

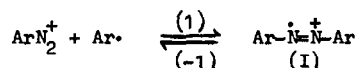
ON THE ADDITION OF RADICALS TO ARENEDIAZONIUM IONS

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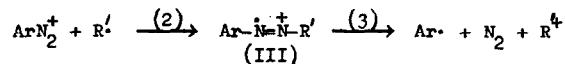
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In 1942 Waters¹ suggested aryl radicals add to the terminal nitrogen of arenediazonium ions, reaction (1), and this was confirmed by a kinetic study of the free-radical chain reaction between toluene-*p*-diazonium ions and methanol² (and since extended to other reducing agents³) and as a result of these studies Packer suggested that the free radical detected by Dixon and Norman⁴ by esr in benzenediazonium ion-dithionite solutions was the azobenzene radical cation (I) rather than the phenyldiazenyl radical, Ar- $\ddot{N}=N\cdot$ (II). Very recently Bargon and Seifert⁵ have



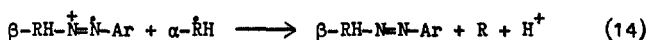
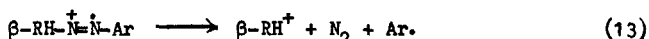
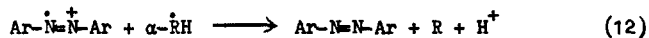
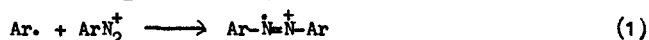
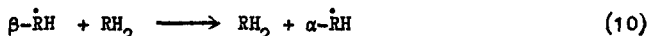
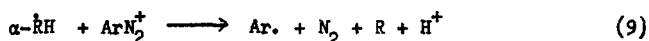
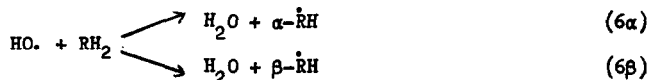
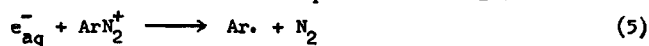
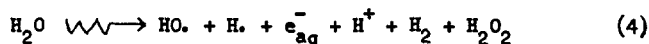
shown by CIDNP studies and MO calculations that the observed radical is not (II) and that the *g* value is very close to that calculated for (I). By considering reaction (1) to be reversible, ie (I) to be unstable, they were able to explain ¹⁵N-scrambling effects in labelled arenediazonium ions and reinterpret CIDNP effects in coupling reactions. They further suggested that radical reductions of diazonium ions might occur by addition of alkyl radicals to diazonium ions followed by the rapid decomposition of the arylazoalkane radical cation (III), reaction (2) and (3), rather than by electron transfer from the reducing radical to the



diazonium ion to give (II) as presumably occurs in polarography.

We now report kinetic evidence (a) for the addition of alkyl radicals to diazonium ions, but (b) against (I) or (III) breaking down rapidly as shown in (-1) and (3) and (c) against reduction occurring via addition to give (III). Consider the following general scheme for reaction in aqueous solution initiated by γ -radiation; where RH₂ represents a reducing agent (an alcohol, formate, acetaldehyde), and α -RH and β -RH are the radicals formed by abstraction

of a hydrogen atom α and β respectively to the oxygen atom:



We have found three different classes of kinetics with change in reducing agent. For methanol and formate (where $\beta\text{-}\dot{\text{R}}\text{H}$ cannot be formed) we find a plot of $\underline{G}(-\text{ArN}_2^+)$, the number of diazonium ions destroyed per 100 eV of energy absorbed, against $[\text{RH}_2]/[\text{ArN}_2^+]$ to be linear with a very small intercept, and that there is no dose-rate effect. This is consistent with propagation by reactions (8) and (9) and termination by (1) and (12), this mechanism leading to the expression

$$\underline{G}(-\text{ArN}_2^+) = \frac{1}{2}\underline{G}_r(2 + \underline{k}_8[\text{RH}_2]/\underline{k}_1[\text{ArN}_2^+])$$

where \underline{G}_r is the primary radical yield, $\underline{G}_{\text{OH}} + \underline{G}_{\text{H}} + \underline{G}_{e_{\text{aq}}^-}$, on radiolysis of water and has the value approximately 6 (100 eV)⁻¹. (Reaction (12) was not properly considered in our earlier papers^{2,3} and the factor of 1/2 was omitted.) The kinetics are quite inconsistent with reaction (-1) being rapid, as if it were $\underline{G}(-\text{ArN}_2^+)$ would be proportional to $[\text{RH}_2]^{1/2}$, $\underline{D}^{-1/2}$ and independent of $[\text{ArN}_2^+]$, where \underline{D} is the dose-rate. Our data show that \underline{k}_{-1} must be less than 10 s⁻¹ and correspondingly that \underline{k}_1 must be greater than 10⁶ mol l⁻¹.

When both α - and β -hydrogen abstraction can occur (with ethanol, propan-2-ol and acetaldehyde) we again find no dose-rate effect and a linear plot of $\underline{G}(-\text{ArN}_2^+)$ against $[\text{RH}_2]/[\text{ArN}_2^+]$, but extrapolation to zero $[\text{RH}_2]/[\text{ArN}_2^+]$ gives values of $\underline{G}(-\text{ArN}_2^+)$ of 157, 164 and

149 (100 eV)⁻¹ in the three cases respectively. Changing from (CH₃)₂CHOH to (CD₃)₂CHOH leads to an increase in both intercept and slope showing β-abstraction to occur.⁶ A mechanism involving propagation by reactions (8), (9) and (10) and termination by (11) and (14) leads to the expression

$$\begin{aligned} \underline{G}(-\text{ArN}_2^+) &= \frac{1}{2}G_r + \frac{1}{2} \left(1 + \frac{k_{8\alpha}}{k_{8\beta}} \right) \left\{ \frac{G_{e^-}}{k_{6\alpha} + k_{6\beta}} + \left(\frac{k_{6\alpha}}{k_{6\alpha} + k_{6\beta}} \right) G_{\text{OH}} \right. \\ &+ \left. \left(\frac{k_{7\alpha}}{k_{7\alpha} + k_{7\beta}} \right) G_{\text{H}} \right\} + \frac{1}{2}G_r \left(1 + \frac{k_{8\alpha}}{k_{8\beta}} \right) \frac{k_{10}[\text{RH}_2]}{k_{11}[\text{ArN}_2^+]} \end{aligned}$$

which is consistent with our data and with the postulate of Seifert that alkyl radicals, β-RH in this system, add to diazonium ions. However our kinetics are quite inconsistent with reaction (13) occurring as this would lead to a measurable inverse dose-rate effect if $k_{13} > 10 \text{ s}^{-1}$ and if it were rapid would prevent chain termination. Thus our results do not support the suggestion that (III) breaks down rapidly according to reaction (3) where R' is a simple alkyl radical.

With benzyl alcohol as reducing agent we find $\underline{G}(-\text{ArN}_2^+)$ to be proportional to $[\text{ArN}_2^+]$ and $D^{-1/2}$ and independent of $[\text{RH}_2]$. This is consistent with propagation by reactions (8) and (9) but with (8) being sufficiently fast and (9) sufficiently slow for termination by (15)³. This mechanism leads to the expression

$$\underline{G}(-\text{ArN}_2^+) = \frac{G_{e^-}}{k_{6\alpha}} + k_9 (100 \frac{N_A G_r}{k_{11}} \frac{D}{k_1})^{1/2} [\text{ArN}_2^+]$$

where N_A is Avogadro's constant. On changing the substituent on ArN_2^+ we find k_9 increases in the order p-CH₃O, p-CH₃, p-Cl, which is the order of increasing positive half-wave reduction potential measured polarographically and corresponding to a one-electron transfer to give (II) as intermediate, with p-NO₂ being the most positive (easily reduced).⁷ On the other hand from the system with methanol or formate as reducing agent we find that the ratio k_8/k_1 increases in the order p-CH₃, p-Cl, p-NO₂. In this system the substituent effect would probably manifest itself mainly through ArN_2^+ in reaction (1) rather than through Ar. in (8) or (1) because Ar. is a σ-radical and thus should be fairly insensitive to para substituents, whereas addition of a radical to the diazonium ion will almost certainly involve the latter's π-orbitals. If this is so, then the substituent effect in ArN_2^+ for addition of Ar. is the reverse of that for reduction by C₆H₅CHOH. Although the conclusion above that reaction (3) does not occur rapidly when R' = β-RH did not preclude it being rapid when R' = α-RH (as α-RH⁺ would be more stable than

β -RH⁺), these substituent effects do suggest that reduction by α -RH does not in fact occur by addition to give (III) followed by breakdown, but is rather an electron transfer process.

Full details of this work will be published elsewhere.

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