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THE AZOBENZENE RADICAL CATION, AN INTERMEDIATE DURING DIAZONIUM REACTIONS

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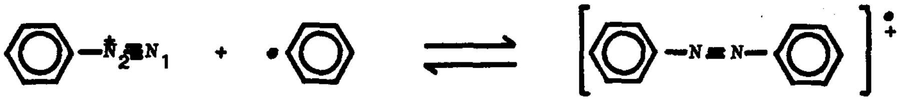
The initial step of diazonium reductions has been formulated as a one-electron transfer from the reducing agent to the diazonium cation (I)[1], resulting either in the formation of nitrogen and a phenyl radical (II)[2] or in the phenyldiazenyl radical (III) as an intermediate[3]. Evidence for III has been claimed by Dixon and Norman[4], who obtained an ESR spectrum during the reduction of I with sodium dithionite. The spectrum showed a quintet splitting characteristic for two equivalent nitrogens with a_N=9.3 Gauss. Later Beckwith and Norman measured the g-value of this radical to be 2.0035[5]. However, Packer and coworkers[6] questioned the ESR assignment, because they found no transient absorption spectrum or other evidence for III during the pulse radiolysis induced reduction of I. Lately, III has been characterized in other systems[3,7]. CIDNP studies during the decompositions of phenylazo alkenes indicate that the g-value of III is smaller than that of the free electron (g_e=2.0023). However, no corresponding ESR signal is found in diazonium reductions. The ESR data of Norman and Dixon disagree badly with the CIDNP results, as the former suggest that III is a π-radical. To resolve this discrepancy we have performed a molecular orbital calculation using the Pople INDO·SCF method[8]. The calculations show that III prefers a bent σ-radical structure. To check the calculations we have determined the signs of some proton and fluorine hyperfine coupling constants (hfs) of fluoro substituted phenyldiazenyl radicals, which we generated from the corresponding phenylazotriphenylmethanes. The calculated signs and values agree with those obtained from computer-simulated CIDNP spectra only for the bent σ-radical structure of III, in which case the nitrogens are inequivalent (a_{N1}=5.8 G, a_{N2}=14.5 G). However, in the linear π-radical arrangement the nitrogens would be almost equivalent (a_{N1}=5.1 G, a_{N2}=4.8 G). We, therefore, conclude that the assignment of the ESR spectrum observed during the reduction of I to III is wrong. Instead we postulate that this ESR spectrum is caused by the azobenzene radical cation (IV). The formation of IV has already been suggested by Waters[9] to result from the addition of II to I:



I II IV

We also have calculated the hfs for IV with the INDO method considering three transoid conformations[10]: a coplanar arrangement, an orthogonal structure and the phenyl rings parallel but staggered. With the orthogonal structure being energetically favored by about 14 Kcal/mole all conformations yield equivalent nitrogen splittings of a magnitude as observed by Dixon and Norman. The averaged value (a_N=9.5 G) agrees particularly well with their experimental value. The g-value of IV[5] is also compatible with those of other nitrogen-containing radical cations[11]. We further assume that the formation of IV is reversible, implying that IV is unstable in solution. This view is supported by mass-spectrometry studies of azobenzenes[12], which decompose via IV into I and phenyl cations in the gas phase. With the reversible formation of the symmetric intermediate IV we can explain the ^{15}N-scrambling in labelled I[13], and the formation of the puzzling sideproduct azobenzene during diazonium reductions[14].

The ^{13}C- and ^{15}N-CIDNP studies of Lippmaa give evidence for the occurrence of III during the thermolysis of diazoaminobenzene[14] but show that III does not account for the ^{15}N-CIDNP in diazonium reductions[15]. Furthermore, these authors found ^{15}N scrambling and spinpolarization in I itself during its reduction with phenolate. This provides additional evidence in favour of a reversible formation of IV. Apparently the CIDNP is built up in IV, from where it is transferred back to I and even further on into its coupling product with phenolate, the p-hydroxyazobenzene (V). Consistently, V shows the same CIDNP pattern as I[15], whereas according to the radical pair theory of CIDNP it should show a pattern complementary to I if V would result from a free-radical combination between III and a phenoxy radical as proposed by Bubnov[16]. In this latter case the p-hydroxyphenyl moiety of V should also show ^{13}C-CIDNP, but its failure proves that V is not a radical-combination product. Thus, Lippmaa's studies clearly show that the diazonium coupling reaction with phenolate is an ionic process and not a free-radical mechanism as falsely concluded by Bubnov. Instead, a side reaction yielding II and then IV accounts for the CIDNP in I and V. The total conversion of I into free radicals might represent a minor reaction pathway as judged from nitrogen scrambling and azobenzene- and arene formation[2], but this is enough to cause CIDNP in the coupling product V.

We want to point out that not all diazonium reductions must necessarily include an electron transfer. Although it is a likely step in polarographic reductions[3] free radicals might reduce I differently: Any alkyl radical could add to I yielding a phenylazoalkane radical cation, which would immediately cleave into II, N_2 and a carbonium ion, thus circumventing the intermediate formation of III. Consistently ESR spectra of alcohol derived radicals are quenched rapidly upon addition of I[5], and it has been considered[6] that the failure to observe the ESR spectrum of II in these systems might be due to its combining with I.

The situation encountered here parallels the conclusions drawn from ESR spectra observed during the decomposition of aryl acylnitrosamines[17]. There a π-radical spectrum, which had been initially attributed to the phenylazooxy radical[18], was later shown to be caused by a nitroxide, resulting from the addition of II to the starting material. The phenylazooxy radical identified later is also a σ-radical[19].

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