

THE HEPTAFULVALENE TRIANION RADICAL

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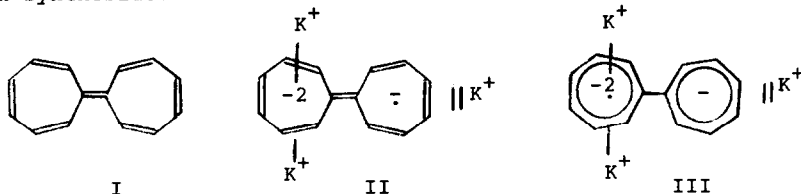
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Since our initial report on trianion radicals, in which the phenanthrene-quinone and oxalate trianion radicals were described,¹ only a few additional examples of this class of compound have been discovered.^{2,3} We now wish to report that the relatively simple hydrocarbon heptafulvalene (I) forms a quite stable trianion radical (I^{-3}).

The heptafulvalene dication,⁴ cation radical,⁵ and anion radical⁵ have been synthesized and studied. In the latter the odd electron is instantaneously



localized on a single tropenyl ring, though cases of slow (methyl THF, -120° , K^+), intermediate (MTHF, -90° , K), and rapid (DMF, electrolytic) exchange of the odd electron and the metal counterion between the two tropenyl rings have been observed. The MO occupied by the odd electron is essentially an antisymmetric tropenyl ABMO which remains largely unperturbed in the heptafulvalene system because it possesses a node at the ring juncture carbon. Another such tropenyl ABMO is potentially available on the other tropenyl ring for trianion radical formation. In the present research it was found that I^- (DME, K) is rapidly exchanging even at -70° , unlike I^- (MTHF or THF, K). The reaction of I^- with excess alkali metal leads initially to nearly diamagnetic solutions (I^{-2}). After 10-30 min potassium, but not sodium,

produces a new radical (I^{-3}): esr (DME, K) G 7.55(2H), 4.92(2H). The hyperfine splittings (hfs) closely resemble those of I^- : esr (MTHF, K, -120°) G 8.22(2H), 5.02(2H). However the rings of I^{-3} are inequivalent even in DME and at all temperatures studied (-70° to RT). Titrations demonstrated the uptake of 3 atoms of potassium/molecule of I; the new species is indeed a trianion radical. To further verify this, I^{-3} was generated in a different manner. First, biphenyl anion radical was added to I (1:1 mole ratio) kept at 78° ; I^- resulted instantly (color change, esr). Then, separately, a 4:1 ratio of biphenyl anion radical to I was combined: the new species resulted immediately. Finally, the addition of I to I^{-3} (2:1 ratio) at -78° gave I^- with a signal intensity increase of greater than twofold. Evidently the new species has the ring system of I intact.

Structure II is proposed for I^{-3} . The similarity of the esr hfs of I^- and I^{-3} is plausible in that the odd electron in each occupies the same kind of tropanyl MO. The much slower exchange in I^{-3} is explicable in terms of tighter ion pairing in the dianionic moiety of II than in the monoanionic one of I^- . Alkali metal salts of the tropenide dianion radical are exceptionally tightly ion paired, as indicated by their large metal hfs and the slowness of metal exchange. We propose that the monoanionic moiety of II exists in a solvent separated ion paired state, at least in DME, on the basis of the relatively rapid exchange found for I^- and the tendency of DME to promote this type of ion pairing. In contrast to the tropenide dianion radical, I^{-3} exhibits no metal hfs, since its odd electron density is on the more weakly ion paired ring. We consider structure III specifically excluded.

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