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REACTIONS OF PERYLENE CATION RADICAL WITH HALIDE IONS[1,2]

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The ways in which nucleophiles may react with cation radicals have recently been discussed in terms of the Dewar-Zimmerman rules.[3-6] A nucleophile which adds either slowly or not at all to a cation radical is thought to be forbidden by symmetry properties from undergoing bond-forming orbital overlap with the cation radical.[3,6] In such circumstances the nucleophile may then undergo an electron transfer reaction with the cation radical. Central to this idea are the reactions of perylene cation radical with halide ions. That is, it had been found that perylene cation radical appeared to be inert to reaction with fluoride ion, and to be reduced by chloride, bromide, and iodide ions,[7] and these observations were considered to be a critical test in favor of the symmetry-forbiddenness proposal.[3,6] Most recently, the kinetics of reaction of perylene cation radical with chloride, bromide, and iodide ion have been measured, and it is concluded that only iodide ion clearly reduces the cation radical by direct electron transfer. In contrast, the second-order rate constants suggest that chloride, and perhaps bromide ion, too, reduces the cation radical by way of an initial nucleophilic addition followed by loss of halogen atom from the adduct.[8]

There are numerous examples of anodic fluorinations in the literature. These are also thought to be genuinely reactions of anodically formed cation radicals with fluoride ion.[5] Furthermore, forceful arguments have been made for the case that metal-fluoride (e.g., CoF_3) fluorinations of aromatic hydrocarbons are also cation-radical reactions.[9] In contrast, successful reactions of isolated cation radical salts with fluoride ion have never been reported. This distinction has led, in part, to contradictory views on the use of the Dewar-Zimmerman rules.[4,5]

In view of these anomalies we have been re-investigating the reactions of perylene cation radical with halide ions, and a preliminary report of our results appears to be warranted.

Reaction with fluoride ion is indeed very slow. The major product is perylene, but fluoroperylene is also formed and is detectable by mass spectrometry. A solution of 116 mg of $P^{\cdot+}ClO_4^-$ (made by exchange of perylene in ethyl acetate solution with dibenzodioxin cation radical perchlorate, and assayed iodometrically as 86% cation radical content) in 75 ml of acetonitrile was stirred with solid KF until the cation radical color had disappeared (five days). The filtered solution was evaporated, and the residue was dissolved in methylene chloride, washed with water and dried over K_2CO_3 to give 52 mg of solid. This appeared from tlc to be only perylene. Nevertheless, mass spectrometry on the crude product showed that fluoroperylene was present, m/e by mass matching 270.0852; required: 270.0845.[10] The relative intensities of m/e 252:270 were 100:5.17, but since these ions originated from two substances in a mixture the data indicate only that the perylene was the major component. All attempts to separate the perylene and fluoroperylene by tlc have failed. Our conclusion is that fluoride ion does add to the isolated perylene cation radical but only indifferently. Although anodic fluorination of perylene itself has not been reported,[5] the great difference between other successful anodic reactions and the poor reactivity of the perylene cation radical may be a general phenomenon and lie in the way in which an initial adduct, formed albeit reluctantly, (eq. 1) is oxidized. This may be facile at an anode (eq. 2) but not so facile by $ArH^{\cdot+}$ (eq. 3). A similar explanation may apply to the metal-fluoride fluorinations. The reaction which led to so much perylene is not known, but may be one with the solvent system during the long time of contact.[7]

$$ArH^{\cdot+} + F^- \rightleftharpoons ArHF^{\cdot} \qquad (1)$$

$$ArHF^{\cdot} - e^- \longrightarrow ArHF^+ \longrightarrow ArF + H^+ \qquad (2)$$

$$ArHF^{\cdot} + ArH^{\cdot+} \longrightarrow ArH + ArF + H^+ \qquad (3)$$

Reaction of perylene cation radical with both chloride and bromide ion gives both mono- and dihalogenoperylene. The products have been identified, again by mass spectrometry, and they are separable by multi-plate tlc and column chromatography. Thus, reaction of 75 mg of $P^{\cdot+}ClO_4^-$ (91% cation radical content) in 25 ml of acetonitrile with 1 g of LiCl gave 59 mg of product. Preparative scale tlc separation was not possible unless very small amounts (0.25 mg) of the mixture were used. By this technique three products were obtained from aliquots of the mixture for mass-matching spectrometry, in order of increasing R_f: perylene (10 mg), chloroperylene (8.3 mg, believed to be 3-chloroperylene) m/e 286.0612, reqd. 286.0549, and a dichloroperylene (6.1 mg, believed to be 3,9-dichloroperylene) m/e 320.0135, reqd. 320.0159. Each tlc product was contaminated by small amounts of neighbor-band product. Column chromatography eventually gave essentially pure chloroperylene, mp 238-240°, m/e 286.0550.[10] A sample of 3,9-dichloroperylene, mp 295-296°, m/e 320.01598[10] for chromatographic controls was prepared from perylene and PCl_5.[11,12] This reaction also gave, after multi-plate tlc, the same monochloroperylene as obtained in the cation-radical reaction. The monochloroperylene appears never to have been isolated or reported before, however.

Reaction of perylene cation radical with bromide ion has given analogous mass spectrometric results but separation of pure mono- and dibromoperylene has not yet been carried out.

The reason for the difference between the present results and the former[7] is not known, but may be in the timing of the quenching with iodide ion which was used in the former (but not the present) chloride and bromide reactions, and in not then recognizing the difficulties of separating perylene and fluoroperylene by tlc.

The formation of both mono- and dihalogenoperylenes from the chloride and bromide ion reactions suggests that the halogenations may be electrophilic ones following electron exchange. The alternative is successive half-regeneration reactions of the normal cation radical-nucleophile type, the first with $P^{\cdot +}$ and a second with subsequently-formed halogeno-$P^{\cdot +}$. Such reactions are ordinarily second order in cation radical, i.e., overall third order in reactants. The recently reported kinetics for the disappearance of $P^{\cdot +}$ are more in line with a follow-up electrophilic halogenation.[8] It is quite unlikely that fluoroperylene is formed in this way, though. The pattern of reactions appears to be that fluoride ion may follow the usual half-regeneration reaction but only to a limited extent, and that iodide ion reduces perylene completely. Between these extremes the paths of the chloride and bromide ion reactions are still uncertain.

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