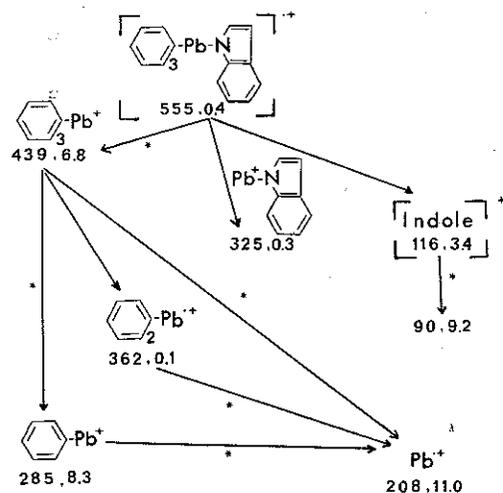


Fig. 6. Fragmentation scheme for triphenylleadindole.

Figure 7 shows the fragmentation pathways for triphenylleadcarbazole ion. Again the ion fragments obtained are quite similar to the other triphenyllead complexes.

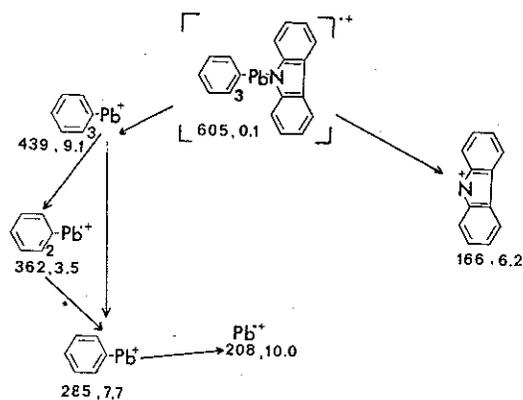


Fig. 7. Fragmentation pathways for triphenylleadcarbazole.

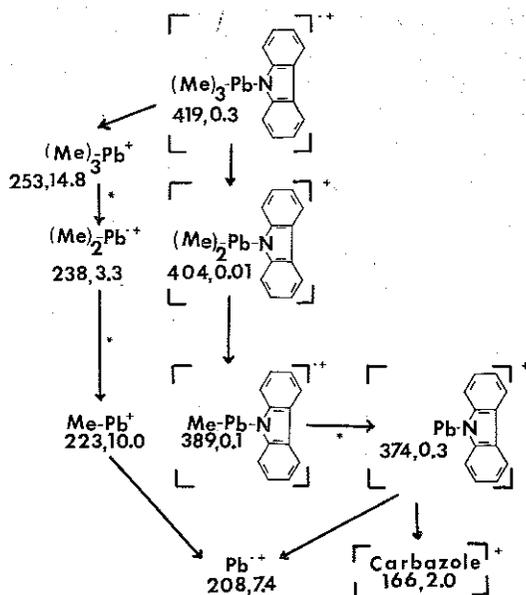


Fig. 8. Fragmentation scheme for trimethylleadcarbazole.

In addition to the triphenyllead complexes of nitrogen heterocycles, studies were made of the behavior of a series of analogous trimethyllead complexes. Figure 8 shows the fragmentation scheme for trimethylleadcarbazole. A low intensity parent ion is observed at mass 419. Fragmentation of trimethyllead compounds follows a fragmentation pathway which is quite similar to the triphenyl compounds. Loss of methyl groups produces low intensity ions at mass 404, and mass 389. Rupturing of the methyllead bond in this ion yields a low intensity leadcarbazole ion at mass 374, and further fragmentation of the weak lead-nitrogen bond leads to the formation of the slightly more abundant carbazolyl ion and the lead ion. Cleavage of the molecular ion at the weak lead-nitrogen bond provides a series of methyllead ions of relatively great intensity.

A comparison of the ions appearing in the spectrum of trimethylleadpyrrole with trimethylleadcarbazole indicates that the fragmentation pathway is nearly identical with respect to both the nature of the ions formed, and their relative intensities. In fact, the similarity is so striking that their spectra are nearly superimposable, except for the weight difference of the carbazole and pyrrole.

The conclusions to be drawn from this study appear perhaps to be rather trivial, since, as with the spectra obtained for most organo-metallic compounds, the spectra are both simple and predictable [13]. In summary, however, a few observations and comparisons can be made. Fragmentation of the parent ion is extensive in all cases. The relative abundance is 1% of total ionization or less. Triphenyllead derivatives have a more intense molecular ion than trimethyllead

derivatives. This is expected as there is greater resonance in the triphenyl system. The parent ions are approximately the same intensity for the three triphenyl systems.

The lead-phenyl (i.e. lead-carbon) bond appears to be stronger than the lead-nitrogen bond in all cases. Likewise, the lead-carbon bond is stronger than the lead-nitrogen bond in the trimethyl heterocyclic systems. This gives rise to the predominant ions in the spectrum, which are the lead aryls or lead alkyls, and the lead ion itself. The lead ion increases in intensity however, going from pyrrole to indole to carbazole, illustrating the expected stability of the lead-nitrogen bond with the increased resonance of the heterocyclic ring system. The series of ions arising from cleavage of the lead-nitrogen bonds is much less abundant, but yields ultimately the ions corresponding to the nitrogen heterocyclic forming the complex. These ions and fragments, though very small, nevertheless are important in identifying the organic moieties present in the complex.

REFERENCES

- 1 Gerhard Sauermann, U. S. Army Materials and Mechanics Research Center, Watertown, Mass., U.S.A.
- 2 R. E. Sacher, Ph.D. Thesis, Boston College, Boston, Mass., 1970.
- 3 M. Fishwick and M. G. H. Wallbridge, *J. Chem. Soc., A*, (1971) 57.
- 4 F. Flockling, J. R. C. Light, *J. Chem. Soc., A*, (1968) 717.
- 5 P. N. Preston, P. J. Rice and N. A. Weir, *J. Mass Spectrom. Ion Phys.*, 1 (1968) 303.
- 6 J. Diekman, J. B. Thompson and C. Djerassi, *J. Org. Chem.*, 32 (1967) 3904.
- 7 D. B. Chambers, F. Flockling, J. R. C. Light and M. Weston, *Chem. Commun.*, 9 (1966) 281.
- 8 J. H. Beynon, J. W. Amy and W. E. Baitinger, *Chem. Commun.*, (1969) 723.
- 9 J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger and T. Y. Ridley, *Anal Chem.*, 45 October 1973, 1023A.
- 10 M. Barber and R. M. Elliott, presented at the Twelfth Annual Conference on Mass Spectrometry and Allied Topics ASTM Committee E-14, Montreal, Canada, 1964.
- 11 J. H. Futrell, K. R. Ryan and L. W. Sieck, *J. Chem. Phys.*, 43 (1965) 1832.
- 12 K. R. Jennings, *J. Chem. Phys.*, (1965) 4176.
- 13 M. L. Bazinet, W. G. Yeomans and C. Merritt, Jr., *Int. J. Mass Spectrom. Ion Phys.*, 16 (1975) 405.