7.62-7.21 (m, 3), 4.61 (m, 1), 4.21 (m, 1), 3.49 (m, 2), and 2.98 (m, 4); *m/e* 205.089 (calcd, 205.089).

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# Spectroscopy of Radical Cations. The McLafferty Rearrangement Product in Fragmentation of *n*-Butylbenzene and 2-Phenylethanol Ions

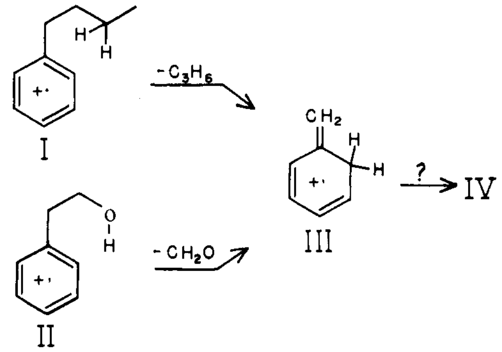
**Robert C. Dunbar***† **and Robert Klein**

*Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106.* *Received October 8, 1976*

**Abstract:** Photodissociation spectroscopy was applied to the question of the structure of the ultimate *m/e* 92 ion resulting from fragmentation of *n*-butylbenzene and 2-phenylethanol parent ions. Identical spectra were obtained for *m/e* 92 derived from these two precursors, and ruled out either the toluene or cycloheptatriene structure. Exhaustive photodissociation using the time-resolved photodissociation method indicated that the *m/e* 92 population consisted of at least 75% of a single structure, and that the fragmentations to give *m/e* 92 yield less than 10% of the toluene structure and less than 20% of the cycloheptatriene structure. Comparison with theory and with the known 1,3,5-hexatriene spectrum was consistent with and suggestive of retention of the methylenecyclohexadiene structure predicted by the McLafferty fragmentation mechanism.

Optical spectroscopy of gas-phase ions can be conveniently investigated taking advantage of the fragmentation processes which frequently follow photon absorption. This approach has been termed photodissociation spectroscopy, and has proven to be of value in determining structures of gas-phase ions[1] and in elucidating electronic properties of radical cations.[1,2] The obvious possibilities of this technique for spectroscopic study of interesting ions resulting from rearrangement fragmentation of larger parent ions have as yet not been pursued, and the present experiments were undertaken to bring this approach to bear on the product ion of one such electron impact induced fragmentation reaction.

The McLafferty rearrangement process yielding $C_7H_8^+$ from *n*-butylbenzene (I) and 2-phenylethanol (II) parent ions is well understood in principle.[3,4] The McLafferty mechanism



leads to the initial formation of III. An abundance of evidence (recently summarized by Levsen, McLafferty, and Jerina[4]) indicates that the rearrangement does follow this path, and it may be assumed without much question that III is formed

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† Alfred P. Sloan Fellow, 1973-1975.

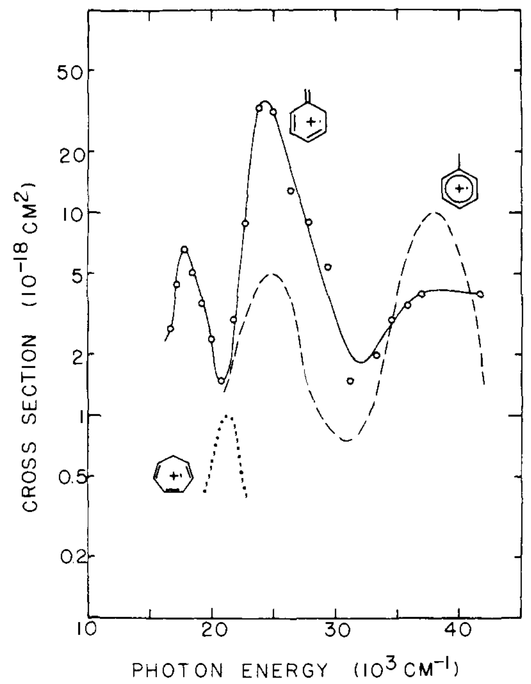
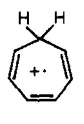
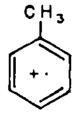


**Figure 1.** Photodissociation spectra of isomeric $C_7H_8^+$ radical ions. The indicated methylenecyclohexadiene structure for IV ions is of course uncertain, as discussed in the text.

initially and has at least a transitory existence. Much less clear is the question of subsequent rearrangements of this initial III structure. For III ions possessing sufficient internal energy to fragment, labeling and metastable decomposition evidence suggests that direct decomposition of III is in competition with rearrangement to other structures, with cycloheptatriene cation (V) the most plausible rearrangement product.[3] The competition between these two processes depends on the internal energy, with rearrangement being favored at lower energies.



V



VI

The focus here will be on those III ions which do not have sufficient energy to fragment. The most unambiguous evidence for this case is the ICR study of Bursey et al.,[5] which clearly showed that on a time scale of $\sim 10^{-2}$ s, there is no rearrangement of III ions to toluene ions (VI). However, as has been pointed out,[4] other rearrangement processes are not ruled out on this evidence.

Collisional activation data[4] show no difference between the final product IV and the cycloheptatriene ion V, although the authors note that this may be coincidental (as the present work would indicate to be the case). There appears to be no conclusive evidence about the structure of the stable form of the nondecomposing products of reactions 1 and 2, and the photodissociation spectroscopic approach seemed well suited to addressing this question.

## Experimental Section

The techniques of photodissociation spectroscopy using the ion cyclotron resonance ion trap have been described.[1,6,7] A plot of the photodisappearance of trapped ions as a function of irradiating wavelengths constitutes the photodissociation spectrum for the ion involved; the position and intensity of the peaks in the spectrum is characteristic of the ion structure in much the same way as the optical absorption spectrum would be.

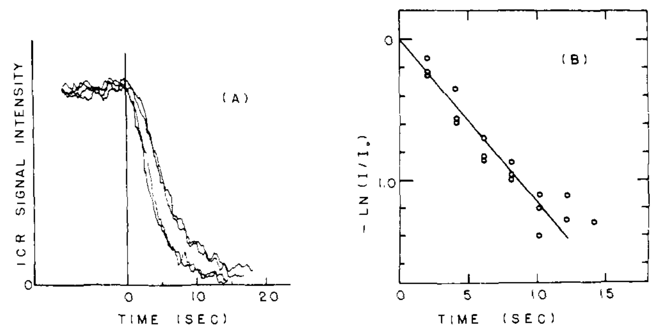


**Figure 2.** Exhaustive photodissociation, or "time-resolved", results for IV ions at 4050 Å. (A) Time-resolved curves. The upper pair of curves (two duplicate runs) represent the ion decay curve obtained for $m/e$ 92 after termination of ion production at time zero. The lower pair of curves are similar data with irradiation at 4050 Å commencing at time zero. (B) A logarithmic plot of the results from A obtained by point-by-point division of the light-on curve by the light-off curve. The simple exponential decay to more than 75% extent of photodissociation suggests a homogeneous ion population.

The only unusual feature of this work arose because photodissociation of the parent ions of I and II yields a sufficient amount of $C_7H_8^+$ to interfere with the determination of the photodissociation properties of IV. It was found possible to use cyclotron ejection[8] to remove the interfering parent ions rapidly and quantitatively from the cell, and with careful tuning of the ejection frequency, conditions were achieved under which there was no observed photoproduction of $C_7H_8^+$. As a further precaution in some of the butylbenzene work, trapping ejection[9] of the parent ion was used at the same time as cyclotron ejection; simultaneous trapping and cyclotron ejection fields gave very efficient parent-ion suppression.

The "time-resolved" mode of ICR photodissociation is a recent technique.[6] The real-time decay of the ICR signal corresponding to trapped ions is followed; the ion decay curve in the presence of illumination is compared with the dark decay curve to yield a profile of the real-time photodisappearance kinetics of the trapped ion population. The resulting curve should approach the baseline exponentially with time constant corresponding to the photodissociation cross section, and deviations from exponential decay are an immediate and clear indication of the presence of two or more spectroscopically distinct ion structures.

Experiments were carried out at pressures ranging from $2 \times 10^{-9}$ to $3 \times 10^{-8}$ Torr, with ion trapping times of 10-30 s. An electron energy of 15-16 eV gave abundant $C_7H_8^+$ without excessive production of smaller fragment ions.

## Results and Discussion

Figure 1 shows the photodissociation spectra of IV and[10] of the two $C_7H_8^+$ ions usually considered as likely rearrangement products from III. It is clear at once that the spectrum of IV corresponds to a species which is neither toluene nor cycloheptatriene, nor a mixture of the two. Results obtained for ions derived from I and II were identical.

The spectrum of IV clearly lacks the strong UV peak characteristic of toluene cation VI, while the peak at 4000 Å is six times more intense, and it is clear that at most a small fraction of the IV population can have the toluene structure.[10] The spectrum of IV does not resemble that of cycloheptatriene cation V either, but this is inconclusive since V has such a small photodissociation cross section. More definitive evidence comes from the "time-resolved" photodissociation result shown in Figure 2. The time-resolved photodissociation curve for IV indicates that at least up to the point where 75% of the IV ions have been dissociated, the decay is perfectly exponential, with no suggestion of the presence of a significant fraction of nondissociating ions. Since V is known[11] to be nondissociative at 4050 Å, the fact that at least ~75% of the IV population dissociates at 4050 Å with uniform cross section rules out the presence in the cell of more than about 25% of the cycloheptatriene structure.

We conclude that, on a time scale of seconds, a major fraction (half or more) of the IV population consists of ions which have not rearranged to either the V or VI structures. In order to draw quantitative conclusions about the IV population, we must take into account the fact that in these trapped-ion experiments a reactive $C_7H_8^+$ structure will be depleted, while less reactive structures will accumulate. To account for this process, the reaction rates of IV, V, and VI cations with parent *n*-butylbenzene were directly measured, and were found to be in the ratios 1:0.8:0.6. Since IV ions are the *most* reactive (and thus have the shortest lifetime in the trapping ICR cell), the conditions of the photodissociation experiment will tend to overestimate the amounts of V and VI ions in the IV population. We can accordingly strengthen our conclusions about the purity of the IV population:[12] the IV population consists of at least 75% of a single species, and is contaminated by less than 10% of toluene cations VI and less than 20% of cycloheptatriene cation V.

We cannot at this point prove that III and IV are the same species,[13] but we may ask whether the spectrum obtained for IV is reasonable for the substituted, partially cyclic triene structure of III. Information on this point comes from theory and from the known photodissociation spectrum of hexatriene cation. Zahradnik and Carsky[14] have calculated the electronic spectrum for the model *trans*-1,3,5-hexatriene radical ion, and predict an intense peak at 22 500 $cm^{-1}$ and smaller peaks at 13 000 and 41 000 $cm^{-1}$. Hexatriene radical cation shows a photodissociation spectrum in acceptable agreement with these predictions,[14-16] with a strong peak at 27 500 $cm^{-1}$, a smaller peak at 16 000 $cm^{-1}$, and another peak near 40 000 $cm^{-1}$. It is evident that qualitatively the spectrum of IV fits the expected pattern for a conjugated triene. Quantitative comparision of IV with hexatriene cation shows a shift of the red peak of hexatriene toward the blue, and a shift of the near-UV peak toward the visible. It can be noted that a similar pattern of peak shifts is seen in conjugated dienes[17] upon going from the straight-chain (predominantly trans) to the cyclized (enforced cis) radical cation species. We conclude that the spectrum of IV is strongly suggestive of retention of the methylenecyclohexadiene structure III; although other structures cannot be ruled out, the very intense peak in the blue is probably inconsistent with structures not having a degree of conjugated unsaturation comparable to III.

At the referee's suggestion, the nature of the *m/e* 92 ion from *n*-butylbenzene was examined at 40 eV electron energy, in order to test whether the increased internal energy available at higher ionizing energy might lead to increased isomerization of III to V or VI. Cross sections for photodissociation of this species were found to be $31 \times 10^{-18}$ $cm^2$ at 25 000 $cm^{-1}$ and $4.5 \times 10^{-18}$ $cm^2$ at 35 700 $cm^{-1}$. These values are not different within experimental error from the values obtained at 16 eV ionizing energy (Figure 1), and we conclude that the *m/e* 92 ion produced at 40 eV still has predominantly the methylenecyclohexadiene ion structure. (For these results, the limit on contamination by V and VI is somewhat weaker, with about 35% of (V + VI) being a reasonable upper limit.) Thus the evidence does not suggest ready interconversion among $C_7H_8^{+\cdot}$ structures for nondecomposing methylenecyclohexadiene ions III, although for more energetic, decomposing $C_7H_8^+$ ions it may well be that the III structure is accessible and interconverting with other structures as has been suggested.[18]

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