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1, 4 Dehydrobenzene: A Stable Species

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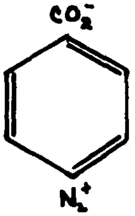
We would like to report the observation of a relatively stable C_6H_4 species which we infer is probably 1,4-dehydrobenzene. Our investigation is based on studying the photoinitiated decomposition of benzendiazonium-4-carboxylate (I). The transient intermediates were the species initially of interest, so that flash-initiated decomposition was used for the study, in conjunction with time-resolved mass spectroscopy and flash-absorption optical spectroscopy. Methods were essentially the same as those described in studies of the ortho-isomer;[1,2] the only difference is the additional care required in the handling of the more sensitive para-isomer, I.

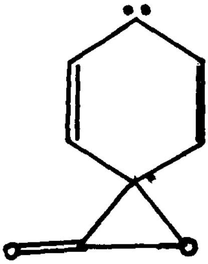


I

The ultraviolet absorption spectrum of the transient gaseous decomposition products from flash-initiated decomposition of I shows a continuum flatter and broader than that of benzyne, extending from at least 2900 mμ to the short wavelength limit of the spectrograph. A possible flat maximum occurs in the region 244-246 mμ. The continuum is present at times 50 μsec to at least 1/2 second after flashing, but not one minute or more later. The spectrum also shows phenol bands at 274.9, 267.9, and 266.2 mμ, after 800 μsec. These bands are most intense when only 2 or 3 μ moles of starting material are used. (A "large" sample would be 10 μ moles.) Two new narrow transient bands, at 328.4 and 339 mμ, present at least 1/2 sec after photolysis, appear within about 200 μsec after photolysis and disappear within minutes. We have not been able to assign these bands or the continuum to any previously known spectrum.

The time-resolved mass spectrum is our principal means of identifying the species of interest, and its analysis is the main concern of the following discussion. The spectrum is relatively rich compared with that obtained from the ortho starting material.[2] The para isomer I apparently does not decompose exclusively to give N_2, CO_2, and a fragment of mass 76 (C_6H_4), although this process accounts for over 90% of the fragment intensities. (Masses 28 and 44 are always the strongest peaks, by far.)

Before discussing the main channel of decomposition, let us examine the alternative path briefly. The principal masses which cannot be ascribed to direct loss of N_2 and CO_2 are 92 and 94. The latter is clearly phenol from the optical spectrum. Both appear within 50 μsec of 76; 92 occasionally appears first, always much more intense than 94. After another 300-400 μsec, the relative intensities are reversed. Mass 93 is always much weaker than 92 or 94. We interpret this pattern to mean that a C_6H_4O fragment is one of the decomposition products of I, probably proceeding through the intermediate II which can lose



II

either CO or an oxygen atom. Carbon monoxide has been identified as a reaction product by Stiles and Burckhardt.[3] The C_6H_4O fragment itself is probably the species observed by Wasserman and Murray,[4] a dehydrophenoxy triplet. This type of molecule has been discussed in some detail by Dewar and Narayanaswami.[5] From our experiments, one cannot determine whether the species we observe is in a carbene-like singlet or an aromatic phenoxy triplet, but the early appearance time and low collision frequency makes the singlet seem quite possible. Wasserman and Murray, on the other hand, have unequivocally observed a stable triplet.

The mass spectrum shows very small amounts of masses 104 (C_6H_4 + 28, presumably CO), and 120 ($C_6H_4CO_2$) during the first 300 µsec; both disappear long before mass 92. Consequently, 92 cannot be a fragmentation product from the ion-molecule of either 104 or 120.

In the main mode of decomposition, at electron accelerating potentials of 45 volts or more, all the C_n fragments are represented, with an informative distribution of intensities. They appear as follows: 12 (300-400 µsec, then decaying 400-600 µsec); 26, 27 (400 µsec, 27 stronger and slower to disappear, apparently a fragmentation product of 76 at potentials above 35 v); 37-44 (40 very weak); 50 (major fragment peak ascribable to $C_6H_4^+$ parent, present even at 32 v); 63-66 (66, the strongest, persisting 2 min; 65 missing or weak at earliest times, suggesting that 66 is C_4H_2O at earliest times and cyclopentadiene later; 66 is too strong to be due entirely to fragmentation).

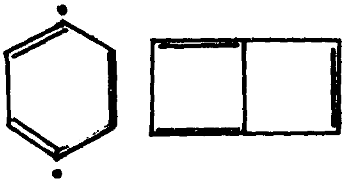
The most surprising part of the mass spectrum is the C_6 region. As we expected, mass 76 is present from the earliest times and is the strongest peak in the mass spectrum, after 28 and 44. It is about 50% stronger than mass 50 at high electron accelerating potentials and possibly stronger still, relative to 50, at 32 volts. The surprise is the fact that <u>76 is not a transient peak, but persists for as much as 2 minutes</u>, after 28 and 44 have dropped back to background. Mass 74 is also present, at 1/4-1/2 the intensity of 76 and is apparently a cracking product of 76. Masses 75 and 78 are present throughout, with about half the intensity of 74; 77 is still weaker.

Certain masses conspicuous by their absence are the possible transient dimer and trimer of 76 at 152 and 228. Instead, a badly resolved broad peak at about 198 ± 4 appears for 400-600 μsec, perhaps $(C_6H_4)_2CO_2$.

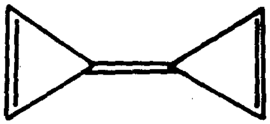
Other peaks conspicuous for their weakness are 51 and 52, particularly by comparison with the results from the <u>ortho</u> isomer of I.[2] We can infer that $C_4H_3^+$ and $C_4H_4^+$ fragments are very rarely formed in the decomposition of the positive ion of mass 76. Masses 60 and 61 are absent; mass 62 is occasionally barely detectable. The weakness of mass 39 is strongly suggestive that the C_3H_3 moiety is absent in the parent ion; again, the contrast with benzyne[2] adds weight to the inference.

We consider now the structure of the fragment of mass 76. It was suggested by Fisher and Lossing[6] that the mass 76 from thermal decomposition of <u>para</u>-diiodobenzene was due to rearrangement, perhaps to III. This and IV are the most

$CH{\equiv}C{-}CH{=}CH{-}C{\equiv}CH$



or



III

IV

V

reasonable and likely structures for the assignment. Other less likely but possible structures include the bicyclopropane V, hexa-1-ene-3,5 diyne (VI), 3-methylene-penta-1,4-diyne (VII), benzyne and its meta-dehydro isomer, and a variety of cumulene and highly strained ring systems. Its known ultraviolet spectrum[7] eliminates VI. The compound VII has a relatively strong mass peak at 72;[7] the product from I gives no mass 72. The mass spectra of benzyne and (attributed to) its meta isomer differ clearly from that reported here.[2,8] The cumulene and small-ring structures are relatively unlikely for a variety of reasons--the requirement of hydrogen shifts, in most cases, and the strain energy in others. Structure V is conceivably the correct structure, and cannot now be excluded on any ground except unconventionality. (By the same token, IV might well seem at least as outlandish.) The mass spectrum of III has been observed for the mass range 48-76.[7] The reported spectrum differs sharply in one significant way from the one we observed, in the C_5 region; III gives only 60, 61 and 62, with 61 the largest. Even after photolysis, as long as 76 is visible, we observe no 61, while 63 and 64 persist. Some intensities in the mass spectrum of III also differ from those we observe: 74 from III has about 27% the intensity of 76, while in our spectra, the figure is roughly 50%. The relative intensities of 49 and 51, both weak peaks, are reversed from those from III. We are therefore strongly inclined to prefer structure IV for the mass 76 species from I.

We infer from the preceding argument that the relatively stable C_6H_4 product of the photoinitiated decomposition of I is either species IV or species V. Species IV seems somewhat more likely, only on the rather weak grounds of its similarity to the precursor.

The variation in the mass spectrum with time might be due to isomerization (e.g., IV to V) or to intersystem crossing from a singlet to a triplet state. It could also be due to vibrational relaxation, since the collision frequency in the sample tube after photolysis is of order 1 μsec^{-1}, so that the entire "early" interval represents about 300-400 collisions.

The continuous absorption is most reasonably attributed to the species of mass 76, (presumably a singlet), since it is the only parent mass having essentially the same disappearance time as the continuum. The bands, however, are also present in the spectrum from the meta isomer of I, and the transient mass spectrum from this species is quite different from that of either the ortho or para isomer,[2,8] so we cannot attribute the bands to our persistent substance of mass 76.

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