models used. All values of the experimental effects are independent of temperature, Table II, and the variations in the computed values are also negligible in the range covered by experiment.

It should also be pointed out that at the pressure employed in this study, approximately 1000 Torr, a small fraction of the initially formed hot thiirane molecules undergo unimolecular fragmentation to reform the reactants. Since the rate constants for this unimolecular reaction of the deuterated molecules would be somewhat smaller than that of the light ethylene, the transmission coefficient ratios to be applied in eq I would slightly differ from unity. This introduces a small error in the isotope effect determinations, of the order of less than 1% which is well within the overall error limits of the measurements.

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# Doubly Charged Ions from Labeled Toluenes. Isotope Effects, Preference Factors, and Hydrogen Randomization

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**Abstract:** The doubly charged ion mass spectra of toluene, toluene-$\alpha$-$d_3$, toluene-*2,3,4,5,6*-$d_5$, and toluene-$d_8$ have been obtained. From these spectra it has been calculated that for the fast reactions occurring in the ion chamber of the mass spectrometer there is a preference factor for loss of an individual side-chain atom over the loss of an individual ring atom of 3.3:1; there is an isotope effect for loss of an H· atom over loss of the corresponding D· atom of 1.3:1. For reactions involving loss of $H_2$, HD, and $D_2$ fragments, it is shown that randomization of H and D atoms in toluene-$\alpha$-$d_3$ and in toluene-*2,3,4,5,6*-$d_5$ is essentially complete.

The gas-phase chemistry of ionized toluene has long been of interest, largely because of the intriguing problems presented by the structure of the molecular ion and of the $C_7H_7^+$ ion formed by loss of H·. Using isotopic labeling, previous investigators have sought to answer two immediate questions: Is there a "preference factor" for losing an H· (or D·) atom from the side chain rather than from the ring; and, is there an isotope factor which favors the loss of H· over the loss of D· from the same position in the molecule? For "fast" processes, that is, for reactions occurring in the ion chamber, it has been shown[2] that there is a preference factor of 1.32 for loss of methyl hydrogen over the loss of ring hydrogen, and also, that there is an isotope effect of 1.58. Studying the metastable transitions of toluene molecular ions, that is, the "slow" processes occurring in the first field-free region of the double-focusing mass spectrometer, it was found[3] that there is no preference factor in fragmentations involving the loss of a neutral hydrogen atom, but that there is an isotope factor of 3.5 favoring loss of H· over the loss of D·.

In this study we were interested in the behavior of doubly charged toluene molecular ions. One of our objectives was to calculate the preference factor in fast fragmentations involving loss of neutral H· or D· from the doubly charged molecular ions using labeled toluenes. Since these ions readily lose $H_2$, HD, and $D_2$, we also wished to examine the extent to which each of these molecules is lost, and thus to determine the amount of randomization in the doubly charged molecular ions prior to these processes. Meyerson[4] has reported that H· loss from doubly charged toluene molecular ions is not preceded by extensive scrambling whereas $H_2$ loss is.

## Experimental Section

All spectra were recorded with an RMH-2 double-focusing mass spectrometer, modified so as to allow the direct introduction of a collision gas into the first field-free region.[5] Ionizing voltage used was 70 eV, emission current 1 mA, source temperature 200°, and accelerating voltage 5 kV. All reagents used were commercial samples of highest available purity. Isotopic purity of the labeled compounds was better than 99%.

## Results and Discussion

After a doubly charged ion has undergone a charge-exchange reaction with a collision gas in the first field-free region of a double focusing mass spectrometer, it can be transmitted through the electric sector set at $2E$, where $E$ is the voltage at which the main beam of stable ions is transmitted, and it can subsequently be mass analyzed by the magnetic sector.[6] In this way, a "doubly charged" ion mass spectrum ("$2E$ spectrum") can be obtained without any interference from singly charged ions.

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Using benzene as collision gas in the first field-free region, doubly charged ion spectra were recorded for toluene, toluene-$d_8$, toluene-$\alpha$-$d_3$ (for brevity, toluene-$d_3$), and toluene-*2,3,4,5,6*-$d_5$ (for brevity, toluene-$d_5$). The sensitivity at which these spectra could be plotted was very good, being only a factor of $10^3$ less than the sensitivity for the main beam of singly charged ions. The doubly charged ion spectra are shown in Table I and they represent the average of ten scans for each compound. The spectrum for toluene shows up an error of one mass unit in the published mass measurement of the doubly charged ions.[6]

**Table I.** Doubly Charged Ion Mass Spectra of Toluene and Labeled Toluenes[a]

| Ion mass | Toluene | Toluene-$\alpha$-$d_3$ | Toluene-*2,3,4,5,6*-$d_5$ | Toluene-$d_8$ |
|---|---|---|---|---|
| 100 | | | | 12.4 |
| 98 | | | | 12.8 |
| 97 | | | 10.2 | |
| 96 | | | 11.2 | 56.6 |
| 95 | | 9.5 | 11.8 | |
| 94 | | 5.7 | 28.9 | 2.1 |
| 93 | | 30.6 | 17.7 | |
| 92 | 7.7 | 25.9 | 2.3 | 2.1 |
| 91 | 14.5 | 6.6 | 1.3 | |
| 90 | 47.1 | 1.8 | 1.5 | 1.2 |
| 89 | 3.2 | 1.3 | 1.1 | |
| 88 | 3.1 | 2.5 | 7.8 | 12.4 |
| 87 | 2.3 | 9.2 | 5.4 | |
| 86 | 22.0 | 6.4 | 0.7 | 0.3 |

[a] Each spectrum is normalized to 100 and corrected for $^{13}C$ contributions.

In order to compare the molar sensitivities of toluene-$d_0$ *vs.* toluene-$d_8$ and toluene-$d_3$ *vs.* toluene-$d_5$, two equimolar mixtures were prepared. The sum of all the $C_7$ ions due to the various compounds was obtained. Using this quantity as a measure of the total ion current, since it accounts for better than 99% of it, the sensitivity ratio of toluene-$d_8$ to toluene-$d_0$ was found to be 1.14, while the ratio of tolene-$d_3$ to toluene-$d_5$ was found to be close to 1.00 (within 1%).

Comparison of the loss of neutral H· from the toluene-$d_5$ and toluene-$d_3$ doubly charged molecular ions shows that there is a great difference in the probability of losing a side chain *vs.* a ring atom. Statistically, this ratio would be expected be

$$\frac{\text{probability of loss of H}\cdot\text{ from the } d_5 \text{ compound}}{\text{probability of loss of H}\cdot\text{ from the } d_3 \text{ compound}} = 3/5 = 0.60$$

Looking at the peaks at masses 96 and 94 in toluene-$d_5$ and toluene-$d_3$, respectively, the actual ratio is seen to be 11.2/5.7 = 1.96. Therefore, we can define a preference factor $p$ for losing an H· atom from the side chain rather than from the ring as $p = 1.96/0.60 = 3.27$. It should be noted that this result is independent of any isotope factor for loss of H· *vs.* D· atoms.

Let us now take toluene-$d_5$ and look at the peaks representing loss of two atoms, *i.e.*, $H_2$, HD, and $D_2$ from the doubly charged molecular ions. The resulting fragment ions are at masses 95, 94, and 93, respectively. While masses 94 and 93 can arise only from loss of HD and $D_2$, respectively (since loss of three atoms has a negligible probability), mass 95 includes contributions from loss of both $H_2$ and D· from the doubly charged molecular ion. Let us assume that the extent to which a D· atom is lost can be estimated from the peak due to ions $(M - D)\cdot^{2+}$ in toluene-$d_8$, which carry 12.8% of total ion current. There are 5 D's and 3 H's in toluene-$d_5$, but taking into account the preference factor for losing a side-chain H, this is equivalent to 5 D's and (3.27 × 3) H's as far as probability of fragmentation is concerned.

Therefore, we would expect that the fraction of the ion current carried by the ions $(M - D)\cdot^{2+}$ would be $12.8\,[5/(5 + 3.27 \times 3)] = 4.3\%$. This means that the rest of the peak at mass 95 represents the current due to ions $(M - H_2)^{2+}$, which amounts to $11.8 - 4.3 = 7.5\%$ of the total ion current. Thus, the measured ratio of $(M - H_2)^{2+}:(M - HD)^{2+}:(M - D_2)^{2+} = 7.5{:}28.9{:}17.7$ or 7.8:30:18.4. If complete hydrogen/deuterium randomization in the toluene-$d_5$ doubly charged molecular ions is assumed, and there is no effective isotope factor, the statistical probabilities for loss of $H_2$:HD:$D_2$ would be 6:30:20. In the formation of the neutral $H_2$ fragment, for example, not only are two C–H bonds broken, but an H–H bond is made. It is not known how large an isotope factor will operate under these conditions and so the simplifying assumption has had to be made that it is unity. It is shown later, for the case of simple removal of a single atom of H· or D· where a C–H or C–D is broken and there is no compensating effect for formation of a new bond, that the isotope factor is only 1.3 suggesting that the effective value in the loss of $H_2$, HD, and $D_2$ will indeed be close to the value 1.0. The result thus shows that, with the above assumption, for the case of loss of two atoms (presumably as a molecule of $H_2$, HD, or $D_2$) the scrambling of hydrogen and deuterium in toluene-$d_5$ is nearly complete.

Let us now assume that the preference factor for losing an H· atom from the side chain rather than from the ring, which was calculated above, holds also for the loss of a D· atom. We can then compare the losses of $H_2$, HD, and $D_2$ from toluene-$d_3$ doubly charged molecular ions. As in the case of toluene-$d_5$, the abundances of ions of formula $(M - HD)^{2+}$ and $(M - D_2)^{2+}$, which occur at masses 92 and 91, can be read from the spectra with no correction. However, the peak at mass 93 again has a contribution from both loss of $H_2$ and D· from the molecular ion. Using exactly the same approach as above, it can be calculated that the ion $(M - D)\cdot^{2+}$ will account for $12.8\,[(3 \times 3.27)/(5 + 3 \times 3.27)] = 8.5\%$ of the total ion current. Therefore, the contribution of ions $(M - H_2)^{2+}$ to mass 93 is $30.6 - 8.5 = 22.1\%$ of the total ion current. This gives the ratio of $(M - H_2)^{2+}:(M - HD)^{2+}:(M - D_2)^{2+}$ peaks as 22.1:25.9:6.6 or 20:23.4:6. Again assuming complete randomization and no isotope effect, this ratio would be expected to be 20:30:6. Therefore, the toluene-$d_3$, as well as the toluene-$d_5$ results, shows that almost complete hydrogen scrambling accompanies the loss of $H_2$ from the doubly charged toluene molecular ion.

Now that the contributions from $(M - D)\cdot^{2+}$ and $(M - H_2)\cdot^{2+}$ have been separated, we can check the ratio of D· loss in toluene-$d_5$ and toluene-$d_3$ in order to justify the assumption that the preference factor is equal for both loss of H· or D·. Using the values of the abundance of the $(M - D)\cdot^{2+}$ peaks obtained above it can be calculated that the ratio $(M - D)\cdot^{2+}$ in toluene-$d_3$/$(M - D)\cdot^{2+}$ in toluene-$d_5$ is 8.5/4.3 = 1.98, while the statistical probability would be expected to be 3/5 = 0.60. Thus, the preference factor for losing a D· atom from the side chain rather than from the ring is $p$ = 1.98/0.60 = 3.30, which is in excellent agreement with the value calculated for loss of hydrogen.

Comparing the abundances of the ions $(M - H)\cdot^{2+}$ in toluene-$d_0$ and $(M - D)\cdot^{2+}$ in toluene-$d_8$, the isotope effect can be calculated. This ratio is 14.5/12.8 = 1.13 which has to be corrected to allow for the molar sensitivity ratio of 1.14. Thus

$$i = \frac{\text{abundance of } (M - H)\cdot^{2+} \text{ in toluene-}d_0}{\text{abundance of } (M - D)\cdot^{2+} \text{ in toluene-}d_8} \times 1.14 = 1.29$$

The other way of obtaining the isotope effect is to compare the loss of H· from toluene-$d_5$ with the loss of D· from toluene-$d_3$, *i.e.*, side-chain atom *vs.* side-chain atom. Thus

$$i = \frac{\text{abundance of } (M - H)\cdot^{2+} \text{ in toluene-}d_5}{\text{abundance of } (M - D)\cdot^{2+} \text{ in toluene-}d_3} = \frac{11.2}{8.5} = 1.32$$

Alternatively, one can compare the loss of H· from toluene-$d_3$ with the loss of D· from toluene-$d_5$, *i.e.*, compare the probability of losing ring atom *vs.* ring atom. In this way we obtain

$$i = \frac{\text{abundance of } (M - H)\cdot^{2+} \text{ in toluene-}d_3}{\text{abundance of } (M - D)\cdot^{2+} \text{ in toluene-}d_5} = \frac{5.7}{4.3} = 1.33$$

## Conclusions

A major feature of our results is that the inverse relationship between isotope effect and preference factor for loss of H· from singly charged toluene molecular ions is also applicable to doubly charged ions. Thus, for slow reactions which involve relatively low energy ions, the isotope effect is large while the preference factor is small; for fast reactions, involving ions of relatively high energy, the opposite is true for both singly and doubly charged ions. This relationship between the reactions of singly and doubly charged molecular ions does not, however, provide any direct information on the structures of these ions.

The observation that hydrogen randomization occurs in the doubly charged ions under examination prior to $H_2$ loss but to only a small extent prior to H· loss is in accord with expectation based on the behavior of singly charged ions.[7] Fragmentation accompanied by bond formation is susceptible to competition by low activation energy/low frequency factor isomerization processes while simple cleavages are not, even when both decompositions are sampled in the ion source.

The good agreement between the three methods for determining the isotope effect for the $M^{2+}\cdot - H\cdot$ reaction speaks for the validity of the general approach. Two implicit assumptions, however, may be discussed here. Firstly, the method used to obtain the doubly charged ion spectrum involves formation of a singly charged ion by charge exchange. This reaction may transfer sufficient energy for the singly charged ion to fragment before leaving the field-free region, thus depleting the spectrum of the ion in question. It is known that "resonant" collisions of this type can transfer large energies (>10 eV)[8] and the consecutive process $92^{2+}$ + neutral $\rightarrow 92^{+} \rightarrow 91^{+}$ has been observed in toluene in the first field-free region. For the type of analysis done in this work in which the doubly charged spectra of isotopically labeled compounds were compared, the effect of unequal depletion of doubly charged ions *via* reactions of the corresponding singly charged ions will be minimal; in other cases the $2E$ spectrum may not accurately represent doubly charged ion abundances in the source.

The second assumption made above is that the doubly charged molecular ion of toluene is the precursor of all the doubly charged fragment ions. This is actually not strictly true since the process $93^{2+} \rightarrow 91^{2+} + 2$ was observed to contribute to the formation of $91^{2+}$ in the first field-free region. This process is believed to make only a small contribution to the total doubly charged ion current but an accurate measure of this contribution has not been made.

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