

[CONTRIBUTION, ISSUED AS NRC No. 6351, FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA]

Free Radicals by Mass Spectrometry. XXIII. Mass Spectra of Benzyl and α - d_2 -Benzyl Free Radicals

BY R. F. POTTIE¹ AND F. P. LOSSING

RECEIVED DECEMBER 15, 1960

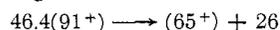
The mass spectra of benzyl and αd_2 -benzyl ($C_6H_5CD_2$) free radicals have been investigated using electron impact on free radicals formed by the thermal decomposition of bibenzyl and tetradeuterio-bibenzyl ($C_6H_5CD_2$)₂. The major peaks in the spectrum of benzyl radical, using 50 v. electrons, correspond to those found in the spectra of toluene and bibenzyl. Also present is a metastable ion at mass 46.4, corresponding to the process $C_7H_7^+ \rightarrow C_6H_5^+ + C_2H_2$. The distribution of H and D in the $C_6H_5^+$ ion present in the 50 v. mass spectrum of $C_6H_5CD_2$ radical shows that this fragment ion is derived from a $C_7H_7^+$ ion in which the H and D atoms on the original ring and side group positions have been completely randomized. The isotopic distribution in the $C_6H_5^+$ fragment ion is found to be essentially unchanged as the electron energy is lowered from 50 v. to a value just above the appearance potential for $C_6H_5^+$ ion formation.

Introduction

Experiments with C^{13} and D labelled derivatives of benzyl have shown that the formation of the ion of mass 91 by electron impact proceeds by way of a rearrangement in which the ring and side-group carbons and hydrogens become indistinguishable.²⁻⁴ From this evidence, which seems to be incontrovertible, it has been proposed that the ion of mass 91, which is a prominent one in the mass spectra of all benzyl derivatives, is the symmetrical cyclo- C_7H_7 (tropylium, tropenyl, cycloheptatrienyl) ion and not benzyl as had been assumed. This evidence is based mainly on the distribution of labelled atoms in the $C_6H_5^+$ fragment ion which is formed from $C_7H_7^+$ ion by loss of C_2H_2



The presence of a metastable peak at mass 46.4 confirms this origin of the $C_6H_5^+$ ion



These experiments necessarily deal with $C_7H_7^+$ ions which have carried over from the primary dissociation sufficient energy to bring about a further dissociation into $C_6H_5^+$ and C_2H_2 , and there is so far no experimental method for determining the structure of the undissociated $C_7H_7^+$ ions formed at or just above the appearance potential ($C_7H_7^+$). There are, moreover, some discrepancies among the appearance potential data, the ionization potential of benzyl radical and the bond dissociation energies of benzyl derivatives which have not been resolved.⁴⁻⁷ Recent measurements⁷ on cycloheptatrienyl radicals indicate that within the present experimental error ΔH_f (cycloheptatrienyl⁺) is the same as ΔH_f (benzyl⁺), that is, 217 ± 6 kcal./mole. Consequently it appears that the identity of $C_7H_7^+$ fragment ions formed at the appearance potential thresholds cannot at present be established from measurements of the energetics of their formation.

(1) National Research Council Postdoctorate Fellow 1958-1960.

(2) P. N. Rylander, S. Meyerson and H. M. Grubb, *J. Am. Chem. Soc.*, **79**, 842 (1957).

(3) S. Meyerson and P. N. Rylander, *J. Chem. Phys.*, **27**, 901 (1957).

(4) S. Meyerson, P. N. Rylander, E. Eliel and J. D. McCollum, *J. Am. Chem. Soc.*, **81**, 2606 (1959).

(5) D. O. Schissler and D. P. Stevenson, *J. Chem. Phys.*, **22**, 151 (1954).

(6) J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, *ibid.*, **22**, 1948 (1954).

(7) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *J. Am. Chem. Soc.*, **82**, 5593 (1960).

In view of the foregoing work on the formation of tropylium ions by rearrangement in dissociative ionization processes, it is of interest to see whether a direct ionization of a benzyl radical also leads to the same isomerization. The present work describes experiments in which the mass spectra of benzyl radicals and of αd_2 -benzyl radicals have been compared, with particular reference to the isotopic constitution of the $C_6H_5^+$ ions formed by subsequent dissociation of the ionized radicals.

Experimental

Materials.—The sample of tetradeuterio-bibenzyl ($C_6H_5CD_2$)₂ was prepared by Dr. L. C. Leitch and Mr. R. Renaud of these Laboratories. Mass spectrometric analyses at low electron energies showed that the only significant impurity was 9% of the trideuterio compound.

Production of Radicals.—The benzyl radicals were produced by thermal decomposition of bibenzyl in a capillary fused-silica furnace attached to a mass spectrometer. The apparatus and techniques used have been described in earlier papers of this series.^{8,9} At 1050° the bibenzyl was about 90% decomposed, as shown by the height of the mass 182 peak remaining at this temperature. The only products were benzyl radicals and a small amount of toluene, which presumably was formed by abstraction of H-atoms from substances adsorbed on the walls of the ionization chamber. There was no evidence for any species arising from H-atom abstraction from the bibenzyl. After subtraction of the spectra of toluene and of the undissociated bibenzyl, the spectrum remaining was attributable to the benzyl radical.

The spectrum of the αd_2 -benzyl radical was obtained in the same way from tetradeuterio-bibenzyl. In this case it was found that the toluene formed was almost entirely $C_6H_5CD_2H$, with only a trace of $C_6H_5CD_3$. This confirms the conclusion given above that the toluene was not formed by abstraction from bibenzyl. The spectrum of $C_6H_5CD_2H$ was calculated on statistical grounds from the spectrum of $C_6H_5CD_3$. After subtraction of the spectra of undissociated tetradeuterio-bibenzyl and the two isomeric toluenes, the remaining spectrum was attributed to the αd_2 -benzyl radical.

It is clear that no rearrangement of benzyl radical to cycloheptatrienyl radical occurred prior to ionization. As mentioned below, the vertical ionization potential of the $C_6H_5CD_2$ radical produced in these experiments was found to be in good agreement with that of undeuterated benzyl radical reported earlier. The ionization potential of the cycloheptatrienyl radical on the other hand, is over a volt lower than that of benzyl.⁷ The presence of a small amount of cycloheptatrienyl radical would therefore be easily detectable using low energy electrons.

Results and Discussion

The mass spectrum obtained for the benzyl radical, using 50 v. electrons, is given in Table I.

(8) J. B. Farmer and F. P. Lossing, *Can. J. Chem.*, **33**, 861 (1955).

(9) F. P. Lossing and J. B. de Sousa, *J. Am. Chem. Soc.*, **81**, 281 (1959).

Although peak ratios down to mass 26 were measured, those below mass 39 have not been listed because of the cumulative probability of error at the lower masses as a result of possible side reactions. The spectrum of the radical has a number of points of interest. It may be noted that the ratios of fragment ion intensities at masses 89, 65, 63 and 39 to that of the ion at mass 91 are much larger than in toluene and other benzyl derivatives. As shown in Table I these ions arise from loss of H_2 , C_2H_2 , C_2H_4 and C_4H_4 from the parent $C_7H_7^+$ ion. Presumably a $C_7H_7^+$ ion formed by ionizing the benzyl radical with 50 v. electrons has appreciably more excitation than a $C_7H_7^+$ ion formed by dissociation of a precursor which was itself produced by 50 v. electrons, and the fragmentation is correspondingly enhanced. The spectrum also shows a metastable ion of 46.4 corresponding to a dissociation of $C_7H_7^+$ into $C_5H_5^+$ and C_2H_2 , similar to that found in the spectra of benzyl derivatives. A peak of relatively large intensity at mass 45.5 evidently arises from formation of the doubly charged radical ion $C_7H_7^{++}$. This ion also appears in the mass spectrum of toluene.

TABLE I
SPECTRUM OF BENZYL RADICAL ($C_6H_5CH_2$) WITH 50 V. ELECTRONS (C^{13} CORRECTED)

m/e	Observed spectrum of $C_6H_5CH_2$	Process $C_6H_5CH_2 + e \rightarrow$
91	100	$C_7H_7^+$
90	10.7	$C_7H_6^+ + H$
89	20.4	$C_7H_5^+ + 2H$
88	2.0
66	0.4	$C_5H_6^+ + C_2H$
65	70.9	$C_5H_5^+ + C_2H_2$
64	5.1	$C_5H_4^+ + C_2H_3$
63	21.2	$C_5H_3^+ + C_2H_4$
62	8.1	$C_5H_2^+ + C_2H_5$
61	2.1
52	4.5
51	9.7
50	7.8
46.4	0.4	Metastable $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$
45.5	2.9	$C_7H_7^{++}$
39	20.2	$C_3H_3^+ + C_4H_4$

A portion of the mass spectrum found for the $C_6H_5CD_2$ radical is given in Table II, after correction for C^{13} contributions and for toluene formation as described above. For comparison are given the intensities for isotopic ions calculated, following Meyerson, et al.,² on the basis of three different models for the $C_7H_7^+$ ion. The calculated intensities in Table II are based on the intensities of the corresponding mono-isotopic ions in the spectrum of the undeuteriated benzyl radical, neglecting possible kinetic isotope effects. The distribution of D atoms in the $C_5H_5^+$ ions is decisive in choosing among the three possible structures for the $C_7H_7^+$ precursor ion. If this precursor had the benzyl structure and if no interchange of D and H occurred, then the expected peak ratios would be those in column (a) in Table II. For this calculation it has been assumed that there are five ways in which a neutral acetylene molecule can be

TABLE II
SPECTRUM OF DIDEUTERIO-BENZYL RADICAL ($C_6H_5CD_2$) WITH 50 V. ELECTRONS (C^{13} CORRECTED)

m/e	Observed spectrum (mean)	Calculated on basis of obsd. $C_6H_5CH_2$ spectrum		
		(a) Benzyl structure	(b) Cyclic C_7H_7 with D-atom neighbors	(c) Cyclic C_7H_7 with D-atoms randomized
93	100	100	100	100
92	7.7		7.7	7.7
91	14.6		14.5	15.8
90	8.7		6.6	7.6
89	2.0		3.5	2.1
67	33.2(loss of C_2H_2)	>56.7	40.5	33.8
66	36.5(loss of C_2HD)	<5.1	22.4	35.2
65	14.2(loss of C_2D_2)	<14.2	17.8	9.3
64	13.9		8.8	13.5
63	12.8		13.0	10.2
62	5.7		3.1	3.3

lost from the parent ion, four of which lead to loss of C_2H_2 and one leading to loss of C_2D_2 . The intensity of the $C_5H_5D_2^+$ ion (loss of C_2H_2) should therefore be $4/5$ times the ratio of mass 65/mass 91 in the spectrum of the undeuteriated benzyl radical. This intensity, 56.7 for $m/e = 67$, is a minimum figure since there may be only four ways to lose acetylene rather than five.² The loss of C_2HD , giving rise to $m/e = 66$, should in any case be zero on the basis of this model. A mass 66 peak can, however, arise from the loss of C_2H_3 . By comparison with the spectrum in Table I it can be seen that the intensity at mass 66 arising in this way cannot be greater than 5.1% of the mass 93 peak. It is evident that the observed intensities for masses 67 and 66 cannot be reconciled with the formation of C_5 ions from a precursor having the benzyl structure.

Column (b) in Table II gives intensities calculated on the assumption of a symmetrical seven-membered ring structure in which the two D-atoms of the side-group are attached to neighboring carbon atoms. It is evident that this conformation, although involving the least rearrangement, does not yield the correct intensities for masses 66 and 67. The third model (c), a symmetrical seven-membered ring structure with the two D-atoms randomized, gives the best fit to the observed intensities at masses 66 and 67.

Some experiments on the effect of electron energy on the relative frequency of loss of C_2H_2 , C_2HD and C_2D_2 from the parent ion were also carried out. These measurements had the advantage of being free from interference from the loss of C_2H_3 fragments, since the appearance potential for this process is considerably higher than for C_2H_2 loss. The relative intensities (normalized to 100 for the total intensity for loss of acetylene) of masses 67, 66 and 65 at electron energies a few volts above the threshold for $C_5H_5^+$ ion formation are given in Table III. The agreement with the intensity distribution based on model c, the symmetrical seven-membered ring with the two D atoms randomized, is quite good. A small bias in favor of loss of C_2HD and C_2D_2 is apparent. This may arise from a small isotope effect on the frequency of

rupture of C-C bonds in the vicinity of D-atoms. It is interesting to note that there is no sign of a systematic change in the isotopic distribution with electron energy.

TABLE III
RELATIVE INTENSITIES FOR LOSS OF C₂H₂, C₂HD AND C₂D₂
FROM IONIZED BENZYL RADICAL AT LOW ELECTRON
ENERGIES

Electron energy (volts, uncorrected)	Intensity (normalized to sum 100)		
	65	66	67
14.87	7.8	47.0	45.2
13.95	7.4	47.2	45.4
13.39	7.5	47.2	45.3
13.00	7.5	47.0	45.5
Calcd.			
(a)	20.0	0.0	80.0
(b)	14.3	28.6	57.1
(c)	4.8	47.6	47.6

The vertical ionization potential of the C₆H₅CD₂ radical was found to be 7.71 v., in satisfactory agreement with 7.76 v. found previously for the undeuteriated benzyl radical.⁶ Although the ionization of benzyl radicals at and just above the threshold must, according to the Franck-Condon principle, lead to formation of benzyl ion and not cycloheptatrienyl ion,⁷ nevertheless, the present

results indicate that a benzyl ion so formed can rearrange when the energy of the impacting electron is only a few volts above the ionization threshold. Whether all benzyl ions undergo such rearrangement at higher electron energies is not clear. The present results show only that those C₇H₇⁺ ions which dissociate to form C₅H₅⁺ + C₂H₂ have all undergone a prior rearrangement. Since the C₅H₅⁺ ion is, however, the most abundant fragment in the 50 v. spectrum of ionized benzyl radical, it would appear that with 50 v. electrons a large fraction, at least 50%, of the benzyl ions must have rearranged.

There are two main difficulties in understanding the rapid isomerization of benzyl ion to tropylium ion. The first is that according to a recent estimate⁷ the isomerization is not particularly exothermic and indeed may be nearly thermoneutral. The second is that the model which gives the closest approximation to the isotopic distribution observed earlier⁴ and in the present work requires that the two D-atoms on the original side group do not end up on adjacent carbons of the seven-membered ring but are randomly distributed. It is not easy to see how this can occur without rather large configurational distortions and consequently relatively large activation energy barriers.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE LABORATORY OF NUCLEAR SCIENCE, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Osmotic Coefficients and Activity Coefficients in Mixed Electrolyte Solutions

BY GEORGE SCATCHARD

RECEIVED DECEMBER 8, 1960

The excess free energy per mole of ionic strength in mixed electrolyte solutions is expressed as a linear function of this property of the solutions of single electrolytes at the same ionic strength, plus a quadratic term in the ionic strength fractions and plus higher deviation terms of the expansion around the midpoint, of which the cubic term is usually sufficient. Other properties are obtained by appropriate differentiations, the osmotic coefficients and activity coefficients by differentiation with respect to the logarithm of the ionic strength. The method is applied to freezing points, "isopiestic," and solute activity measurements. The deviations from linearity in ionic strength fraction are relatively smooth functions of the ionic strength which may be expressed approximately as integral power series. The relatively complicated linear terms may usually be expressed approximately by the Debye-Hückel functions with a different size parameter for each electrolyte plus integral power series in the ionic strength. The relations of this method to Brønsted's principle of specific ion interaction, to Harned's rule and to Friedman's application of the Mayer theory are discussed.

Several years ago Scatchard and Prentiss¹ gave analytical expressions for the free energies of solutions of non-electrolytes, electrolytes or both in terms of the concentrations of each species and calculated from these expressions the osmotic coefficients and the activity coefficients of the solutes. Introducing the excess free energy directly and changing from F to G , we rewrite equation 3 of the second paper as

$$G^{\circ}/RT = (G - G^*)/RT + \sum_i n_i (1 - \ln n_i/n_0 w_0) + \sum_{ij} n_i A_{ij} \sqrt{I} + \sum_{ij} n_i n_j (B_{ij} + C_{ij} \sqrt{I})/n_0 w_0 + \sum_{ijk} n_i n_j n_k (D_{ijk} + E_{ijk} \sqrt{I})/(n_0 w_0)^2 + \dots \quad (1)$$

in which G is the free energy of the system, $G^* = n_0 G_0^{\circ} + \sum_i n_i G_i^{\circ}$, the free energy in the standard state of zero concentration of all solutes; w_0 is one thousandth of the molecular weight of the solvent, n_0 is the number of moles of solvent and

n_i the number of moles of the i 'th solute species. We may define I as the ionic strength,² and the A , B , C , D , E 's are parameters characteristic of the species designated in the subscripts, of the solvent, and of the temperature and pressure. They also noted that the higher terms of the Debye theory require a term proportional to $I \log I$. Current theory^{3,4} gives the higher terms in this series as $\sum_{\sigma \geq 0} S_{\sigma} \kappa^{\sigma} (\kappa^2 \ln \kappa)$ instead of $\sum_{\sigma \geq 1} S_{\sigma} \kappa (\ln \kappa)^{\sigma}$ as given by Scatchard and Prentiss. In practice the higher terms merge with those in equation 1.

The mixed concentration scale is necessary if

(2) Scatchard and Prentiss defined I as $\sum_i m_i z_i^2$, or twice the ionic strength, to be consistent with their definition of $M = \sum_i m_i$, and we have used it in this sense ever since. Although many people have liked our symbol I , they have usually used it as $\sum_i m_i z_i^2/2$. It therefore seems advisable to change to this later definition. If the parameters of our papers are used, the A 's, C 's and E 's must be multiplied by $\sqrt{2}$.

(3) J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950).

(4) J. C. Poirier, *ibid.*, **21**, 965, 972 (1953).

(1) G. Scatchard and S. S. Prentiss, *J. Am. Chem. Soc.*, **56**, 1486, 2314, 2320 (1934).