1:2 and some theoretical support for this view has been proposed, notably by Fano.

There have been a number of attempts at relating quantitative knowledge of the primary physical effects to the resultant chemical effects. It is not the purpose of this introduction to survey these attempts. Some of them have been very useful in guiding further experimentation. These essentially speculative treatments have been concerned with a number of factors, the possible effects of which have been considered individually and also in their relationships to other factors. They include: mechanism of neutralization; the contribution of negative ions and negative ion formation; the fate of excited molecules and the effect of excitation level, state of aggregation and of other molecules, surfaces, etc., on the fate of such excited molecules; the phenomenon of energy transfer; Stern–Volmer reactions of excited molecules and of excited free radicals; and, rather recently, ion–molecule and electron–ion–molecule reactions. From a more chemical point of view the speculations extend to the fate of free radicals, both "cold" and "hot," and to the effect of temperature on that fate.

With all this speculation and incipient theory it is apparent that much more extensive and reliable information is required before one can expect to make reasonable predictions in radiation chemistry. In the radiation chemistry of organic compounds especially, a strictly pragmatic approach to radiation chemistry may be particularly useful. Not only can the observations and correlations resultant from careful, detailed work give useful information, the immediate applications of which would be readily apparent, but, much more importantly the subtle variations of study possible in the radiation chemistry of organic compounds (*e.g.*, by detailed studies of a homologous series) may eventually give us a clearer understanding of the physical processes precedent to the chemistry and thus in turn give us a sound basis for prediction. In this Symposium, there are represented in a systematic way some of the purely chemical approaches to the solution of some fundamental problems of radiation chemistry.

ORGANIC IONS IN THE GAS PHASE. VI. THE DISSOCIATION OF *p*-XYLENE UNDER ELECTRON IMPACT

BY SEYMOUR MEYERSON AND PAUL N. RYLANDER

Research Department, Standard Oil Company (Indiana), Whiting, Indiana

Received June 24, 1957

The most abundant ions obtained from xylenes and other polymethylbenzenes by electron impact result from the loss of a methyl radical. Although other alkylbenzenes preferentially cleave a bond once removed from the ring, the polymethylbenzenes appear to cleave a ring-to-alkyl bond. Mass spectra of a series of labeled *p*-xylenes confirm the conclusion, based on a study of appearance potentials, that the resulting ions do not have the tolyl structure. Further, these spectra indicate drastic rearrangement before dissociation. Consequently, the methyl group lost does not contain solely the elements of an original side-chain.

The mass spectrum of a compound gives the distribution by mass of the ionized products that result from electron impact. Unfortunately, the spectrum tells nothing about the identity of an ion except its mass—or, more accurately, the ratio of mass to charge. The masses of the more abundant ions from most compounds can be accounted for by postulating cleavage of one or more bonds in the original molecule. Such a simple explanation is attractive and has been the basis for many assumptions about the nature and origin of ions produced by electron impact.

Although such assumptions have facilitated empirical correlation of mass-spectral data, without supporting evidence they may be no more than convenient fictions and have little significance for problems involving actual chemical processes. For example, chemical reactions induced by electron impact seem to have important implications for radiation chemistry and perhaps other areas. Also, appearance potentials of ions, interpreted in terms of reactions more often assumed than established, have been widely used to compute bond-dissociation energies and other thermochemical values. Although the simplest assumptions continue to be useful in providing initial hypotheses, such assumptions must be proved valid by independent observations before they can be accepted as descriptions of actual chemical particles and events.

The most abundant ions obtained from xylenes and other polymethylbenzenes by electron impact have masses 15 units lower than the parent molecules.[1,2] These masses correspond to loss of a methyl group and suggest cleavage of a ring-to-methyl bond. When the process is considered to be such cleavage, however, appearance potentials of the ions derived by loss of methyl from toluene, the three xylenes and mesitylene are not mutually consistent.[3] These potentials lead to heats of formation of the ions from the xylenes and mesitylene far lower than that of the ion from toluene, and close to that of the ion derived from ethylbenzene by the loss of methyl. This finding has led various investigators to suggest that the ion derived from toluene is actually phenyl,[4] but that those derived from the other compounds have rearranged to benzyl[3] or tropylium[5] ions. Regardless of the structure attributed to the ions, the methyl lost was assumed

---

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

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

(3) F. H. Field and J. L. Franklin, *J. Chem. Phys.*, **22**, 1895 (1954).

(4) However, see P. N. Rylander and S. Meyerson, *ibid.*, **27**, 1116 (1957).

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

implicitly to be one of the original side-chains.

Evidence bearing on the origin and configuration of an ion can be obtained from the distribution of labeled atoms in the ion derived from labeled molecules, and in its further decomposition products. To throw further light on the dissociation of polymethylbenzenes under electron impact, we therefore studied the mass spectra of *p*-xylene and four labeled *p*-xylenes: α-*d*, α,α'-d_2, o-*d*, and α-C^{13}. To provide a possible basis for generalizing from *p*-xylene, we obtained the spectrum of *m*-xylene-α,α'-d_2 for comparison with that of the *para* isomer.

Theoretical

Individual steps in a decomposition path can often be identified conclusively from the locations of metastable peaks in the mass spectrum.[6-8] Such evidence reveals two important paths for *p*-xylene. Metastable peaks at

$$78.4\ (106^+) \longrightarrow (91^+) + 15$$

and

$$46.4\ (91^+) \longrightarrow (65^+) + 26$$

establish the path

$$C_8H_{10}^+ \xrightarrow{-CH_3} C_7H_7^+ \xrightarrow{-C_2H_2} C_5H_5^+ \qquad (a)$$

A metastable peak

$$59.7\ (105^+) \longrightarrow (79^+) + 26$$

establishes the path

$$C_8H_{10}^+ \xrightarrow{-H} C_8H_9^+ \xrightarrow{-C_2H_2} C_6H_7^+ \qquad (b)$$

The assumption that the methyl lost in path a is an original side-chain could be checked readily. If it were valid, the per cent. labeling of the resulting $C_7H_7^+$ ions from the labeled xylenes should be

$$\frac{\alpha\text{-d}}{50} \quad \frac{\alpha,\alpha'\text{-}d_2}{100\ \text{(singly labeled only)}} \quad \frac{\text{o-}d}{100} \quad \frac{\alpha\text{-C}^{13}}{50}$$

Any significant deviation from these values would show that rearrangement had occurred. Moreover, if rearrangement had occurred in the formation of $C_7H_7^+$, it should be reflected in the distribution of the label in the $C_5H_5^+$ resulting from further breakdown.

The hydrogen atom lost in the first step of decomposition path b might reasonably be expected to come from a side-chain, with the formation of a *p*-methylbenzyl ion. However, such a simple explanation seemed questionable in view of evidence that the toluene molecule–ion rearranges to a seven-membered ring before losing a hydrogen atom.[5,9] The $C_6H_7^+$ ion was of further interest because of the uncertainty about its identity when derived from monoalkylbenzenes.[10] The spectra of labeled xylenes might be expected to clarify the processes in this path, and possibly those leading to the formation of other fragment ions as well.

Experimental

p-Xylene-α-*d* was kindly supplied by E. L. Eliel, of the University of Notre Dame. *p*-Xylene-α,α'-d_2 was made by reducing Eastman White Label *p*-di-(chloromethyl)-benzene with lithium aluminum deuteride. *p*-Xylene-o-*d* was prepared from 2-bromomagnesium-*p*-xylene by addition of D_2O. *p*-Xylene-α-C^{13} was prepared by the reaction of Eastman $C^{13}H_3I$, of 66% isotopic purity, and *p*-tolyllithium in ether; the product, after washing with water and concentration by distillation, was separated by gas chromatography. A portion of the *p*-xylene-α,α'-d_2 was treated with HF–BF_3 under conditions that have been shown to effect complete side-chain isomerization to *m*-xylene.[11,12] Unlabeled *p*-xylene was an API Standard Sample.

Spectra were recorded on a Consolidated Model 21-102 mass spectrometer. Isotopic species in the samples of labeled *p*-xylenes, determined at reduced ionizing voltage,[13,14] were

	α-*d*	α,α'-d_2	o-*d*	α-C^{13}
Unlabeled, %	4.8	3.6	20.8	34.0
Singly labeled, %	95.2	23.3	79.2	66.0
Doubly labeled, %	..	72.3	..	..
Triply labeled, %	..	0.8	..	..

All spectra were corrected for naturally occurring C^{13}; the spectra of the labeled species were corrected for the contributions of unlabeled xylene and, in the case of the xylene-d_2 spectrum, of xylene-d_1. Traces of aliphatic hydrocarbon appeared in the spectra of *p*-xylene-α,α'-d_2 and -α-C^{13}, but the other spectra revealed no components other than xylene. Partial spectra of the labeled *p*-xylenes are shown in Table I. Complete spectra will be submitted for issuance as part of the API "Catalog of Mass Spectral Data."[15]

TABLE I

PARTIAL SPECTRA OF *p*-XYLENES

Corrected for naturally occurring C^{13}

Mass, *m/e*	Unlabeled	α-*d*	α,α'-d_2[a, b]	o-*d*	α-C^{13}[b]
109	...	...	0.6	...	...
108	...	...	100.0	...	...
107	...	100.0	39.3	100.0	100.0
106	100.0	47.0	10.8	46.6	52.9
105	51.6	7.8	5.3	6.4	4.5
93	...	...	32.1	...	...
92	...	97.5	142.4	153.9	99.7
91	172.7	77.7	4.6	19.7	72.7
90	1.3	2.2	2.6	3.2	2.8
81	...	...	4.5	...	...
80	...	6.11	7.0	6.23	6.53
79	8.36	7.58	10.9	9.16	8.47
68	...	...	0.6	...	...
67	...	0.64	2.0	0.86	0.65
66	1.18	5.95	8.9	8.82	6.25
65	12.8	8.24	4.8	5.71	7.48

[a] Uncorrected for 1% xylene-d_3 (corresponding to 0.8% in the original sample). [b] Contains traces of aliphatic hydrocarbon.

Distribution of Label in Fragment Ions.—The abundance of $C_nH_m^+$ ions from unlabeled xylene is measured by the relative intensity at mass $M = 12n + m$ in the mass spectrum. In the spectrum of a labeled xylene, $C_nH_m^+$ ions are distributed be-

---

(6) P. N. Rylander and S. Meyerson, *J. Am. Chem. Soc.*, **78**, 5799 (1956).

(7) M. B. Wallenstein, A. L. Wahrhaftig, H. Roesnstock and H. Eyring, in "Symposium on Radiobiology," ed. by J. J. Nickson, John Wiley and Sons, Inc., New York, N. Y., 1952.

(8) H. M. Rosenstock, A. L. Wahrhaftig and H. Eyring, *J. Chem. Phys.*, **23**, 2200 (1955).

(9) S. Meyerson and P. N. Rylander, *ibid.*, **27**, 901 (1957).

(10) S. Meyerson and P. N. Rylander, *J. Am. Chem. Soc.*, **79**, 1058 (1957).

(11) D. A. McCaulay and A. P. Lien, *ibid.*, **74**, 6246 (1952).

(12) The mass spectrum of the *m*-xylene-α,α',-d_2 was found to be indistinguishable from that of the *p*-xylene-α,α',-d_2. This observation was taken to indicate that no methyl hydrogen had exchanged during isomerization.

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

(14) D. P. Stevenson and C. D. Wagner, *J. Am. Chem. Soc.*, **72**, 5612 (1950).

(15) Amer. Petroleum Inst., Research Project 44, "Catalog of Mass Spectral Data," Carnegie Inst. of Technology, Pittsburgh, Pa., 1947–.

tween masses M and $M + 1$, the latter being attributed to the labeled species. However, the intensity at M may include some contribution from labeled $C_nH_{m-1}^+$ and so cannot be used, in general, to compute the distribution of the label in $C_nH_m^+$ ions.

Distribution of the label can be estimated readily if the next-heavier ion $C_nH_{m+1}^+$ is absent or nearly absent from the unlabeled xylene spectrum. The relative intensity I_1 at M for unlabeled xylene gives the total yield of $C_nH_m^+$—the sum of the labeled and unlabeled species in the case of the labeled xylene. The relative intensity I_2 at $M + 1$ for the labeled xylene gives the yield of labeled $C_nH_m^+$. The difference $I_1 - I_2$ is attributed to unlabeled $C_nH_m^+$. This general procedure assumes negligible isotope effect on the dissociation process.

Where the yield of $C_nH_{m-1}^+$ is negligible relative to that of $C_nH_m^+$, as seen in the spectrum of the unlabeled compound, the distribution of the label among ions of the latter formula may be determined directly; the intensities at masses M and $M + 1$ give the yields of unlabeled and labeled $C_nH_m^+$ ions, respectively. This procedure may be used, for instance, for the $C_7H_7^+$ ion from xylene, with results nearly identical to those obtained by the general procedure.[16] However, the absence of interference from the next-lighter ion is peculiar to the $C_7H_7^+$ ion among all those studied in the xylene spectrum. In the interests of uniformity, therefore, we have employed the general procedure throughout.

The yield of labeled $C_nH_{m-1}^+$ can be estimated from the difference between the relative intensity at mass M and the computed yield of unlabeled $C_nH_m^+$. Per cent. labeling of the $C_nH_m - 1^+$ ions can then be computed with confidence where the total yield of $C_nH_m^+$ is much smaller than that of $C_nH_{m-1}^+$. In the spectra of the singly labeled xylenes, for example, the abundance of labeled $C_5H_5^+$ of mass 66 can be computed despite the presence of $C_5H_6^+$. The mass-66 intensity of unlabeled xylene is taken as a measure of total $C_5H_6^+$ yield. The mass-67 intensity of a singly-labeled xylene is attributed to labeled $C_5H_6^+$. The difference between these values then measures the yield of unlabeled $C_5H_6^+$ and is subtracted from the mass-66 intensity of the labeled xylene to obtain the yield of labeled $C_5H_5^+$. Where the specified condition is not met, such a computation should be accepted with caution, because errors, from whatever source, are cumulative.

The $C_7H_7^+$ and $C_5H_5^+$ Ions.—The per cent. labeling of $C_7H_7^+$ ion from each singly labeled xylene is given by the ratio of the relative intensity at mass 92 for the labeled xylene to that at mass 91 for unlabeled xylene. Similarly, the per cent. doubly labeled $C_7H_7^+$ ion from xylene-d_2 is given by the ratio of the mass-93 intensity for this compound to the mass-91 intensity for unlabeled xylene. Unlabeled $C_7H_7^+$ from the singly labeled xylenes and singly labeled $C_7H_7^+$ from xylene-d_2 were obtained by difference from 100%.

The observed distribution of variously labeled $C_7H_7^+$ ions from the labeled xylenes is markedly different from that expected if the methyl group lost were an original side-chain

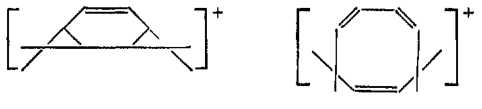
	α-d	α,α'-d_2	o-d	α-C^{13}
Unlabeled	44	..	11	42
Singly labeled	56	81	89	58
Doubly labeled	..	19	..	..

Rearrangement must therefore have occurred either before or during dissociation.

The distribution of deuterium from the deuterated xylenes can be accounted for on the assumption that the methyl group lost is an original side-chain that has had a 50:50 chance of exchanging one hydrogen with a ring hydrogen. The observed distribution agrees closely with that calculated on this basis

	α-d	α,α'-d_2	o-d
Unlabeled	42	..	12
Singly labeled	58	83	88
Doubly labeled	..	17	..

Models that would meet the statistical requirements for deuterium labeling are the electromeric structures[17]:



Each methyl is considered to give rise to a CH_2 group; and the CH_3 subsequently lost may be formed from either of these and a hydrogen atom from an adjacent CH group. These statistics require that no appreciable amount of CH_3 be lost without first being involved in a rearrangement. Even this rather extensive rearrangement is not adequate to account for the xylene-α-C^{13} data, which indicate that 58 minus 42, or 16%, of the methyl radicals lost contain carbons originally in the ring.

The yields of labeled $C_5H_5^+$ relative to that of labeled $C_7H_7^+$ from the singly labeled xylenes are given by the mass-66 intensities in the spectra, recalculated with a value of 100.0 assigned to the intensity at 92. The mass-66 intensities thus obtained

α-d	o-d	α-C^{13}
5.6	5.6	5.7

imply that the atoms originally in the ring and in the side-chains were no longer distinguishable in the $C_7H_7^+$ ion. For complete equivalence of the atoms, the values should be identical and equal to 5.3, five-sevenths the mass-65 intensity in the unlabeled xylene spectrum, recalculated with a value of 100.0 assigned to the mass-91 intensity. The data suggest that the bulk of the $C_5H_5^+$ ions are derived from a $C_7H_7^+$ precursor, as in the dissociation of toluene and other monoalkylbenzenes,[5,9] but that some likewise stem from other precursors, presumably $C_8H_{10}^+$ and $C_8H_9^+$.

Heats of formation of $C_7H_7^+$ ions, calculated from the appearance potentials from the three xylenes and ethylbenzene, are 243, 244, 239 and 234 kcal., respectively.[3] Good agreement among heats of

---

[16] Agreement of the $C_7H_7^+$ results by the two computing procedures supports the assumption of negligible isotope effect in the formation of this ion.

[17] *Cf.*, A. C. Cope, A. C. Haven, Jr., F. L. Ramp and E. R. Trumbull, *J. Am. Chem. Soc.*, **74**, 4867 (1952).

formation of ions of the same empirical formula but derived from different compounds has often been used to suggest that the ions have the same structure.[3,9] On this basis, it is tempting to suggest that the structure of $C_7H_7^+$ from the xylenes is the same as that from ethylbenzene, which has been shown to be tropylium.[5,9] This suggestion would be consistent with the evidence of the $C_5H_5^+$ data that the atoms in $C_7H_7^+$ have lost identity.

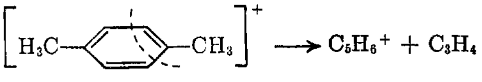
The $C_8H_9^+$ and $C_6H_7^+$ Ions.—Relative intensity at the parent-mass-less-one measures the loss of protium atoms from the molecule–ion. In the spectrum of unlabeled xylene, this intensity measures the total yield of $C_8H_9^+$ ion. If any deuterium is lost from deuterated xylene, the intensity will be less than that for unlabeled xylene. The parent-less-one intensities show that individual ring and methyl hydrogens are lost about equally. These intensities agree closely with the values calculated for complete equivalence of the ten hydrogens

	α-*d*	α,α′-*d*$_2$	o-*d*
Observed	47	39	47
Calculated	46	41	46

Such agreement implies loss of identity of the hydrogens and suggests extensive rearrangement before or during dissociation.

Similarly, the per cent. labeling of the $C_6H_7^+$ ion from xylene-α-C^{13} implies complete equivalence of the carbon atoms in the $C_8H_9^+$ ion. If $C_6H_7^+$ originates solely by the loss of acetylene from $C_8H_9^+$ the per cent. labeling is measured by the ratio of the mass-80 intensity of xylene-C^{13} to the mass-79 intensity of unlabeled xylene, both spectra being recalculated with a value of 100.0 assigned to the parent-less-one intensity. The value obtained is 76, in good agreement with the 75 expected for a process in which two out of eight equivalent atoms have been lost. The spectra cannot reveal whether equivalence of the carbon atoms was achieved in the xylene molecule–ion or in the $C_8H_9^+$ ion. Rearrangement processes by which the hydrogens and the carbons become equivalent may, therefore, be either the same or different. The configuration of the $C_6H_7^+$ ion is uncertain; however, as in the dissociation of ethylbenzene and α-chloroethylbenzene,[10] this ion is clearly not derived solely from the original benzene ring.

The $C_5H_6^+$ Ion.—The $C_5H_6^+$ ion, a distinctly minor product of xylene decomposition, is the one product observed that can be accounted for by bond cleavage in a molecule–ion with the conventional xylene configuration. Because it is the heaviest five-carbon ion produced, it is subject to no interferences, and the intensities due to labeled $C_5H_6^+$ from labeled xylenes can be determined unambiguously despite their small values.[18] Atoms originally in the ring and in methyl side-chains have not lost their identities. The observed isotopic distribution can be accounted for by the loss from the molecule-ion of methylacetylene, which contains the elements of a methyl side-chain, the attached carbon, and an adjacent CH group



The observed mass-67 intensities due to labeled $C_5H_6^+$ agree with the values calculated for this process

	α-*d*	o-*d*	α-C^{13}
Observed	0.64	0.86	0.65
Calculated	.59	.89	.59

Other Xylenes.—The pronounced similarity of the mass spectra of the isomeric xylenes[1,2,5] is not limited to the unlabeled compounds. The spectra of *m*-xylene-α,α′-d_2 and *p*-xylene-α,α′-d_2 are indistinguishable, and one would expect the spectra of other labeled *m*-xylenes also to be indistinguishable from those of the corresponding *p*-xylenes. There can be little doubt that decomposition under electron impact of *m*-xylene, and, indeed, of *o*-xylene closely resembles that of the *para* isomer.

Conclusion

Drastic rearrangements are involved in the processes by which *p*-xylene gives rise to $C_7H_7^+$ and $C_5H_5^+$ and to $C_8H_9^+$ and $C_6H_7^+$. Furthermore, these are rearrangements not of radical ions but of molecule-ions. Mounting evidence[4,5,9,19] suggests that such rearrangements may be far more common than has been supposed. Without supporting evidence, mass spectra cannot be safely interpreted in terms simply of bond cleavage in the original molecule.

Acknowledgments.—We are indebted to D. A. McCaulay for preparing the *p*-xylene-α,α′-d_2 and *m*-xylene-α,α′-d_2, and to E. L. Eliel for supplying the *p*-xylene-α-*d* and for helpful suggestions.

---

[18] Xylene-d_2 was an exception; small aliphatic peaks at masses 69–71 in the spectrum of this sample suggest that the peaks at masses 67 and 68 may also contain contributions from aliphatic contaminants.

[19] S. Gordon and M. Burton, *Disc. Faraday Soc.*, **12**, 88 (1952).