Tetrahedron Letters No.33, pp. 2811-2813, 1969. Pergamon Press. Printed in Great Britain.

MASS SPECTROMETRY OF TRIS(TRIMETHYLSILYL)PHOSPHATE

Mikio Zinbo and William R. Sherman (1)

Department of Psychiatry, Washington University School of Medicine

St. Louis, Missouri 63110

(Received in USA 2 May 1969; received in UK for publication 9 June 1969)

The volatility conferred on many substances by derivatization with the trimethylsilyl (TMSi) group has made this method one of great importance in gas chromatography and, more recently, in mass spectrometry. The ability to perform difficult separations and to examine the purified substances by combined gas chromatography-mass spectrometry (GC-MS) provides the chemist with a powerful tool for the structural analysis of substances in simple and complex mixtures. Recently TMSi derivatives of nucleotides (2) and phosphorylated carbohydrates (3) have been subjected to combined GC-MS. Several fragment ions in these spectra contain phosphate in ester linkage with TMSiOH. As an aid in the interpretation of these spectra it was of interest to us to learn the extent to which tris(TMSi)phosphate (I) gave rise to the same ions.

The cyclohexylamine salt of orthophosphoric acid was prepared and crystallized from water by the addition of acetone. The salt was then dried and completely silylated with bis(TMSi-$\underline{d}_0$ or $\underline{d}_9$)acetamide:TMSiCl-$\underline{d}_0$ or -$\underline{d}_9$:pyridine in a ratio of 3:5:2 v/v/v. The bis(TMSi-$\underline{d}_9$)acetamide was prepared by the method of McCloskey et al., (4). Tris(TMSi)phosphate (I) previously isolated in pure form by Sauer (5), was separated from solvent and by-products by gas chromatography on a 4' x 1/4" glass column containing 0.1% Dow Corning DC-710 on etched glass beads, Corning code 0201. Spectra were obtained at 70 ev ionizing potential as I eluted from the column in an LKB 9000 combined GC-MS.

Figure 1 presents the mass spectrum of I. In Table 1 we present the mass shifts which are observed in ions from tris(TMSi-$\underline{d}_9$)phosphate. Table 1 also contains the calculated and observed abundances of the A+1 ions which result from the naturally occurring heavy isotope composition of each ionic species. Taken together the TMSi-$\underline{d}_9$ mass shifts and the A+1 ion data give mutually supporting evidence for the empirical formulas given.

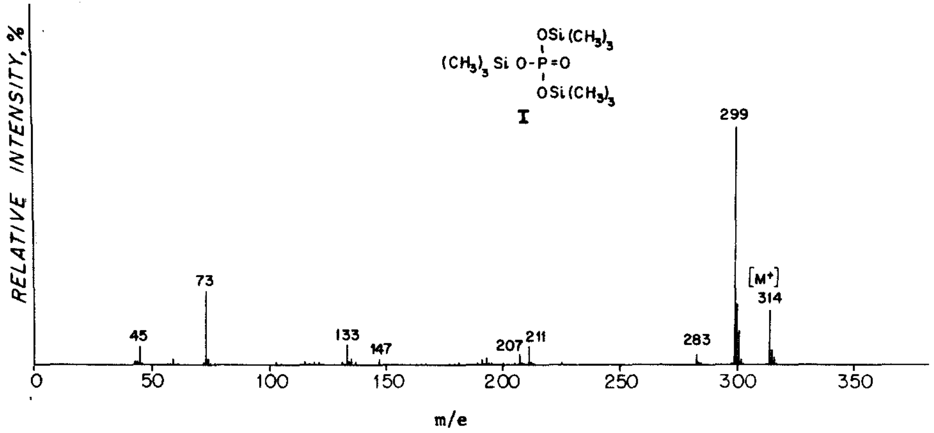

Figure 1

TABLE 1

Mass Spectra of Tris(trimethylsilyl)Phosphate and Tris($\underline{d}_9$-trimethylsilyl)Phosphate

$\underline{m}/\underline{e}$	Tris(TMSi) Phosphate rel. int. (%)	$\underline{m}/\underline{e}$	Tris($\underline{d}_9$-TMSi) Phosphate mass shift (amu)	$(A+1)^+/A^+$ obs.	calc.*	Empirical Formula
314	22.9	341	27	26.6	26.9	$(CH_3)_9Si_3PO_4$
299	100.0	323	24	25.8	25.7	$(CH_3)_8Si_3PO_4$
283	4.5	303	20	24.1	24.6	$(CH_3)_6CH_2Si_3PO_4$
211	7.8	223	12	15.0	15.7	$(CH_3)_4Si_2PO_4$
207	4.5	222	15	22.6	22.4	$(CH_3)_5Si_3O_3$
147	2.4	162	15	17.4	16.8	$(CH_3)_5Si_2O$
133	8.3	142	9	15.3	14.5	$(CH_3)_3Si_2O_2$
73	31.1	82	9	8.2	8.9	$(CH_3)_3Si$
45	7.8	50	5	6.9	6.2	CH_3SiH_2

*Calculated for contributions of ^{13}C (1.08%), ^{2}H (0.02%), ^{17}O (0.04%) and ^{29}Si (5.07%).

The four phosphorus-containing ions in the mass spectrum of I are the molecular ion, m/e 314, and the fragment ions at m/e 299, 283 and 211. A metastable peak identifies m/e 299 as the product formed by loss of a methyl radical from the molecular ion (m* calculated 284.7, observed 285.0). The tris($\underline{d}_9$-TMSi)phosphate spectrum also contains this metastable peak, shifted to m/e 306. The loss of methane from m/e 299 could account for the formation of m/e 283. In a similar way, m/e 211 could be formed from *m/e* 227 by the loss of methane. In the mass spectrum of several TMSi phosphorylated carbohydrates (3) a metastable ion is found which relates *m/e* 211 to 227 (m* calculated and found at 196.1). The spectrum of d_9-TMSi glucose 6-phosphate contains *m/e* 227 shifted to *m/e* 242 suggesting the composition $(CH_3)_5Si_2PO_4H$ for *m/e* 227. *M/e* 227 is observed in the spectrum of I in 1% relative intensity.

It was of particular interest for us to learn whether *m/e* 387, a major ion in the spectra of all TMSi carbohydrate phosphates, could be formed from I. This ion has the remarkable structure tetrakis(TMSi)phosphate (3) and must be formed by either intramolecular migration of TMSi to phosphate oxygen or by an ion-molecule reaction of a TMSi phosphate ester with, perhaps, the abundant TMSi+ ion (*m/e* 73). The absence of *m/e* 387 from our spectrum of I supports an intramolecular rearrangement pathway to this ion.

The ion at m/e 45 was observed by Sharkey et al., (6) and assigned the structure CH_3SiH_2+ and by Diekman et al., (7) who assigned the structure $CH_3O=CH_2+$. The ion we observed appears, from the data in Table I, to be of the former type.

The other fragments observed in the mass spectrum of I are *m/e* 207 and *m/e* 133. These are siloxane ions related, in general, to *m/e* 147 ($Me_3SiO=SiMe_2+$) which is seen in spectra of TMSi carbohydrates (8) and other TMSi ethers (7). An ion at *m/e* 133 is also observed in the mass spectrum of TMSi α-D-glucose (8) and several TMSi phosphorylated carbohydrates (3). In the latter case, the mass shift on formation of the d_9-TMSi derivative is identical to that described in this paper.

The following support for this work is gratefully acknowledged: N.I.H. Research Career Program Award GM-21,863, N.I.H. Research Grant NB-05159, United Cerebral Palsy Research Grant R-218-68, and in part, N.I.H. Grant MH-13002. The mass spectrometer used in this study was funded by Health Science Advancement Award 5 S04 FR06115-02 to Washington University.

1. To whom requests for reprints should be sent.
2. J. A. McCloskey, A. M. Lawson, K. Tsuboyama, P. M. Krueger and R. N. Stillwell, *J. Am. Chem. Soc.*, **90**, 4182 (1968).
3. M. Zinbo and W. R. Sherman, the 156th National Meeting of the American Chem. Soc. (1968).
4. J. A. McCloskey, R. N. Stillwell and A. M. Lawson, *Anal. Chem.*, **40**, 233 (1968).
5. R. O. Wauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).
6. A. G. Sharkey, Jr., R. A. Friedel and S. H. Langer, *Anal. Chem.*, **29**, 771 (1957).
7. J. Diekman, J. B. Thomson and C. Djerassi, *J. Org. Chem.*, **33**, 2271 (1968).
8. D. C. DeJongh, T. Radford, J. D. Hribar, S. Hanessian, M. Bieber, G. Dawson and C. C. Sweeley, *J. Am. Chem. Soc.*, **91**, 1728 (1969).