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The Mass Spectra of Methylcyclopentane and Methyl-C^{13}-cyclopentane

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The mass spectra, as excited by single electron impact by 75 volt electrons, of methylcyclopentane and methyl-C^{13}-cyclopentane are described and briefly discussed. Certain conclusions with respect to the modes of dissociation of the methylcyclopentane ion into fragments are presented.

In connection with the analysis of reaction products arising in the course of the study of the mechanism of the aluminum bromide catalyzed isomerization of methyl-C^{13}-cyclopentane to cyclohexane-C^{13},[1] we have had occasion to compare critically the mass spectra of methylcyclopentane (natural carbon isotope abundance) and the C^{13}-labeled, methyl-C^{13}-cyclopentane. Since the comparison yields facts that are of interest with respect to the nature of the mechanisms of the unimolecular dissociation reactions of molecule–ions formed by single electron impact that are pertinent to the general theory of such dissociation reactions[2] and to the interpretation of the appearance potentials of fragment ions in the mass spectra of cyclanes,[3] we present herewith the results of this study.

The mass spectra were obtained with a modified Westinghouse Type LV instrument.[4] The mass spectra were recorded by scanning the magnetic analyzing field while keeping the ion accelerating potential at −1000 volts. The ions were withdrawn from the ground potential ion source by application of a 5 volt ion repeller potential, equivalent to a field of 13 volts/cm. The energy of the ionizing electrons obtained from a carburized tungsten cathode was a nominal 75 volts, and the ion source temperature was 125 ± 5°.

The methylcyclopentane with natural carbon isotope abundances was a Phillips Research Grade sample that had been treated with N_2O_4 and then percolated through a column packed with Ascarite to remove excess N_2O_4 and then silica gel for the removal of the nitro-olefins and benzene. After this treatment the methylcyclopentane had an optical density (1 cm. path against distilled water in the reference cell) less than 0.2 at all wave lengths greater than 2000 Å. and less than 0.02 at all wave lengths greater than 2200 Å. The intensity of the ions of mass to charge ratio 86 and 71 in the mass spectrum of the portion used indicated the hexane content of the sample to be less than 0.05% m. The methyl-C^{13}-cyclopentane was prepared[5] by the reaction of cyclopentanone with methylmagnesium iodide (*ca.* 50% C^{13}) to form the tertiary alcohol, methyl-C^{13}-cyclopentanol, that was dehydrated by heating with oxalic acid to the olefin. This was hydrogenated to methyl-C^{13}-cyclopentane over Raney nickel. The product was treated with small portions of concentrated sulfuric acid to remove residual olefin and ether.

The mass spectrum of monoisotopic (C^{12}) methylcyclopentane was deduced from that of the "natural" methylcyclopentane by correcting for the C^{13}-containing ions under the assumption of negligible isotope effects on the fragmentation pattern, employing the apparent C^{13} abundance, $1.0_1\%$,[6] indicated by the intensity of the ion of $m/q = 85$ (C_6-C_{12}-C^{13}_1) relative to that of the ion of $m/q = 84$ (C_6H_{12}-C^{13}_0). This mass spectrum is shown in the second column of Table I. In this table of mass spectra the intensities of the ions are recorded as the fraction (times 100) the intensities the ions constitute of the total mass spectral intensity. In computing and tabulating the mass spectra doubly charged ions totaling *ca.* 0.3% of the total intensity were neglected.

TABLE I

THE MASS SPECTRA OF METHYL-C^{12}- AND METHYL-C^{13}-CYCLOPENTANES

75 volt ionizing electrons, ion source temperature 125 ± 5°

m/α	Me^{12}-CP	Me^{13}-CP	% Cor.
85		8.16	
84	8.16	0.29	
83	0.29	.01	
82	.01	.07	
81	.07	.00	Assumed
80	.00	.12	
79	.12	.01	
78	.01	.12	
77	.12	.00	
70	.00	5.84 ± 0.05	13
69	12.0_9	5.4_1 ± .1	63
68	1.38	1.30 ± .03	52
67	0.69	0.55 ± .01	54
66	.06		
65	.20		
57	.00	27.9 ± .3	6
56	31.0	8.0_4 ± .3	79
55	7.07	2.8_9 ± .06	70
54	0.90	0.79 ± .02	53
53	.88	0.40 ± .02	68
52	.16		
51	.44		
50	.32		
44	.00	1.94 ± .02	11
43	2.73	4.19 ± .05	43
42	6.41	10.2 ± .7	41
41	14.3_0	7.5_5 ± .1	65
40	0.92	2.09 ± .03	35
39	4.21	2.65 ± .05	60
38	0.36		
37	.13		
30	.00	0.73 ± .01	10
29	1.79	1.75 ± .03	50
28	1.36	1.96 ± .03	41
27	3.30	2.03 ± .04	57
26	0.29	0.23 ± .01	54
25	.00		
16	.00	0.05_7 ± 0.005	12
15	.20	$.12_2$ ± 0.005	62
14	.01	.01	0

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(1) O. Beeck, J. W. Otvos, D. P. Stevenson and C. D. Wagner, to be submitted for publication.

(2) H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig and H. Eyring, *Proc. Nat. Acad. Sci.* (*USA*), **38**, 667 (1952).

(3) (a) J. L. Franklin and H. E. Lumpkin, *J. Chem. Phys.*, **19**, 1073 (1951); (b) J. L. Franklin and F. H. Field, *ibid.*, **21**, 550 (1953).

(4) D. P. Stevenson and C. D. Wagner, *ibid.*, **18**, 11 (1950).

(5) Preparation and purification by Dr. C. D. Wagner.

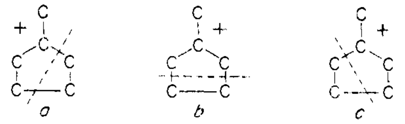
(6) This value is in good agreement with that previously found in butanes and propane, $1.0_2\%$, see ref. 4 above.

The gross isotopic constitution of the "labeled" methylcyclopentane was computed from the intensities of the ions of $m/q = 86$, 85 and 84 in the mass spectrum, by use of the relative intensities of the ions of $m/q = 84$, 83 and 82 in the methylcyclopentane-C_0^{13} mass spectrum, assuming negligible isotope effects on the relative parent and fragment ion sensitivities of the various isotopic species. The quality of the agreement between the total specific intensity of C_6 ions in the mass spectrum of the natural and the labeled material (±2%) provides reasonable assurance that the neglect of isotope effects is warranted. The gross isotopic composition thus found was C_6H_{12}-C_0^{13} = 44.65%, C_6H_{12}-C_1^{13} = 52.65% and C_6H_{12}-C_2^{13} = 2.70% (all ±0.1%). This composition corresponds to a 53.0 ± 0.1% C^{13}-content of the E. K. Co. methyl iodide. The concentrations of the individual isotopic isomers calculated from the gross isotopic composition and the assumption that the C^{13}-content of the cyclopentanone was the same as that of the natural methylcyclopentane are: methyl-C^{13}-cyclopentane = 50.4%, methylcyclopentane-C_1^{13} = 2.2%, methyl-C^{13}-cyclopentane-C_1^{13} = 2.6% and methylcyclopentane-C_2^{13} = 0.1%.

The mass spectrum of the methyl-C^{13}-cyclopentane was deduced from that of the labeled sample in the following manner. First the observed spectrum was corrected for C_6H_{12}-C_0^{13} using the concentration 44.6_5% and the mass spectrum given for this substance in Table I. The residual mass spectrum indicated that among the C_5 ionic fragments *ca.* 50% retain the methyl carbon while *ca.* 100% of the C_4 ionic fragments retain the methyl carbon. Mass spectra for the minor isotopic isomers, Me-CP-C_1^{13} and Me-C^{13}-CP-C^{13} were computed from that of C_6H_{12}-C_0^{13} using these approximate methyl-carbon retention figures along with the further assumption that among the C_3 ionic fragments there is 50% methyl carbon retention, while among the C_2 ionic fragments there is complete randomness with respect to the carbons. Except in the cases of the ion of mass to charge ratio 71 and 58 the corrections for contributions of the minor isotopic species constitute less than 10% of the total correction and thus even quite large errors in the minor species corrections would not introduce significant error in the final methyl C^{13}-cyclopentane mass spectrum as far as the discussion and conclusions we shall reach are concerned. In the case of the ion, $m/q = 71$, only C_6H_{12}-C_2^{13} contributes and the calculated intensity agreed with that observed to within 3%. Again in the case of the ion, $m/q = 58$, only C_6H_{12}-C_2^{13} contributes and in this case the calculated intensity was 16% less than the observed intensity. On the basis of these agreements we conclude that the accuracies of the intensities deduced for the fragment ions of the Me-C^{13}-CP mass spectrum are controlled by the accuracy of the corrections for C_6H_{12}-C_0^{13}. The repeatability of relative mass spectral intensities is ±1% of the individual intensities. This figure has been used in computing the uncertainties of the relative intensities of the ions in the Me-C^{13}-CP mass spectrum shown in the third column of Table I. There are shown in the fourth column of this table (as per cent. of the originally observed intensity) the magnitudes of the corrections.

Fifty per cent. retention of the methyl carbon by C_5-fragment ions in the methylcyclopentane mass spectrum would lead to expected intensities of $m/q = 70$ and 69 of 6.09 and 6.78, respectively, in the methyl-C^{13}-cyclopentane mass spectrum. The observed intensities, 5.8 and 6.4, respectively, are in essential agreement with the "calculated" intensities. This finding of methyl carbon retention by the C_5 ionic fragments is contrary to *a priori* expectation which was that there should be no such retention. The retention indicates that the structure of the $C_5H_9^+$ ion ($m/q = 69$ in the ordinary MCP mass spectrum) is probably not that of a cyclopentyl ion and that those methylcyclopentane ions that dissociate to C_5 ionic fragments largely undergo prior rearrangement to normal hexene ions that subsequently lose a terminal carbon atom. To the extent that this behavior of methylcyclopentane ions is a general one and is representative of the behavior of alkyl-cyclane ions, it is apparent that appearance potentials of ions of the type, $C_mH_{2m-1}^+$, in the mass spectra of R-C_mH_{2m-1} cyclanes, cannot be employed to deduce energetic properties of cycloalkyl radicals or ions. It will be noted that this behavior of the methylcyclopentane ion is in marked contrast to that of such alkane ions as have been studied. In the case of the alkanes, the dissociation of a methyl or ethyl radical by the alkane ion is not preceded by rearrangement.[4]

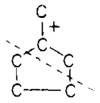
The intensity of the ion of $m/q = 57$ in the methyl-C^{13}-cyclopentane mass spectrum, = 27.9, *vs.* 31.0 for that of $m/q = 56$ in the MCP-C_0^{13} mass spectrum indicates that there is no unique process leading to loss of an ethylene fragment by the $C_6H_{12}^+$ ion. A conceptually simple mechanism that would lead to 100% retention of the methyl carbon by the $C_4H_8^+$ fragment would be

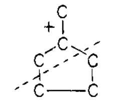


where *a* and *c* would give normal butene ions and *b* an isobutene ion, if the fission process were accompanied by simultaneous proton shift in the $C_4H_8^+$ residue. If the loss of a C_2 unit from the $C_6H_{12}^+$ ion were preceded by rearrangement to a normal hexene ion, as was found to be the case for loss of a C_1 unit, it would be expected that there would be 50% retention of the methyl carbon atom by the C_4 ionic fragment. If the order of 80% of the $C_4H_8^+$ fragments were formed by processes like *a*, *b* and *c* and 20% by prior rearrangement, the intensities of the ions $m/q = 57$ and 56 in the methyl-C^{13}-cyclopentane mass spectrum would be expected to be 27.9 amd 8.5, respectively. Approximate comparison of the initial portions of the ionization efficiency curves of the ions of $m/q = 84$ and 56 in the ordinary methylcyclopentane mass spectrum indicate that C_2H_4 is the neutral fragment that accompanies the $C_4H_8^+$ fragment ion.

The greater than 50% retention of the methyl carbon by the ion $C_3H_7^+$ ($m/q = 44$ in the methyl-

C^{13}-cyclopentane mass spectrum) suggests that a major mode of formation of this ion is by the process


d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where the fission is accompanied by simultaneous hydrogen atom transfer across the bonds that are being broken. The fact that the intensity of m/q = 44 in the labeled compound mass spectrum is but 0.7 times that of m/q = 43 in the mass spectrum of the unlabeled compound indicates that this ion is not formed by a unique process. Other processes that may contribute are (1) prior rearrangement to a normal hexene ion followed by fission of the central bond that would lead to 50% retention of the methyl carbon and (2) secondary dissociation of a $C_5H_9^+$ ion formed as described above. The latter process would lead to but 25% methyl carbon retention.

An essentially random selection of carbon atoms from C_6H_{12} to form two carbon ionic fragments would lead to 33% retention of the methyl carbon atom by the ionic fragments. If the process of formation of the two carbon fragments follows the sequence

$$C_6^+ \longrightarrow C_4^+ + C_2 \longrightarrow C_2^+ + 2C_2$$

we should expect about 40% retention of the methyl carbon by the C_2 ionic fragments, since we found above that there is about 80% methyl carbon retention by the C_4 ionic fragments. The observed intensity of $C_2H_5^+$-C^{13}, 0.73, in the methyl-C^{13}-cyclopentane mass spectrum is 40.5% that of $C_2H_5^+$ in the mass spectrum of the unlabeled methylcyclopentane. The absolute rate theory of Eyring and co-workers[2] would lead to the expectation that the two carbon ionic fragments should be formed as secondary dissociation products rather than as primary dissociation products. This is a consequence of the greater excitation energy required of a molecule ion, $C_6H_{12}^+$, for dissociation to $C_2H_5^+$ (or $C_2H_4^+$, etc.) plus C_4H_7 (or C_4K_8, etc.) than for the complementary dissociation to C_2H_5 (or C_2H_4) plus $C_4H_7^+$ (or $C_4H_8^+$). The higher required excitation energy results from the greater ionization potentials of the C_2 units than of the complementary C_4 units.

Similar evidence that the C_2 ionic fragments in the mass spectrum of neopentane arise through a two stage process, $C_5 \rightarrow C_4^+ + C \rightarrow C_2^+ + C_2 + C_1$, with essentially random selection of carbons in the second stage dissociation has been found by Langer and Johnson[7] in studies of the mass spectra of two C^{13}-labeled neopentanes.

It is well known[8] that methyl ions are formed in the mass spectra of the higher hydrocarbons by at least two different processes. One of these, the dissociation of a doubly charged molecule- (or fragment) ion, leads to a methyl ion with sufficient extra kinetic energy to cause the nominal m/q = 15 ($C^{12}H_3$) peak to have a "high mass" satellite. The manner in which the mass spectra obtained in this investigation were recorded, 1000 volt analyzing potential, did not permit sufficient resolution of the satellites of the $C^{12}H_3^+$ and $C^{13}H_3^+$ peaks for their separate measurement, and thus we cannot make any statements with respect to whether or not the life of the doubly charged ions is sufficiently great to permit "rearrangement" prior to dissociation. The intensities reported in Table I for ions of m/q = 15 and 16 are for the ions with relatively little excess kinetic energy, presumably those formed by secondary or tertiary dissociation of heavier fragment ions. The C^{13}-retention, *ca.* 33%, by the "normal" methyl ions is a factor of two greater than would be expected if the methyl ions were formed from an intermediate state of $C_6H_{12}^+$ in which there was randomization of the carbon atoms.

There are two conclusions with respect to the interpretation of the mass spectrum of a substance that are to be derived from the preceding discussion. These are: (1) it is generally not possible to assign a unique mechanism of formation nor a unique structure to a fragment ion in a mass spectrum of a formally unsaturated hydrocarbon, and (2) the process leading to a particular ion may not be the "obvious" one, and thus careful checks should be made with respect to the probable structure of an ion before energetic conclusions are based on an appearance potential of an ion in a mass spectrum.

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[7] A. Langer and C. Johnson, *J. Phys. Chem.*, **61**, 891, 1010 (1957).

[8] F. L. Mohler, V. H. Dibeler and R. M. Reese, *J. Chem. Phys.*, **22**, 394 (1954).