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Decomposition of Benzenediazonium-3-Carboxylate: Transient 1,3-Dehydrobenzene

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We wish to report the evidence for a transient C_6H_4 species which, from existing information, appears to be 1,3-dehydrobenzene. This substance, identified principally by its mass spectrum, has a lifetime in the gas phase comparable to that of benzyne, the 1,2-dehydrobenzene.

The method of production and identification of the supposed 1,3-isomer follows that used for the long-lived 1,4-isomer[1] and the transient 1,2-isomer.[2,3] Flash-initiated decomposition of an unstable precursor, in this case benzenediazonium-3-carboxylate,[**] generates N_2, CO_2 and organic products. We have studied the process and the products by following both the mass spectrum and the optical spectrum as functions of time.

In order to present the evidence for the transient C_6H_4 and for the assignment of its structure as 1,3-dehydrobenzene, we shall discuss, first, the optical spectrum, and second, the mass spectrum. We then present the analysis of the latter from which the structure is inferred.

OPTICAL SPECTRUM: Optical spectra of the gaseous decomposition products provide some information, albeit less than one might hope. As with <u>ortho</u> and <u>para</u> isomers, there is a transient continuum extending to about 290 mμ. (However with samples 10μ moles or more, the tube is essentially opaque.) The continuum could be detected sometimes as late as 2000 μsec after photolysis. Bands at about 339 and 328 mμ are visible between 45 and 250 μsec but never as late as 1800 μsec. These are apparently identical to unassigned bands obtained from decomposition of the <u>para</u> diazonium carboxylate.

Two products exhibit their known band spectra: benzene (258.9, 247.1, 241.5 mμ, as early as 1800 μsec); and phenol (274.9, 268.2, 266.2 mμ, possibly with excess energy at 2200 μsec, certainly in its normal state later; never earlier than 2200 μsec). One completely unambiguous result which we have been unable to reproduce seems to be worth reporting here. This consisted of four diffuse bands appearing 1800 μsec after photolysis, at 236.5 (weak), 248.5 (very strong), 265.6 (strong) and 282.8 mμ (weak). The pattern is distinctive and similar to that reported for $CH_2{=}CH{-}C{\equiv}C{-}C{\equiv}CH$, namely:[4] 231, 242, 255 and 270 mμ. The wavelength differences, however, are significant and the two species can hardly be the same.

MASS SPECTRUM: The time-resolved mass spectrum is comparable in complexity to that from the para isomer,[1] but shows no persistent mass 76 peak. At the first appearance of photolysis products, the mass spectrum shows very strong peaks at 28 and 44 and, when the electron accelerating voltage is about 45 eV or above, a large variety of other peaks. Like the <u>para</u> diazonium carboxylate, the <u>meta</u> compound shows small peaks at 92 (very weak after 200-500 μsec), 94 (C_6H_5OH), 104 (probably C_6H_4CO, half-life ca 200 µsec) and 120 (presumably $C_6H_4CO_2$, half-life 200-300 µsec). There is also some indication of a broad transient peak at mass 152, presumably a dimer of the primary species at mass 76, with a lifetime of 400-500 µsec. This high mass region was not resolved clearly, so the mass could not be identified with certainty.

Spectra at electron accelerating potential of 33 eV indicate a parent species with mass 76 for 400-600 µsec and mass 78 at all times. With large samples and electron potentials of 45-60 eV, mass 76 is detected at all times, but drops in intensity about 400 µsec after photolysis. When small samples (2 µmoles, estimated) are used, mass 76 can only be seen for about 400 µsec. At maximum, the intensity of the peak is ca five times the noise level. (Mass 78 is surely benzene.)

The following list gives the transient mass pattern from C_1 to C_6 fragments; masses are followed by relative intensities (in unite of typical signal: noise ratios) and lifetimes, if they are short enough to be measurable ($<$ 1.5 msec): 12 (1.5-2, perhaps as long as 400-600 µsec); 14 (3-4); 15 (1.5-2); 16 (3-4); 17 (1.5-2); 18 (3-4); 24 (in large samples only, 2, 200 µsec); 25 (1.5, 200 µsec in moderate samples; 3.5-4 with larger samples, $>$ 800 µsec); 26 (2.5-10, depending on sample size, not observed with smallest samples); 27 (2-12, depending on sample size; persistent with electron potentials 45 v or higher, and always higher than 26); 31 (2.5-3; persistent); 32 (2.2.5; persistent); 39 (2-9, strong for the first 400 µsec, then decreasing);

40-43 (1.5-2, all very weak after ca 300 µsec); 50 (1.5-3, > 800 µsec); 51 (1.5-2, only with large samples, probably only 200 µsec); 58 (1.5); 63 (1.5-7, only with moderately large samples 300-500 µsec); 64, 65, 66 (as high as 5 with largest samples; no more than 500 µsec); 77 (1.5-2, with largest samples). This pattern differs clearly from either of those of References 1 and 2, except for the transient 66 which is probably C_4H_2O due to loss of acetylene from C_6H_4O, mass 92.

ANALYSIS: We infer from the mass pattern that a species of mass 76 is a primary product of the flash-initiated decomposition of benzenediazonium-3-carboxylate. The most reasonable structure which this might have is that of any of the 3 vinyl diacetylenes or of 1,3-dehydrobenzene. Apropos the diacetylenes, a suggestion was made by Fisher and Lossing that the mass 76 species obtained by pyrolytic decomposition of both *meta* and *para* diiodobenzene might be hexa-3-ene-1, 5-diyne, since both parents gave peaks at 76 having the same appearance potential.[6] The mass 76 species obtained from the two corresponding diazonium carboxylates are clearly different, one being (or isomerizing to) a long-lived species and the other, a transient.

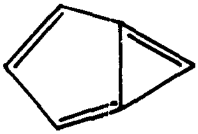
The fragmentation pattern can be interpreted, at least in part, to help us infer the probable structure of the mass 76 species. Specifically, we can compare the pattern with those of diacetylene and vinylacetylene. Neither of these has a peak of any size at mass 39, but both have strong peaks at 38. The latter of these implies that the ion molecule of a rigid conjugated system is unable to rearrange so as to fragment into the very stable and otherwise favored $C_3H_3^+$. Our substance has a rather intense peak at 39 for at least 400 µsec, and none at 38. We conclude that our parent species probably has a C_3H_3 piece in its skeleton.

Most of the remaining masses are consistent with more than one possible structure. Mass 50, for example, would probably be a fragment of all the C_6H_4 species since it comes from loss of acetylene. Rather, the absence of certain peaks helps us to count the vinyldiacetylenes as improbable. These compounds would be expected to lose characteristic fragments, C_3H_2 from hexa-3-ene-1,5-yne and C_2H_3 from hexa-1-ene-3,5-yne, leaving ions of mass 38 and 49, respectively.[4] We do not observe these ions during our 1500 µsec search time. We infer, therefore, that neither species is responsible for the mass 76 species present during the first few hundred µsec. Nevertheless the one optical spectrum at 1800 µsec indicating a vinyldiacetylene suggests that such a species might be formed later by a slow rearrangement.

The hydrochloride has also been studied. It photolyzed with difficulty, gives no mass 76 transient and slowly produces chlorobenzene after photolysis (after 200 µsec).

We conclude by summarizing our observations and inferences. The products from benzenediazonium-3-carboxylate decomposition include a transient parent mass 76. The fragmentation pattern and its time dependence show that the mass

76 species is different from either of those obtained from the *ortho* or *para* isomers of the precursor. Comparison of the fragmentation pattern with model compounds suggests that 1,3-dehydrobenzene is the most likely assignment of the species, probably in a singlet state, but whether I or II is the better representation is entirely open.



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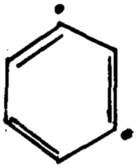

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[**] The starting material, derived from the corresponding 3-aminobenzoic acid, is the most unstable and sensitive of the three isomers and cannot be kept for more than a few minutes, wet or dry, at room temperature without decomposition. The pure dry material detonates even when moved from place to place, and has exploded violently when a small insect alighted on it. Consequently all solutions were used at -78°C and the material was stored at this temperature as a slurry in ether.

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