not necessarily be the one formed in (1). No doubt some of the radicals disproportionate to give oxidation products, as indicated by the formation of small amounts of acetaldehyde during photolysis in ethanol solution. The change in Φ_A/Φ_B with the nature of the solvent would be due to the ease with which the solvent molecules participate in (1) and (3).

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Rochester, New York

[Contribution from the Research Department, Standard Oil Company (Indiana)]

Organic Ions in the Gas Phase. VII. Tropylium Ion from Benzyl Chloride and Benzyl Alcohol

By Seymour Meyerson, Paul N. Rylander, Ernest L. Eliel[1] and John D. McCollum

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The $C_7H_7^+$ ion present in the mass spectra of benzyl chloride and benzyl alcohol appears not to be the benzyl ion. The spectra of variously deuterated species show that the seven hydrogens have completely lost identity. The structure of the $C_7H_7^+$ ion is better represented as tropylium, just as in toluene and ethylbenzene, although its formation and further decomposition are not entirely clear. The appearance potentials of this ion from benzyl chloride, benzyl bromide and benzyl iodide are somewhat lower than the values expected for benzyl ion and suggest that rearrangement occurred before or during dissociation. These appearance potentials lead to an upper limit of 207 to 210 kcal./mole for the heat of formation of the tropylium ion.

Evidence has been presented that the $C_7H_7^+$ ion found in great abundance in the mass spectrum of toluene, as well as in the spectra of higher alkylbenzenes and cycloheptatriene, is the symmetrical tropylium (cycloheptatrienylium) ion rather than the benzyl ion.[2,3] This finding was surprising, and implicit in it was the question of how general such behavior might be. In particular, do non-hydrocarbon benzyl compounds give rise to benzyl ions, or do they likewise rearrange to give tropylium?

The appearance potentials of the $C_7H_7^+$ ion from benzyl halides[4] show clearly that the energetics of $C_7H_7^+$ formation from these compounds are different than those from toluene, ethylbenzene, propylbenzene, dibenzyl and cycloheptatriene.[2,3] Whereas the values for the hydrocarbons all exceed those expected for a benzyl ion by about 16 kcal./mole, those from the benzyl halides were found to be 3 to 5 kcal./mole lower than the expected values.[4] Recent estimates of the bond-dissociation energies $D(C_6H_5CH_2{-}Cl)$[5] and $D(C_6H_5CH_2{-}I)$[6] increase the apparent discrepancy in the halide measurements to 6 to 10 kcal./mole. The pertinent data for the halides are summarized in Table I.

Table I

Energetics of $C_7H_7^+$ Formation from Benzyl Halides

X in $C_6H_5CH_2X$	$D\cdot$ $(C_6H_5CH_2{-}X)$, kcal./mole	Ref.	Calcd. $A\cdot$ $(C_6H_5CH_2^+)$.[a] kcal./mole	Obsd. $A(C_7H_7^+)$,[b] kcal./mole
Cl	68	5	247	239
Br	50.5	7	229	223
	48.5	8	227	
I	43.2	6	222	213
	36.5	8	215	
	39	9	218	

[a] The sum of $D(C_6H_5CH_2{-}X)$ and $I(C_6H_5CH_2)$, the ionization potential of the benzyl radical, 179 kcal./mole, ref. 10. [b] See ref. 4.

To obtain more evidence on the nature of the $C_7H_7^+$ ion formed by electron impact from non-hydrocarbon benzyl compounds, we studied the mass spectra of deuterated benzyl chlorides and benzyl alcohols. We prepared both compounds labeled with a single deuterium atom in the *ortho*, *meta* and *alpha* positions, and with two alpha deuteriums. The *para*-deuterated species were omitted because the three ring-deuterated isomers of every benzene derivative studied previously[2,3,11,12] have given indistinguishable spectra; even if the $C_7H_7^+$ ion proved to be a benzyl ion, one would expect to find spectral differences between the *ortho* and other ring deuterated species, but not between the *meta* and *para*.[2] Benzyl alcohol deuterated in the hydroxyl group was omitted because hydrogen exchange with water on the walls of the spectrometer inlet system would greatly reduce the isotopic purity of such a sample and, consequently, the likelihood of obtaining a useful spectrum.

To establish the decomposition processes at work, the spectra of these compounds were examined for both metastable peaks[13] and distri-

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[1] 1956 summer research participant from Department of Chemistry, University of Notre Dame.

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

[4] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *ibid.*, **22**, 1489 (1954).

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[7] M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950).

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[9] M. Szwarc, *Chem. Revs.*, **47**, 75 (1950).

[10] J. B. Farmer, I. H. S. Henderson, C. A. McDowell and F. P. Lossing, *J. Chem. Phys.*, **22**, 1948 (1954).

[11] S. Meyerson and P. N. Rylander, This Journal, **79**, 1058 (1957).

[12] F. L. Mohler, V. H. Dibeler, L. Williamson and H. Dean, *J. Research Natl. Bur. Standards*, **48**, 188 (1952).

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bution of the label in fragment ions.[14] Also, we measured one appearance potential that seems not to have been reported previously, $A(C_7H_7^+)$ from benzyl alcohol.

Experimental

Materials.—Benzyl chloride and benzyl alcohol were Eastman White Label grade, redistilled. Cryoscopic measurements on the chloride indicated better than 99% purity. The infrared spectrum of the alcohol showed no benzaldehyde or other carbonyl compounds, but the mass spectrum showed 0.5% benzyl chloride and was corrected for this impurity.

Toluene-*o-d* was prepared by converting 0.5 mole of *o*-bromotoluene to the Grignard reagent and treating it with 1.0 mole of deuterium oxide. Most of the ether was distilled off, the complex was decomposed with saturated ammonium chloride, and the product was worked up and distilled. The boiling point was 109–111°, and $n^{20}\text{D}$ was 1.4953–1.4961; corresponding literature values[15] for unlabeled toluene are 110.6° and 1.49693. The yield was 69%, and isotopic purity was 88.2%.

Toluene-*m-d* had been prepared in the course of another investigation.[16] The isotopic purity of the sample used was 80.1%.

Benzyl chloride-*o-d* and -*m-d* were prepared from the corresponding toluenes by treatment with redistilled sulfuryl chloride and benzoyl peroxide.[17] Equimolar amounts of the toluene and sulfuryl chloride with a small amount of benzoyl peroxide—1% by weight of the chloride—were heated at about 100° mantle temperature for 1 hr., cooled, poured on ice and extracted with isopentane. The solution was washed with water, aqueous sodium bicarbonate and again water; it was dried over calcium chloride, concentrated and distilled. The infrared spectrum of an undeuterated sample prepared similarly indicated absence of ring-chlorinated toluenes. Because both unchanged toluene and benzal chloride are obtained as by-products in this reaction, center fractions were collected for infrared and mass spectrometry. Despite this precaution, 2 to 3% benzal chloride-*d* was found in each sample. The mass spectra were not corrected for this material.

Benzyl alcohol-*o-d* and -*m-d* were prepared by hydrolysis of the corresponding deuterated chlorides with boiling 10% aqueous sodium carbonate[18]; the weight of anhydrous sodium carbonate was 80% that of the chloride. Reflux time was 4 to 8 hr. at an oil-bath temperature of 150°; the reaction was terminated when the odor of benzyl chloride disappeared. A small amount of added detergent promoted phase contact. The product was extracted with ether, and the extract was washed with saturated sodium bisulfite solution to remove traces of benzaldehyde. Center distillation fractions were collected for infrared and mass spectrometry.

Benzyl alcohol-*α-d* was prepared by reducing 0.094 mole of freshly purified benzaldehyde with 0.033 mole of lithium aluminum deuteride in ether. Benzyl alcohol-*α-d*$_2$ was prepared similarly from 0.18 mole of methyl benzoate and 0.12 mole of lithium aluminum deuteride. The isotopic purities of the two deuteride samples used, determined by decomposing with water and analyzing the resultant deuterium by mass spectrometer, were 96.6 and 97.2%.

Benzyl chloride-*α-d* and -*α-d*$_2$ were prepared from the corresponding deuterated alcohols. Typically, 0.1 mole of zinc chloride was dissolved in 0.1 mole of hydrochloric acid, and the mixture was cooled to room temperature and added to 0.05 mole of benzyl alcohol.[19] A homogeneous solution resulted, but an oily layer separated after a few seconds. After standing five minutes, the oil was extracted with two portions of isopentane; the organic layer was washed with concentrated hydrochloric acid and ice-water, dried over calcium chloride, concentrated and distilled.

The physical properties, isotopic composition and yields of the benzyl chlorides and alcohols are listed in Table II. Isotopic composition was determined from mass spectra obtained at reduced ionizing voltage.[20]

TABLE II

PROPERTIES AND YIELDS OF BENZYL COMPOUNDS

Species	B.p., °C. (mm.)	$n^{20}\text{D}$ [a]	Isotopic composition % d_0	% d_1	% d_2	Yield, %
			Chlorides			
d_0[b]	71–71.5 (27–28)	1.5389	100.0	0.0	0.0	..
o-d	76–79 (20)	1.5391	11.8	88.2	0.0	52
m-d	71–76 (18)	1.5382	19.5	80.5	0.0	53
α-d	68–70 (16)	1.5385	3.7	94.3	2.0	70
α-d$_2$	75–77 (22)	1.5377	0.0	3.5	96.5	80
Lit.,[c] d_0	73.9 (17)	1.5391	...	..	..	..
			Alcohols			
d_0[b]	98–100 (17)	1.5402	100.0	0.0	0.0	..
o-d	102–108 (25)	1.5399	12.2	87.8	.0	63
m-d	104–105 (23)	1.5392	19.4	80.6	.0	38
α-d	97–99 (16)	1.5392	3.8	93.9	2.3	80
α-d$_2$	106–110 (25)	1.5389	0.0	5.3	94.7	91
Lit.,[d] d_0	93 (10)	1.5396	...	..	..	..

[a] Some of the indices reported actually were measured at temperatures slightly different from 20° and have been corrected by assuming a decrease in $n\text{D}$ of 0.0005 per degree. [b] Unlabeled. [c] From M. S. Kharasch and H. C. Brown, THIS JOURNAL, 61, 2146 (1939). [d] From I. Heilbron and H. M. Bunbury, "Dictionary of Organic Compounds," Vol. I, Eyre and Spottiswoode, London, 1953, p. 270.

Mass Spectra.—Mass spectra were recorded on a Consolidated Model 21-102/21-103c analytical mass spectrometer. They were corrected for isotopic impurities, for naturally occurring C^{13} and Cl^{37}, and, in the parent-mass region of the alcohol spectra, for O^{18}. The relative intensities at mass 126 in the spectra of the ring-deuterated benzyl chlorides are unduly large, exceeding that of the unlabeled chloride at 125. The benzal chloride-*d* impurities are undoubtedly responsible; they would be expected to produce their most abundant ions at mass 126 by loss of a Cl atom. Benzal chloride contributions to other peaks of interest are believed negligible.

The $C_7H_7^+$ ion is the most abundant ion in the mass spectra of the chlorides, shown in Table III. The process by which it is formed is not affected by the presence of deuterium, as evidenced by identical relative intensities of the unlabeled species at 91, singly labeled at 92 and doubly labeled at 93.

TABLE III

PARTIAL SPECTRA OF BENZYL CHLORIDES

Mass, m/e	d_0	*o-d*[a]	*m-d*[a]	*α-d*	*α-d*$_2$
65	57.9	20.6	22.8	23.3	22.1
66	...	43.3	42.6	39.4	29.5
67	...	...	...	...	27.0
90	11.2	25.8	27.0	21.0	11.2
91	516	7.6	8.7	9.4	15.6
92	...	516	516	516	8.5
93	...	...	...	...	516
125	13.2	3.1	4.2	1.8	0.1
126	100.0	20.4	26.4	9.6	3.6
127	...	100.0	100.0	100.0	5.7
128	...	...	...	...	100.0

[a] Uncorrected for benzal chloride-*d*, estimated at 2–3%.

In the spectra of the alcohols, shown in Table IV, the $C_7H_7^+$ ion is a minor dissociation product. The most abundant ion, not shown, is $C_6H_7^+$ of mass 79. The fact that the intensities due to $C_7H_6D^+$ and $C_7H_5D_2^+$ from the labeled species are larger than the intensity due to $C_7H_7^+$ from the unlabeled species differentiates benzyl alcohol from benzyl chloride. This difference implies an isotope effect, either in the rupture of the C–OH bond or, more

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[14] S. Meyerson and P. N. Rylander, *J. Phys. Chem.*, **62**, 2 (1958).

[15] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Inst. of Technology, Pittsburgh, 1953, p. 71.

[16] T. J. Prosser and E. L. Eliel, THIS JOURNAL, **79**, 2544 (1957).

[17] R. H. Clark and H. R. L. Sheight, *Trans. Roy. Soc. Can.*, [3] **23**, 77 (1929).

[18] M. Gomberg and C. C. Buehler, THIS JOURNAL, **42**, 2059 (1920).

[19] J. P. Norris and H. B. Taylor, *ibid.*, **46**, 753 (1924).

[20] D. P. Stevenson and C. D. Wagner, *ibid.*, **72**, 5612 (1950); R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

TABLE IV

PARTIAL SPECTRA OF BENZYL ALCOHOLS

Mass, m/e	d_0	o-d	m-d	α-d	α-d_2
65	9.5	4.0	4.1	4.5	4.3
66	0.6	7.4	7.4	7.2	5.6
67	0.2	0.5	0.4	0.4	5.1
68	0.3	0.2	0.2	0.2	0.3
90	10.1	6.7	7.0	7.0	2.9
91	20.8	9.1	9.6	9.3	6.4
92	0.5	22.5	23.4	23.3	8.1
93	...	0.6	1.1	0.3	24.6
94	...	...	...	0.1	0.2
107	80.7	7.5	7.3	9.1	0.7
108	100.0	73.0	71.5	70.3	18.2
109	...	100.0	100.0	100.0	59.3
110	...	...	...	...	100.0

likely, in competing processes by which molecule-ions are removed. Such competing processes are important in the dissociation of the alcohol but play a lesser part in the dissociation of the chloride.[21]

The appearance potential of the $C_7H_7^+$ ion from benzyl alcohol was estimated by the vanishing-current method,[22] with furan (ionization potential, 9.05 e.v.) as the reference gas. A value of 11.7 e.v. or 270 kcal./mole was obtained, but this must be considered as no more than a rough estimate, because the initial slope of the ionization-efficiency curve was too small to permit confident evaluation of the vanishing point.

Infrared Spectra.—Infrared spectra were recorded on a Perkin–Elmer Model 21 double-beam instrument.

The spectra of the labeled compounds deserve comment.[23] The C–D stretching frequency occurred at 4.38 to 4.45 μ for the ring-deuterated species and at 4.5 to 4.7 μ for the α-monodeuterated species; the dideuterated species showed multiplets in the region of 4.45 to 4.80 μ. All compounds, including the unlabeled species, had a strong band at 6.86 to 6.94 μ. This band evidently is not due to CH_2-bending[24] inasmuch as the $-CH_2$ grouping is absent in the α-deuterated species. A likely source of this band is splitting of the aromatic ring in-plane vibration at about 6.7 μ.[25] (A band at 6.65–6.67 μ is also found in all of our benzyl alcohols and benzyl chlorides.) Similar splitting is found in the spectra of the four halobenzenes (serial no. 1012, 1284, 1289 and 1291),[26] phenol (no. 1213 and 1612),[26] thiophenol (no. 1438 and 1680)[26] and benzonitrile (no. 541).[26] The *ortho*-deuterated compounds showed a strong band at 12.89 to 12.96 μ; the *meta*-deuterated compounds, at 12.37 to 12.55 μ. Corresponding bands, attributed to out-of-plane vibration, have been reported in the spectra of the ring-deuterated toluenes.[27] The *ortho*-deuterated isomers showed the typical[28] pattern of an ortho-di-substituted benzene in the region of 5 to 6 μ.

Labeling Evidence.—The $C_7H_7^+$ ion from the benzyl chlorides must, of course, consist of the atoms comprising the original benzyl group. In the case of the benzyl alcohols, the intensities of the singly labeled species at mass 92 and of the doubly labeled species at 93 are slightly larger than that of the unlabeled species at 91. Evidently no deuterium is lost from ring or α-positions in the formation of $C_7H_7^+$. Thus, this ion is formed by loss of the original hydroxyl group and, as with the chlorides, consists of the atoms of the original benzyl group.

The metastable peaks in the spectra of the unlabeled, singly labeled and doubly labeled species of both the chloride and the alcohol

$$46.6 \quad (91^+) \longrightarrow (65^+) + 26$$
$$47.7 \quad (92^+) \longrightarrow (66^+) + 26$$
$$48.3 \quad (93^+) \longrightarrow (67^+) + 26$$

establish the decomposition

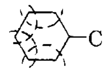
$$C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2$$

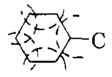
as a source of the $C_5H_5^+$ ion. This process has also been reported in the dissociation of toluene, ethylbenzene and *p*-xylene under electron impact.[2,14] It seems to be characteristic of $C_7H_7^+$ ions regardless of the parent molecule.

Relative intensity of the unlabeled compounds at mass 65 measures total $C_5H_5^+$ yield; mass-66 intensity measures $C_5H_4D^+$ yield from the singly labeled compounds; and mass-67 intensity measures $C_5H_3D_2^+$ yield from the doubly labeled compounds. The observed intensities of the chlorides agree well with those calculated on the assumption that the seven hydrogens in the $C_7H_7^+$ precursor were completely equivalent[2,14] and are clearly inconsistent with the benzyl configuration

	o-d, mass 66	m-d, mass 66	α-d, mass 66	α-d_2, mass 67
Obsd.	43.3	42.6	39.4	27.0
Calcd. for symmetrical $C_7H_7^+$	41.4	41.4	41.4	27.6
Calcd. for benzyl ion	43.4 or 46.3	29.0 or 34.7	57.9 or 46.3	57.9 or 46.3

The two values calculated for each benzyl ion are based on alternative assumptions that this ion can split out acetylene in four or five ways[2]





Because the relative intensity of unlabeled benzyl alcohol at mass 91 and of the singly and doubly labeled species at 92 and 93 are not equal, the intensities at masses 65, 66 and 67 were recalculated relative to the corresponding $C_7H_7^+$ intensities taken as 100. Thus normalized, the observed intensities can be compared with the values calculated for the breakdown of a symmetrical $C_7H_7^+$ ion and of a benzyl ion

	o-d, mass 66	m-d, mass 66	α-d, mass 66	α-d_2, mass 67
Obsd.	32.9	31.6	30.9	20.7
Calcd. for symmetrical $C_7H_7^+$	32.6	32.6	32.6	21.8
Calcd. for benzyl ion	34.3 or 36.5	22.8 or 27.4	45.7 or 36.5	45.7 or 36.5

Again, the observed intensities agree well with the values calculated for complete equivalence of the seven hydrogens in the $C_7H_7^+$ precursor and are thus inconsistent with the benzyl structure.

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[21] The relative importance of processes leading to the $C_7H_7^+$ ion is indicated by the fraction this ion constitutes of total fragment-ion yield: 0.037 for benzyl alcohol; 0.48 for benzyl chloride.

[22] L. G. Smith, *Phys. Rev.*, **51**, 263 (1937).

[23] We are indebted to G. M. Barrow, R. R. Hopkins and E. W. Clower for help in interpreting the infrared spectra.

[24] N. Sheppard and D. M. Simpson, *Quart. Revs.*, **7**, 19 (1953), state that the CH_2-bending wave length range is 6.80–6.94 μ.

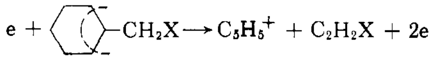
[25] We are indebted to Professor William A. Klemperer of Harvard University for suggesting this explanation.

[26] Infrared Spectral Data, American Petroleum Institute Research Project 44.

[27] J. Turkevich, H. A. McKenzie, L. Friedman and R. Spurr, THIS JOURNAL, **71**, 4045 (1949); G. Van Dyke Tiers, *J. Chem. Phys.*, **19**, 1072 (1951); G. Van Dyke Tiers and J. H. Tiers, *ibid.*, **20**, 761 (1952).

[28] C. W. Young, R. B. DuVall and N. Wright, *Anal. Chem.*, **23**, 709 (1951).

The differences between observed and calculated values for both the chlorides and the alcohols may well be real. They may result from an isotope effect, or they may reflect a small contribution to $C_5H_5^+$ production by another process



Supporting evidence was found for the analogous process as a minor contributor of $C_5H_5^+$ production in the dissociation of toluene.[3]

The spectra of the labeled benzyl chlorides and benzyl alcohols lead to the same finding as did those of labeled toluenes and ethylbenzenes.[2,3] The $C_5H_5^+$ ion is derived from a $C_7H_7^+$ ion in which the atoms originally in the α-position and various ring positions had become indistinguishable. Again, the simplest explanation would seem to be that the $C_7H_7^+$ ion has a completely symmetrical structure—that of tropylium.

However, something further is required to account for the spectra of the doubly labeled species. Complete equivalence of the two deuterium and five protium atoms in $C_7H_5D_2^+$ from benzyl chloride-α-d_2 and benzyl alcohol-α-d_2—as also observed[2] in this ion from ethylbenzene-α-d_2 and -α,β-d_5—indicates that the two atoms originally on the α-carbon are no longer associated in any non-random fashion in the $C_7H_7^+$ ion. The contrary assumption that these atoms are located on adjacent carbons in the tropylium ion leads to expected intensities at mass 67 of 33.1 for benzyl chloride-α-d_2 and 26.1 for benzyl alcohol-α-d_2, in poor agreement with the observed 27.0 and 20.7.

Three possible interpretations can be offered to account for the observed randomization: (a) ring expansion is more involved than simply inserting the α-carbon between the already attached ring carbon and an *ortho* carbon and moving an α-hydrogen to the attached carbon; (b) the hydrogen atoms are highly mobile in the $C_7H_7^+$ ion or within the benzyl group of the molecule-ion; (c) further rearrangement occurs before or during the dissociation

$$C_7H_7^+ \longrightarrow C_5H_5^+ + C_2H_2$$

Support for (a) can be derived by analogy from two competing reactions of the toluene ion

$$C_6H_5CH_3^+ \longrightarrow C_6H_5^+ + CH_3$$

and

$$C_6H_5CH_3^+ \longrightarrow CH_3^+ + ?$$

These reactions appear to involve a rearranged molecule-ion in which complete equilibration does *not* take place, but in which the five ring hydrogens have become equivalent in relation to the methyl group.[29]

If true, (b) makes a symmetrical intermediate unnecessary. High mobility of the hydrogen atoms in a benzyl ion would appear to be a sufficient condition. However, the proposal that $C_7H_7^+$ from toluene is tropylium rather than benzyl is supported also by C^{13} labeling and by the pronounced similarity of the toluene spectrum to that of cycloheptatriene.[3]

As for (c), nothing is known about the mechanism of the dissociation or about the nature of the $C_5H_5^+$ ion. Further decomposition steps following one in which the atoms have completely lost identity are not amenable to study by the labeling technique. However, some loss of symmetry must precede dissociation, and the ease with which cycloheptatriene forms transannular bonds[30] suggests that the tropylium ion might similarly rearrange under the proper conditions.

Energetics.—Insofar as one can judge from the labeling evidence, the $C_7H_7^+$ ions from toluene and related hydrocarbons and from benzyl chloride and benzyl alcohol are identical. However, this evidence is based on the products of further decomposition and so reflects the behavior of those $C_7H_7^+$ ions having enough energy to decompose further. An appearance potential, on the other hand, refers to the particular process by which an ion is formed in the lowest electronic state of sufficient transition probability to give detectable quantities of the ion. Thus, information obtainable from labeling evidence and from appearance potentials refers to groups of $C_7H_7^+$ ions of different energy content and not necessarily of the same structure. The labeling evidence therefore cannot establish the cause of the difference in energy requirements for the formation of $C_7H_7^+$ from the hydrocarbons and from the benzyl halides.

The value found for $A(C_7H_7^+)$ from benzyl alcohol leads, surprisingly, to the conclusion that this compound behaves like toluene, etc., rather than like the benzyl halides. This value, 270 kcal./mole, exceeds by 18 kcal./mole the value expected for a benzyl ion: the sum of the bond-dissociation energy $D(C_6H_5CH_2\text{–}OH)$, 73.4 kcal./mole[31] and the ionization potential of the benzyl radical, 179 kcal./mole.[10] The difference is close to the excess energy of 16 kcal./mole in the values of $A(C_7H_7^+)$ from the hydrocarbons.[2,3,10] However, the value from benzyl alcohol must be considered provisional; the numerical agreement could be fortuitous.

On the other hand, as shown in Table I, the observed values of $A(C_7H_7^+)$ from the benzyl halides are lower than the values calculated for a benzyl ion. If the differences are attributed to uncertainties in the appearance-potential and dissociation-energy measurements, the $C_7H_7^+$ ion may be first formed as a benzyl ion. However, if the difference is real, the $C_7H_7^+$ ion from benzyl halides *even as first formed* is not benzyl. The tropylium structure for this ion is a reasonable alternative and is compatible with the appearance-potential data if the tropylium ion is assumed to be somewhat more stable than benzyl ion.

The values obtained for $A(C_7H_7^+)$ from benzyl chloride, bromide and iodide, when combined with appropriate thermochemical data, lead to maximum values of 209, 210 and 207 kcal./mole for $\Delta H_f(C_7$-

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[29] P. N. Rylander and S. Meyerson, *J. Chem. Phys.*, **27**, 1116 (1957).

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H_7^+).[32] $\Delta H_f(C_6H_5CH_2^+)$ is calculated to be 216.5 kcal./mole from $\Delta H_f(C_6H_5CH_2)$ = 3.57 kcal./mole[9,33] and $I(C_6H_5CH_2)$ = 179 kcal./mole.[10] On the basis of various estimates of resonance energy,[2] the tropylium ion should be more stable than the benzyl ion by −5 to 19 kcal./mole. Thus the value of 207 to 210 kcal./mole for $\Delta H_f(C_7H_7^+)$ is entirely compatible with the assumption that the $C_7H_7^+$ ion is tropylium.

A similar calculation for the benzyl-containing hydrocarbons leads to maximum values of 231 to 236 kcal./mole for $\Delta H_f(C_7H_7^+)$.[3] The differing energy requirements of the hydrocarbons and halides to form apparently the same product would seem to be a matter of the ionized states that are accessible by electron impact. Little is known of the potential-energy hypersurfaces involved or of the selection rules for excitation-ionization by electron impact other than that Franck–Condon restrictions apply[34] and that subsequent dissociation may take enough time to allow rearrangements.[13,35] Apparently, the $C_7H_7^+$ ion from the halides, unlike that from the hydrocarbons, is formed from a state of the molecule-ion with little or no energy beyond the minimum required for the dissociation.

Interpretation of Appearance Potentials.—Appearance potentials often have been used to estimate bond dissociation energies.[36] For the process

$$e^- + XY \longrightarrow X^+ + Y + 2e^-$$

the energetic relationship is written as an inequality

$$A(X^+) \geq D(XY) + I(X)$$

to accommodate possible excess excitation or kinetic energy. The method assumes that the dissociation products X^+ and Y have the structure of the original groups in the molecule XY and, therefore, that the bond X—Y is the only one involved in the process.

Directly measured ionization potentials of free radicals[4,10,37] have shown that the inequality is, in some instances, in the *opposite* direction from that expected if dissociation involves no structural rearrangement. The spectra of labeled compounds testify to the prevalence of such rearrangements in both molecule-ions and ionic dissociation products.[2,3,11,14,29,38] Without independent supporting evidence, appearance potential measurements cannot establish the nature of a dissociation process.

Despite such rearrangements, bond-dissociation energies derived from electron-impact data often agree closely with values obtained in other ways. Such agreement arises from the nature of the indirect method of computation,[39] which is most often used because of the lack of directly measured ionization potentials of the appropriate free radicals. In this method, the appearance potentials of the same ion produced from two different but related molecules are measured, and the difference is combined with thermochemical data to give the required dissociation energy. If both measured appearance potentials contain the same energy excess *or deficiency*, it drops out when the difference is taken. Thus, the indirect method can give the correct value for a dissociation energy even though the actual process and the identity of the resultant ion are markedly different from those that have been assumed.

The term "rearrangement peak" in the literature of mass spectrometry denotes a peak that cannot be accounted for without some rearrangement. The term is misleading, in that it implies that peaks not so designated result from processes that do not involve rearrangement. In view of the evidence that rearrangements are extremely common in ionization-dissociation processes, all peaks might well be regarded as involving rearrangement unless proved otherwise.

Whiting, Indiana

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(32) If $A(C_7H_7^+)$ is assumed equal to the endothermicity of the reaction

$$e + C_6H_5CH_2X \longrightarrow C_7H_7^+ + X + 2e$$

then

$$\Delta H_f(C_7H_7^+) = \Delta H_f(C_6H_5CH_2X) + A(C_7H_7^+) - \Delta H_f(X)$$

where

$$\Delta H_f(C_6H_5CH_2X) = \Delta H_f(C_6H_5CH_2) + \Delta H_f(X) - D(C_6H_5CH_2 - X)$$

further

$$\Delta H_f(C_6H_5CH_2^+) = \Delta H_f(C_6H_5CH_2) + I(C_6H_5CH_2)$$

The $C_7H_7^+$ ion may be formed in an excited state so that $A(C_7H_7^+)$ contains excess energy. The expression for $\Delta H_f(C_7H_7^+)$ then places an upper limit on this value. Both of the calculated values, $\Delta H_f(C_7H_7^+)$ and $\Delta H_f(C_6H_5CH_2^+)$ depend on $\Delta H_f(C_6H_5CH_2)$ which is controversial (see ref. 33). Since both values have the same dependence on $\Delta H_f(C_6H_5CH_2)$, the maximum $\Delta H_f(C_7H_7^+)$ will be lower than $\Delta H_f(C_6H_5CH_2^+)$ whatever the accuracy of $\Delta H_f(C_6H_5CH_2)$. The thermochemical values used, in kcal./mole, are: $D(C_6H_5CH_2{-}Cl)$ = 68, from ref. 5; $D(C_6H_5CH_2{-}Br)$ = 50.5, from M. Szwarc, B. N. Ghosh and A. H. Sehon, *J. Chem. Phys.*, **18**, 1142 (1950); $D(C_6H_5CH_2{-}I)$ = 43.2, from ref. 6; and $\Delta H_f(C_6H_5CH_2)$ = 37.5, $\Delta H_f(Cl)$ = 29.0, $\Delta H_f(Br)$ = 26.7, and $\Delta H_f(I)$ = 25.5, from ref. 9.

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