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ON THE REACTION OF NAPHTHALENE ANION RADICAL WITH WATER

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We wish to report the results of experiments that provide insights into the mechanism of the reaction of aryl anion radicals with water. In both this reaction and the related carbonation reaction, half of the original hydrocarbon is recovered unchanged and dihydro derivatives of the parent aromatic hydrocarbons are formed, in the absence of excess alkali metal.(1,2,3) A mechanism (I) proposed by Paul, Lipkin, and Weissman(4), to account for these observations, involves the sequence of steps shown in equations 1-3.

$$ArH^{\overline{\cdot}} + H_2O \longrightarrow ArH_2\cdot + OH^- \tag{1}$$

$$ArH_2\cdot + ArH^{\overline{\cdot}} \longrightarrow ArH_2^- + ArH \tag{2}$$

$$ArH_2^- + H_2O \longrightarrow ArH_3 + OH^- \tag{3}$$

Two attractive alternate mechanisms which can account for the observed products involve disproportionations: first a radical disproportionation reaction (II) (eq. 4, 5);

$$ArH^{\overline{\cdot}} + H_2O \longrightarrow ArH_2\cdot + OH^- \tag{4}$$

$$2\ ArH_2\cdot \longrightarrow ArH_3 + ArH \tag{5}$$

and second, a radical anion disproportionation (III) to give the thermodynamically less favored(5) (but probably more reactive) dianion (eq. 6, 7, 8).

$$2\ ArH^- \longrightarrow ArH^{=} + ArH \qquad (6)$$

$$ArH^{=} + H_2O \longrightarrow ArH_2^- + OH^- \qquad (7)$$

$$ArH_2^- + H_2O \longrightarrow ArH_3 + OH^- \qquad (8)$$

It is known that partial protonation of certain aryl anion radicals with stearyl alcohol in the presence of excess alkali metal yields a solution of the dihydro anion (ArH_2^-)(6), and that under certain conditions some aryl anion radicals disproportionate to dianion and hydrocarbon.(5a,7) (eq. 6). And it is known that very recently a stable dianion of naphthalene was prepared using lithium in tetrahydrofuran.(8) Nevertheless, it was not known whether either of these species is of importance in the reaction with water, nor had any test of the proposed mechanism been performed. We anticipated that information concerning the validity of the above mechanisms could be provided by a study of the products resulting from reaction with labeled water.

A solution of sodium naphthalene prepared from 1.60 g. (12.5 mmole) of naphthalene and 0.30 g. (13 mmole) of sodium in 40 ml. of tetrahydrofuran was quenched with 2.0 ml. of H_2^3O (1 millicurie/ml.). The products were isolated by addition of water and extraction with pentane. Separate experiments indicated that recovered material accounted for 95-98% of the original naphthalene. Analysis of the reaction products, performed on a radioassaying gas chromatography apparatus, indicated 40.7% dihydronaphthalenes, 58.7% naphthalene, and 0.6% tetralin. *All* of the radioactivity was concentrated in the dihydronaphthalenes and tetralin. This was confirmed by isolating the naphthalene by recrystallization (mp 80-80.5°) and subsequent analysis of large samples. Hence, no low level activity was present in the naphthalene. The analytical method would have detected 0.1% of the activity found for dihydronaphthalene.

In a separate experiment tritiated water (1 millicurie/ml.) was added slowly to a tetrahydrofuran solution of sodium naphthalene over a period of two hours. The water was metered in by a "constant rate syringe drive" apparatus. The recovered material (69% yield) consisted of 83% naphthalene, 15% dihydronaphthalenes, and 2% tetralin. The remainder of the material presumably goes to "dimer."(9) Naphthalene isolated from this reaction mixture and analyzed as above again was completely devoid of radioactivity.

If one can make the reasonable assumption that reaction with water results in attachment of the proton by a normal sigma bond, protonation of the anion radical indelibly marks it for reduction. Proton, hydrogen atom, or hydride ion transfer between the originally protonated species, or any species derived from it, and naphthalene anion radical or neutral naphthalene, is ruled out unless both products of such an act are eventually converted to dihydronaphthalenes.

Clearly mechanism II must not be valid because this scheme predicts that the recovered naphthalene would be labeled according to the following considerations. The radical formed by reaction of the radical anion and tritiated water should have a corresponding activity since no kinetic isotope effect is expected for proton abstraction reactions by strong bases.(10) Disproportionation of such a labeled radical to naphthalene and dihydronaphthalene would of course lead to incorporation of tritium in the recovered naphthalene.

Moreover, the results suggest (but do not demand) that mechanism III is unlikely for the following reasons. The equilibrium depicted in equation 6 must be very rapid if the scheme is to account for the results. When an excess of water is added rapidly, reactions 7 and 8 must be rapid and moreover irreversible. When small quantities of water are added slowly, however, the concentration of ArH_2^- is expected to build up and proton transfer between ArH_2^- and $ArH^=$ would seem plausible. This, of course, results in incorporation of tritium into naphthalene. Indeed these experiments, which provide the first test of Paul, Lipkin, and Weissman mechanism, reinforce the proposed scheme.

In addition to information about the mechanism of the quenching reaction, our analytical scheme provides the detection of tetralin, heretofore unreported. The data provide insights into the probable path of tetralin formation. The fact that no activity is found in the naphthalene while the tetralin does have activity rules out a reaction in which the dihydronaphthalene (ArH_3) undergoes base-catalyzed disproportionation, in a manner similar to the reaction of 1,3-cyclohexadiene in the presence of strong base.(11) It is evident that no dihydronaphthalene can be converted to naphthalene in the tetralin formation process. A scheme to account for these facts is given in equations 9-12.

$$ArH_3 + ArH^{\overset{-}{\cdot}} \longrightarrow ArH_3^{\overset{-}{\cdot}} + ArH \tag{9}$$

$$ArH_3^{\overset{-}{\cdot}} + H_2O \longrightarrow ArH_4\cdot + OH^- \tag{10}$$

$$ArH_4\cdot + ArH^{\overset{-}{\cdot}} \longrightarrow ArH_4^- + ArH \tag{11}$$

$$ArH_4^- + H_2O \longrightarrow ArH_5 + OH^- \tag{12}$$

The critical step in this process, electron transfer from the naphthalene anion radical to dihydronaphthalene, is quite plausible since the reduction potential of 1,2-dihydronaphthalene is of the same magnitude as that of naphthalene.(12) A scheme involving disproportionation of the dihydronaphthalene radical anion to give a dinegative species is far less likely in view of the anticipated high energy of this intermediate. Insofar as the formation of dihydronaphthalene from naphthalene and the formation of tetralin from dihydronaphthalene are related these considerations contribute additional support that mechanism II is unlikely.

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