Tetrahedron Letters No.40, pp. 3469-3472, 1969. Pergamon Press. Printed in Great Britain.

# ALTERATION OF THE BENZENE MOLECULAR ION AND SUBSTITUTED BENZENE MOLECULAR IONS BY THEIR MODE OF FORMATION IN THE MASS SPECTROMETER

Maurice M. Bursey,* Fred E. Tibbetts, III, and William F. Little
Venable Chemical Laboratory, The University of North Carolina
Chapel Hill, North Carolina 27514
Marvin D. Rausch and Glenn A. Moser
Department of Chemistry, The University of Massachusetts
Amherst, Massachusetts 01002

(Received in USA 16 June 1969; received in UK for publication 29 July 1969)

Interest in the fragmentation of formally similar ions from different sources arose several years ago in connection with theoretical studies of rate processes in mass spectra (1). The earliest studies, on metastable ions formed by charge exchange (2) and on metastable ions of the composition $C_6H_{13}^+$ from different molecules (3), did not indicate that initial preparation of the ion significantly affects decomposition. More recently it has been shown that metastable intensities for formally similar decompositions are correlated in some cases with the number of vibrational degrees of freedom in the precursors of the metastable parent (4) and with substituent parameters (5). Isomeric ions may be distinguished by relative metastable ion abundances for competing decompositions of the ions (6), though before claiming identity or distinction of structures for the supposed isomers it is important to compare the intensities of more than one pair of metastable peaks (7).

The singly charged ion formed by electron impact on benzene in the mass spectrometer fragments to give a mass spectrum quite similar to that from hexa-3,5-dien-1-yne (8), and there has been speculation that $C_6H_6^{+\cdot}$ is not a cyclic species, as a result. Scrambling of deuterium and protium in partially labeled benzenes is more or less complete before the major fragmentations

---

* Fellow of the Alfred P. Sloan Foundation, 1969-71.

(9, 10). This may be a result of valence isomer formation by the molecular ion (10), or it may be a result of hydrogen scrambling on an intact carbon skeleton (11), or both processes may contribute.

We report now that the benzene molecular ions produced by fragmentation of benzenechromium tricarbonyl on electron impact reproducibly show a fragmentation pattern distinct from that of benzene ionized directly under similar conditions. The normal mass spectra have significantly different intensities of fragment peaks, the metastable ions are of greatly different intensities with respect to each other, and the ratios of metastable ion intensities to their individual precursors are likewise very different in the two spectra. Illustrative data for the metastable peak intensities are reported in the Table.

These same pronounced differences with respect to the spectra of the parent arenes also occur reproducibly in the metastable spectra of anisolechromium tricarbonyl, dimethylanilinechromium tricarbonyl, and styrenechromium tricarbonyl,* as the Table indicates. The utter lack of correspondence in metastable intensities, and the failure to observe metal-containing ions (other than $Cr^+$ and those containing the entire arene and/or CO) which might act as precursors to the metastable parents, suggest that in each of these cases a different form of the arene, the sole source of all organic ions, is produced by π bond cleavage to generate eventually all of the metastable ions observed. The phenomenon of significant alteration of ions produced from aromatic compounds by their mode of formation may not be general, though it seems widespread. We are currently comparing deuterated compounds to note if there is an alteration in the scrambling of hydrogens in the $C_8H_8^{+\cdot}$ from styrene derivatives paralleling the altered characteristics of the metastable intensities in these compounds.

On the other hand, the metastable spectrum of $C_6H_6^{+\cdot}$ generated from benzenetungsten tricarbonyl is similar to that of $C_6H_6^{+\cdot}$ from benzene itself. (The normal peaks have different intensities.) In cases where similarity is found in a pattern, the precursor might have arisen through thermolysis of the organometallic compound; this might be expected for the tungsten compound, where a probe temperature of 140° was necessary to give a satisfactorily intense metastable spectrum in our instrument, a Hitachi RMU-6E. All of the other organometallic spectra were recorded with sample introduction by the direct probe at ambient temperature into an un-

---

* The normal peak intensities also vary for the styrene case, but in such a way that most of the metastable-to-precursor intensities have some resemblance. This may be coincidence.

Table. Relative Intensities of Metastable Peaks from the Decomposition of $ArH^{+\cdot}$ from Different Sources (Most Intense m* in Spectrum of ArH = 100)

| m* | $C_6H_6$ | $C_6H_6Cr(CO)_3$ | $C_6H_6W(CO)_3$ |
|---|---|---|---|
| 34.7 | 100 | 100 | 100 |
| 33.8 | 33 | 178 | 32 |
| 32.9 | 17 | 2 | 23 |
| 19.5 | 35 | 200 | 28 |

| m* | $C_6H_5N(CH_3)_2$ | $[C_6H_5N(CH_3)_2]Cr(CO)_3$ |
|---|---|---|
| 116.4 | 69 | 12 |
| 89.2 | 21 | 24 |
| 88.5 | 100 | 100 |
| 72.1 | 57 | 22 |
| 70.5 | 12 | 6 |
| 46.5 | 5 | -- |
| 33.9 | 25 | 26 |
| 32.9 | 4 | -- |
| 23.5 | 4 | -- |
| 16.1 | 3 | 13 |
| 14.6 | 21 | 20 |

| m* | $C_6H_5OCH_3$ | $(C_6H_5OCH_3)Cr(CO)_3$ |
|---|---|---|
| 57.6 | 17 | -- |
| 56.3 | 100 | 100 |
| 45.6 | 25 | 27 |
| 44.6 | 2 | -- |
| 35.2 | 1 | -- |
| 34.8 | 2 | -- |
| 33.8 | 7 | 44 |
| 32.9 | 1 | -- |
| 23.4 | 8 | 24 |
| 19.5 | 1 | -- |

| m* | $C_6H_5C_2H_3$ | $(C_6H_5C_2H_3)Cr(CO)_3$ |
|---|---|---|
| 58.5 | 100 | 100 |
| 57.5 | 80 | 44 |
| 56.6 | -- | 10 |
| 48.1 | -- | 5 |
| 44.5 | -- | 3 |
| 34.9 | 13 | 4 |
| 33.9 | 70 | 16 |
| 32.9 | 10 | 6 |
| 23.3 | 13 | 3 |
| 19.5 | -- | 1 |

heated source. The filament current was turned up only a few seconds before the run in order to prevent further heating of the chamber, so that pyrolysis reactions common (12) in organometallic compounds under mass spectrometric conditions could be avoided as much as possible.

The examples given here illustrate the greatest differences yet reported for ions expected to be similar, to our knowledge. One similar study, on the formation of $C_6H_5OCH_3$ ions from the molecular ions of methyl phenyl carbonate, indicated very similar energy distributions for the $C_6H_5OCH_3^{+\cdot}$ ion from this source and that from direct ionization of anisole (13). Such large differences as observed here indicate very different distributions of states generated by direct electron impact and by fragmentation of a larger ion. At the minimum, the $C_6H_6^{+\cdot}$ produced from the complex would have different energetics, conceivably because it would be expected to be colder than the $C_6H_6^{+\cdot}$ produced directly if less internal energy is available to the ion as a result of its presumably higher appearance potential. At the most, different populations of isomeric $C_6H_6^{+\cdot}$ ions would be present in the two samples. From these data one should be able to identify the normal and metastable peaks of the high-voltage spectrum associated with differing amounts of internal energy. We plan to study this matter further.

We thank the National Science Foundation for support through grants GP 8096 and GU 2059.

## REFERENCES

1. H. M. Rosenstock and M. Krauss, *Adv. Mass Spectrom.*, 2, 251 (1962).
2. W. A. Chupka and E. Lindholm, *Ark. Fys.*, 25, 417 (1963).
3. H. M. Rosenstock, V. M. Dibeler, and F. N. Harllee, *J. Chem. Phys.*, 40, 591 (1964).
4. F. W. McLafferty and W. T. Pike, *J. Am. Chem. Soc.*, 89, 5951 (1967).
5. M. L. Gross and F. W. McLafferty, *Chem. Commun.*, 254 (1968).
6. T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, 88, 5021 (1966).
7. J. L. Occolowitz, 17th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 18-23, 1969.
8. J. Momigny, L. Brakier, and L. D'Or, *Bull. Classe Sci. Acad. Roy. Belg.*, 48, 1002 (1962).
9. C. G. Macdonald and J. S. Shannon, *Aust. J. Chem.*, 15, 771 (1962).
10. K. R. Jennings, *Z. Naturforsch.*, 22a, 454 (1967).
11. *Cf.* S. Safe, *Chem. Commun.*, 534 (1969); M. M. Bursey and T. A. Elwood, *J. Am. Chem. Soc.*, in press.
12. *Cf.* G. A. Junk, H. J. Svec, and R. J. Angelici, *J. Am. Chem. Soc.*, 90, 5758 (1968), and related papers.
13. P. Brown and C. Djerassi, *J. Am. Chem. Soc.*, 89, 2711 (1967).