sidered extremely probable in irradiated methane with (4) very likely accounting for the observed simultaneous hydrocarbon buildup. The buildup by this path would be possible, however, only if electron neutralization of CH_4^+ and CH_3^+ did not occur before (3) and (4) could take place. While there are no data available on neutralization rates in ionized methane, the results of Biondi and Brown[10] on neutralization rates in ionized hydrogen, if extrapolated to ionized methane, suggest that, at the radiation intensities and pressures used in this work and in most high energy radiations, electron neutralization of CH_3^+ and CH_4^+ will be slow compared with (3) and (4) and that these reactions may indeed be occurring.

The energy yields are independent of pressure over a threefold range. This fact is difficult to reconcile with a purely free radical scheme (which would be required if CH_4^+ and CH_3^+ were neutralized before reaction with methane) because of the competition between free radical abstraction and recombination reactions.

The results of this work are not strictly comparable to those of Lind and Bardwell[3] (see Table II) because these authors used higher intensities and higher pressure which would tend to operate in opposite directions on the energy yields. However, it seems quite improbable that the two effects would so exactly counterbalance each other as to give the striking agreement in $G(H_2)$ and $G(CH_4)$. Rather, it seems easier to believe that $G(H_2)$ and $G(CH_4)$ are independent of pressure and intensity over a wide range.

These facts suggest that ion-molecule reactions in irradiated methane may be playing a much larger part than has been generally believed. When the ions are neutralized they may fragment in many ways and so no detailed mechanism can be written without complete speculation as to the neutralization reactions. A detailed scheme would require, in addition, an understanding of the reactions leading to the polymeric material of which at the present time nothing is known.

Acknowledgments.—The author wishes to acknowledge fruitful discussions with Drs. W. E. Doering, F. H. Field and J. L. Franklin and the assistance of Messrs. T. P. Gorman and J. P. Keller in carrying out the experimental work.

BAYTOWN, TEXAS

[CONTRIBUTION FROM THE RESEARCH DEPARTMENT, STANDARD OIL COMPANY (INDIANA)]

Organic Ions in the Gas Phase. III. $C_6H_5^+$ Ions from Benzene Derivatives by Electron Impact

BY SEYMOUR MEYERSON AND PAUL N. RYLANDER

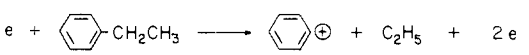
RECEIVED OCTOBER 18, 1956

Alkylbenzenes and alkylbenzene derivatives under electron impact give rise to $C_6H_5^+$ ions. They have been assumed to be phenyl ions formed by cleavage of the side chain from the ring. Spectra of labeled molecules furnish evidence that the $C_6H_5^+$ ions derived from phenyl alkyl ketones and 2-methyl-2-phenylalkanes do have the phenyl structure. On the other hand, those derived from α-chloroethylbenzene and ethylbenzene are formed by a process involving ring cleavage.

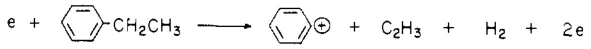
Introduction

The known stability of the benzene ring to chemical attack has led mass spectrometrists to assume that this ring is also stable to electron bombardment. Thus the $C_6H_5^+$ ions found in the mass spectra[1] of all alkylbenzenes heavier than toluene have been assumed to contain the original ring, and to be phenyl ions formed by cleavage of the side-chain from the ring. Similarly, the $C_6H_7^+$ ions have been assumed implicitly to be benzenium[2] ions formed by the same cleavage with concomitant transfer of hydrogen from the side-chain to the ring.

Identification of $C_6H_5^+$ as phenyl has seemed obvious. So firmly was this notion accepted that even the measured appearance potential of 16.3 e.v. for the $C_6H_5^+$ ion from ethylbenzene,[3] which leads to a heat of formation of phenyl ion 61 kcal. higher than the known heat of formation,[4] did not suggest that this ion was other than phenyl. Instead, this high value led to the suggestion[4] that the process could not be represented simply as



but more probably as



The last reaction gives a heat of formation of the phenyl ion more nearly in agreement with the known value.

The spectra of labeled compounds furnish evidence that the $C_6H_5^+$ ion is frequently not a phenyl ion. The precursor of the $C_6H_5^+$ ion in these cases is the $C_6H_7^+$ ion, which is not benzenium. However, some benzene derivatives do yield $C_6H_5^+$ and $C_6H_7^+$ ions that almost certainly are phenyl and benzenium.

Phenyl Ions

$C_6H_5^+$ ions from electron impact of phenyl alkyl ketones and 2-methyl-2-phenylalkanes apparently retain the original ring intact.

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[1] American Petroleum Inst., Research Project 44, "Catalog of Mass Spectral Data," Carnegie Inst. of Technology, Pittsburgh, Pa., 1947-1956.

[2] L. W. Pickett, N. Muller and R. S. Mulliken, *J. Chem. Phys.*, **21**, 1400 (1953).

[3] F. H. Field and J. L. Franklin, *ibid.*, **22**, 1895 (1954).

[4] J. L. Franklin and F. H. Field, *ibid.*, **21**, 2082 (1953).

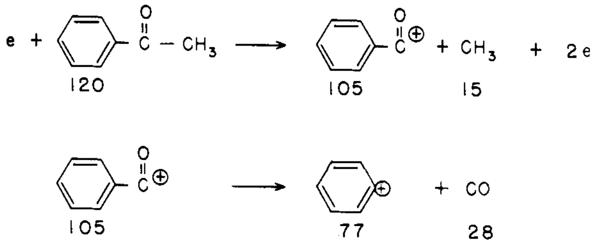
Dissociation of Phenyl Alkyl Ketones.—The mass spectrum of acetophenone contains the metastable peaks[5]

$$92.1\ (120^+) \longrightarrow (105^+) + 15$$
$$56.7\ (105^+) \longrightarrow (77^+) + 28$$

The spectrum of acetophenone-ω-d_3 contains the corresponding metastable peaks

$$89.9\ (123^+) \longrightarrow (105^+) + 18$$
$$56.7\ (105^+) \longrightarrow (77^+) + 28$$

These establish the dissociation path



The principal features of the spectra of these compounds, shown in Table I, can be accounted for by this reaction scheme. Although some $C_6H_6^+$ is formed, this is distinctly a minor product from the dissociation of acetophenone.

TABLE I

PARTIAL SPECTRA OF PHENYL ALKYL KETONES

Corrected for naturally occurring C^{13}

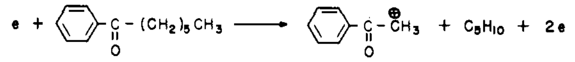
Mass	Acetophenone	Acetophenone-ω-d_3[a]	Hexyl phenyl ketone
190	..	..	6
123	..	30	..
122	..	3	..
120	33	..	68
105	100	100	100
79	..	3	..
78	3	1	4
77	80	82	42

[a] Spectrum uncorrected for 9% acetophenone-ω-d_2.

The spectrum of hexyl phenyl ketone, shown also in Table I, is consistent with this interpretation. The metastable peaks

$$75.8\ (190^+) \longrightarrow (120^+) + 70$$
$$91.9\ (120^+) \longrightarrow (105^+) + 15$$
$$56.7\ (105^+) \longrightarrow (77^+) + 28$$

establish the process



followed by further dissociation of the acetophenone ion, as before. Hydrogen migration characteristically accompanies cleavage of a bond beta to a carbonyl group.[6–8] This spectrum also shows the existence of a competing process to form $C_6H_6^+$ ion, but, again, it is a minor product.

Dissociation of 2-Methyl-2-phenylalkanes.—The mass spectra of 2-methyl-2-phenylalkanes differ markedly in the 77–78–79 region from those of primary and secondary alkylbenzenes. The relative intensity of the $C_6H_7^+$ ion from 2-methyl-2-phenylalkanes, unlike other alkylbenzenes, is nearly equal to or even greater than that of the $C_6H_5^+$ ion.[9] The mechanism by which these ions are formed from 2-methyl-2-phenylalkanes may also differ from that from other alkylbenzenes.[9] This suggestion is reinforced by the virtual absence in the spectra of *t*-butylbenzene and *t*-pentylbenzene of a $C_8H_9^+$ ion, mass 105, which will be shown to be antecedent to both the $C_6H_7^+$ ion and the $C_6H_5^+$ ion in the breakdown of primary and secondary alkylbenzenes.

The spectra of *t*-butylbenzene-α-C^{13} and unlabeled *t*-butylbenzene are given in Table II. Relative intensities at mass 79 in these two spectra are nearly equal; those at mass 80 are, in both cases, zero. The α carbon cannot be part of the $C_6H_7^+$ ion and hence the side-chain must be lost in forming it. The most likely structure for the $C_6H_7^+$ ion is benzenium

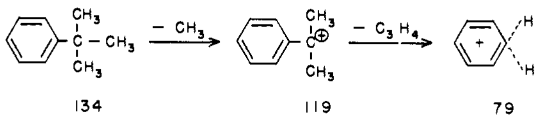


TABLE II

PARTIAL SPECTRA OF *t*-BUTYLBENZENE AND *t*-BUTYLBENZENE-α-C^{13}

Corrected for naturally occurring C^{13}

Mass	Unlabeled	Labeled
135	...	25.2
134	24.5	...
120	...	100.0
119	100.0	1.0
92	...	20.3
91	53.2	33.9
79	11.2	9
78	4.2	14[a]
77	10.9	7

[a] Contains some benzene.

TABLE III

PARTIAL SPECTRA OF α-CHLOROETHYLBENZENE AND α CHLOROETHYLBENZENE-β-d_3

Corrected for naturally occurring C^{13} and Cl^{37}

Mass	Unlabeled	Labeled[a]
143	...	14
142		1.6
140	13	...
139	0.2	...
125	7	7
108	...	100
107	...	11
106	...	8
105	100	6
104	22	2
103	17	1
82	...	4
81	...	7
80	...	5
79	12	8
78	11	7
77	19	4

[a] Spectrum uncorrected for 9% α-chloroethylbenzene-β-d_2.

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(5) P. N. Rylander and S. Meyerson, THIS JOURNAL, **78**, 5799 (1956). See footnote 3 for brief discussion of the significance of metastable peaks and for literature reference.

(6) F. W. McLafferty, *Anal. Chem.*, **28**, 306 (1956).

(7) G. P. Happ and D. W. Stewart, THIS JOURNAL, **74**, 4404 (1952).

(8) A. G. Sharkey, Jr., J. L. Shultz and R. A. Friedel, *Anal. Chem.*, **28**, 934 (1956).

(9) S. Meyerson, *Appl. Spectroscopy*, **9**, 120 (1955).

The metastable peak

$$75.1\ (79^+) \longrightarrow (77^+) + 2$$

in the spectra of *t*-butylbenzene, *t*-pentylbenzene and 2-methyl-2-phenylpentane supports the origin of the $C_6H_5^+$ ion by the reaction

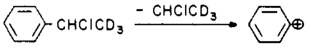
$$C_6H_7^+ \longrightarrow C_6H_5^+ + H_2$$

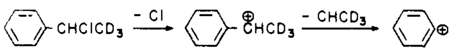
There is no reason to believe this ion is other than phenyl.

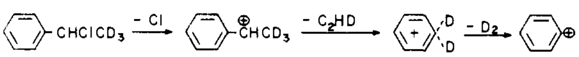
Other $C_6H_5^+$ Ions

The spectra of labeled α-chloroethylbenzene and ethylbenzenes show conclusively that these compounds do not form $C_6H_5^+$ ions by simple rupture of the bond between the ring and substituent. The process at work here involves ring cleavage and appears to be characteristic of the dissociation of primary and secondary alkylbenzenes.

Dissociation of α-Chloroethylbenzene.—Table III gives the mass spectra of α-chloroethylbenzene-β-d_3 and unlabeled α-chloroethylbenzene. The spectrum of the labeled compound is inconsistent with all of the following schemes for the formation of the $C_6H_5^+$ ion







The first two reactions demand that the intensity of the $C_6H_5^+$ ion from labeled and unlabeled α-chloroethylbenzene be equal. This is by no means the case. Even the third reaction prohibits more than two deuterium atoms in the C_6 ion; yet the peak at mass 82 shows that C_6 ions are formed that contain all three deuteriums.

A metastable peak

$$59.4\ (105^+) \longrightarrow (79^+) + 26$$

does support the formation of the $C_6H_7^+$ ion by loss of C_2H_2 from the $C_8H_9^+$ ion, as in the second step of the third reaction. But the peak at mass 82 in the spectrum of the labeled compound indicates that a large part of the C_2H_2 lost came from the ring rather than the side-chain. In this case, the $C_6H_7^+$ is not benzenium and $C_6H_5^+$ derived from $C_6H_7^+$ is not the original phenyl.

Dissociation of Ethylbenzene.—The spectra of variously deuterated ethylbenzenes, given in Table IV, show unequivocally that $C_6H_5^+$ ion does not form from ethylbenzene simply by cleavage of the phenyl-to-ethyl bond. If this were the mechanism, the relative intensities at mass 77 should be the same for the unlabeled compound and for the α-*d*, β-*d*, α-d_2 and α,β-d_5 compounds. Furthermore, phenyl ions formed in this manner from the three ring-deuterated compounds should all be deuterated and have mass 78; the relative intensities at mass 77 in the spectra of these compounds should be not greater than that at mass 76 in the spectrum of the unlabeled compound. Clearly, cleavage of the phenyl-to-ethyl bond is not the mechanism.

Neither is α-bond cleavage accompanied by migration of two hydrogens the source of $C_6H_7^+$ ions. If this were the mechanism, $C_6H_7^+$ ions from the α,β-d_5 compound should all contain two deuterium atoms and have a mass of 81. The observed relative intensity at mass 82, due to $C_6H_4D_3^+$ ions, is almost as great as that at 81, and even more-highly deuterated ions are present. Furthermore, ethylbenzenes labeled with a single deuterium atom in the α-, β-, *o*-, *m*-, and *p*-positions all give about the same number of $C_6H_6D^+$ ions, mass 80. If the ion were composed of the six original ring carbons, the deuterium in the α- and β-positions would have to be transferred exclusively and efficiently to the ring when the side-chain is lost. This assumption is untenable. Clearly, the ring did not remain intact.

TABLE IV

PARTIAL SPECTRA OF LABELED ETHYLBENZENES

Corrected for naturally occurring C^{13}

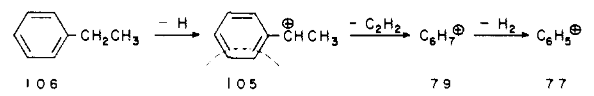
Mass	d_0	α-*d*[a]	β-*d*	*o*-*d*	*m*-*d*	*p*-*d*	α-d_2[b]	α,β-d_5[c]
111	...	...	...	...	...	...	..	29.7
110	...	...	...	...	...	...	..	4.15
109	...	...	...	...	...	...	1.2	1.98
108	...	...	...	...	...	...	30.6	0.38
107	...	30.4	30.4	30.0	30.4	29.7	2.3	0.80
106	30.0	4.51	5.77	5.03	5.02	4.97	0.5	0.80
105	5.63	1.37	0.95	1.13	1.25	1.12	2.6	0.42
84	...	...	...	...	...	...	..	0.19
83	...	...	...	...	...	...	..	0.81
82	...	...	...	...	...	...	..	1.11
81	...	...	...	...	...	...	1.0	1.22
80	...	1.80	2.01	2.11	2.25	2.22	2.6	2.63
79	2.88	3.56	2.21	6.52	6.64	6.68	5.3	5.07
78	6.42	6.60	8.28	5.93	5.96	6.05	10.6	1.58
77	7.60	4.76	5.09	3.12	3.13	3.02	3.1	1.04
76	0.78	0.84	0.86	0.65	0.78	0.86	0.9	0.55

[a] May contain 1–2% ethylbenzene-β-*d*. [b] Spectrum uncorrected for 4% ethylbenzene-d_3. [c] Spectrum uncorrected for 5.1% ethylbenzene-d_4, 0.1%-d_3, and about 3% isomeric-d_5.

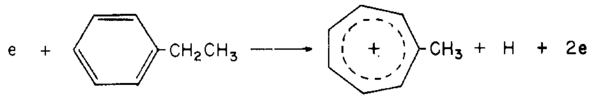
The spectrum of ethylbenzene, in common with those of many other alkylbenzenes,[1] contains the metastable peaks

$$59.4\ (105^+) \longrightarrow (79^+) + 26$$
$$75.1\ (79^+) \longrightarrow (77^+) + 2$$

The indicated sequence leading to formation of the $C_6H_5^+$ ion is



Not all aspects of the process are yet clear. Some of the $C_8H_9^+$ ions are formed by loss of hydrogen from the ring rather than from the α-carbon. Also, the spectra imply greater symmetry in the $C_8H_9^+$ ion than is represented by the phenylethyl ion. Some of the difficulty is dispelled if it is postulated that ethylbenzene molecule-ion rearranges to produce methyltropylium as the hydrogen is lost[10]



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(10) P. N. Rylander, S. Meyerson and H. M. Grubb, THIS JOURNAL, **79**, 842 (1957).

Labeling with C^{13} may clear up the remaining difficulties.

These findings can explain the anomalously high value calculated for the heat of formation of "phenyl" ion from the measured appearance potential of $C_6H_5^+$ from ethylbenzene. The value 16.3 e.v.[3] is the over-all activation energy for the sequence shown. That the preferred route should be a multi-step process rather than simple α-bond cleavage is at first surprising. Cleavage of the α-bond is calculated to require 2.65 e.v., or 61 kcal., less energy than the observed route and might be expected to occur more easily.

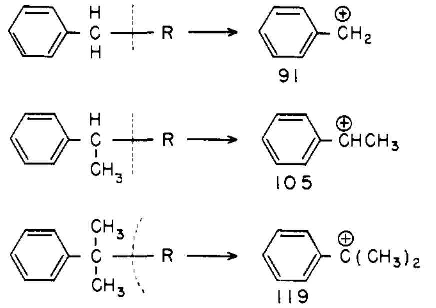
An explanation lies in the fact that any amount of energy sufficient to rupture the α-carbon–carbon bond is more than enough to break a β-carbon–hydrogen bond. Rupture of a β-carbon–hydrogen bond should require only about 11 e.v.; that of an α-carbon–carbon bond rupture, about 13.7 e.v.[3] Thus, even though a huge excess—commonly 70 e.v.—of energy is available in the mass spectrometer for any conceivable decomposition, the preferred decomposition path is determined by the low energy initial step. The process leading to the $C_6H_5^+$ ion is sequential and irreversible, and the preferred path at each step would seem to be that requiring the least energy.

Correlations of Alkylbenzene Spectra.—The metastable peaks

$$59.4\ (105^+) \longrightarrow (79^+) + 26$$

$$\text{and } 75.1\ (79^+) \longrightarrow (77^+) + 2$$

are common in the mass spectra of alkylbenzenes. They suggest that $C_6H_7^+$ and $C_6H_5^+$ ions are derived from other alkylbenzenes in much the same way as from ethylbenzene. Relative intensity of the mass-79 ion can be correlated readily with side-chain structure once it is viewed as being derived from the ion of mass 105. Predominant initial cleavage of alkylbenzenes under electron impact occurs at the β-carbon–carbon bond[9,11]



The observed intensities at 105, shown in Table V, are in accord with this mode of breakdown, and high intensities at 79 are found in those compounds having high intensities at 105.

The apparent discrepancy in the case of 2-methyl-2-phenylalkanes reflects the different nature and origin of the $C_6H_7^+$ ions derived from these compounds. Among primary and secondary alkylbenzenes, those molecules in which the initial cleavage leads directly to a 105 ion have both a high intensity at 105 and a relatively high intensity at 79. A correlation does not prove a hypothesis, but the agreement between the observed intensities and the structure of the side-chain lends credence to the decomposition postulated.

TABLE V

RELATIVE INTENSITIES AT MASSES 105 AND 79

Value of 100.0 assigned to relative intensity of most-abundant ion in each spectrum.

Compound	Mass 105	Mass 79
n-Propylbenzene	3.6	1.3
n-Butylbenzene	8.1	2.7
Isobutylbenzene	0.9	0.8
n-Pentylbenzene	18.5	3.0
2-Phenylpropane	100.0	10.6
2-Phenylbutane	100.0	7.0
2-Phenylpentane	100.0	5.8
2-Phenylhexane	100.0	5.5
t-Butylbenzene	0.6	11.6
t-Pentylbenzene	3.0	7.7
2-Methyl-2-phenylpentane	10.5	6.9

Experimental

Preparation of the deuterated ethylbenzenes[10,12] and C^{13}-labeled *t*-butylbenzene[5] has been described elsewhere. Hexyl phenyl ketone was prepared by the method of Ju, Shen and Wood.[13] The acetophenone-d_3 and chloroethylbenzene-d_3 were kindly supplied by Harold Hart of Michigan State University. All spectra were recorded on a Consolidated model 21-102 mass spectrometer. Per cent. labeling was determined from spectra obtained at reduced ionizing voltage.[14,15]

WHITING, INDIANA

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(11) I. W. Kinney, Jr., and G. L. Cook, *Anal. Chem.*, **24**, 1391 (1952).

(12) H. Hart, THIS JOURNAL, **78**, 2619 (1956).

(13) T. Y. Ju, G. Shen and C. E. Wood, *J. Inst. Petr.*, **26**, 514 (1940).

(14) R. E. Honig, *Anal. Chem.*, **22**, 1474 (1950).

(15) D. P. Stevenson and C. D. Wagner, THIS JOURNAL, **72**, 5612 (1950).