Free-Radical Reductions of Arenediazonium Ions in Aqueous Solution. Part II.[1] Kinetics of Reactions with Formate, Cysteine, Methanol, Hypophosphite, and Phosphite as Reducing Agents

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Two classes of kinetics are exhibited in the γ-radiation-induced radical-chain reduction of toluene-*p*-diazonium ions with the above reducing agents in aqueous oxygen-free solution, the overall reaction being $ArN_2^+ + RH_2 \longrightarrow ArH + N_2 + R + H^+$. In class A, $G(-ArN_2^+)$ is proportional to $[RH_2]/[ArN_2^+]$ and independent of dose rate; and in class B, proportional to $[ArN_2^+]/(\text{dose rate})^{\frac{1}{2}}$ and independent of $[RH_2]$. A reaction sequence to account for these observations is proposed, the relative rates of the reactions involved determining the class of kinetics exhibited. By altering the concentration of ArN_2^+ it is possible to change the behaviour of the system from one class to the other. The rate of hydrogen abstraction by the *p*-tolyl radical from RH_2 is in the order hypophosphite and phosphite > formate > methanol > formic acid. Addition of acid decreased $G(-ArN_2^+)$ in the case of the oxyanions, but not for methanol.

REPLACEMENT of the amino-group on an aromatic nucleus by hydrogen is usually achieved by diazotisation followed by reduction, and a variety of reducing agents and conditions have been reported.[2] The most common reducing agents are hypophosphorous acid and alcohols. Kornblum studied the kinetics of reduction with H_3PO_2 and concluded that it occurred by a free radical chain mechanism[3] [equations (i)—(iii)]. He found a similar

$$ArN_2{-}Y \longrightarrow Ar\cdot + N_2 + Y\cdot \qquad \text{(i)}$$

$$Ar\cdot + H_3PO_2 \longrightarrow ArH + H_2\dot{P}O_2 \qquad \text{(ii)}$$

$$H_2\dot{P}O_2 + ArN_2^+ \longrightarrow Ar\cdot + N_2 + HPO_2\ (\xrightarrow{H_2O} H_3PO_3) \qquad \text{(iii)}$$

but slower and less efficient reaction with phosphorous acid.[4] Recently Beckwith[5] has shown by e.s.r. flow studies that the radical $H\dot{P}O_2^-$ derived from hypophosphite and the radicals $H\dot{P}O_3^-$ and $\dot{P}O_3^{2-}$ derived from phosphite react with arenediazonium ions to produce aryl radicals, providing direct evidence for the second propagating step (iii). He suggests that phosphorous acid is worthy of further investigation as a reducing agent.

De Tar and his co-workers concluded that reductions with alcohols occurred by a somewhat similar chain

$$Ar\cdot + R^1R^2CHOH \longrightarrow ArH + R^1R^2\dot{C}OH \qquad \text{(iv)}$$

$$ArN_2^+ + R^1R^2\dot{C}OH \longrightarrow Ar\cdot + N_2 + R^1R^2CO + H^+ \qquad \text{(v)}$$

reaction[6] [equations (iv) and (v)], and again supporting evidence for this came from e.s.r. flow experiments.[7]

The study of the kinetics of these and related chain reactions of diazonium ions in aqueous media has been made difficult by the problem of initiating the chain reactions quantitatively, the exact nature and rates of the initiating reactions being uncertain.[8] Radiolysis of water or dilute aqueous solution results in the formation of three radicals, hydroxyl, hydrogen atom, and aquated electron, in known yield, and each of these radicals can initiate a chain reaction. Detailed kinetics of a variety of reactions initiated in this way have been reported.[9]

However, no quantitative study of the kinetics of the reduction of arenediazonium ions by free-radical chain reactions has been reported. We are making such a study with particular attention to (*a*) factors affecting chain length, (*b*) the nature of the chain termination steps, (*c*) the effect of substituent groups on the arenediazonium ion, and (*d*) the magnitude of the rate constants. By studying various reducing agents it is hoped that a clearer insight into the relative efficiencies of these reagents will be obtained.

In Part I we described our experiments on the reaction of toluene-*p*-diazonium ions and methanol in aqueous solution initiated by γ-radiation; we found $G(-ArN_2^+)$, the number of diazonium ions destroyed per 100 eV of radiation energy absorbed, to be proportional to $[MeOH]/[ArN_2^+]$ and independent of dose rate, confirming that the propagation steps were those proposed by De Tar and showing further that termination was caused by the reaction of *p*-tolyl radicals with the diazonium ion. We now describe our studies on toluene-*p*-diazonium and anisole-*p*-diazonium ions with formate, hypophosphite, phosphite, and cysteine.

EXPERIMENTAL

Materials.—The diazonium tetrafluoroborates were prepared by precipitation on addition of 40% HBF_4 to diazotised *p*-toluidine and *p*-anisidine, and were recrystallised from warm water. Methanol, cysteine hydrochloride, disodium hydrogen phosphite hydrate (Riedel-de Haen), formic acid (AnalaR), sodium formate, sodium hypophosphite (B.D.H.), and hypophosphorous acid (May and Baker) were used as supplied. Triply distilled water was used throughout.

γ-Radiolysis and Analysis.—Samples (10 or 5 ml) were deaerated by shaking under vacuum in the reaction vessels, each of which had a spectrophotometer cell (2, 5, or 10 mm) attached on a side arm. The concentration of the diazonium ion was measured spectrophotometrically after each of several exposures to γ-radiation from a 100 Ci ^{60}Co source,

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[1] Part I, J. E. Packer, D. B. House, and E. J. Rasburn, *J. Chem. Soc.* (*B*), 1971, 1574.

[2] N. Kornblum, *Org. Reactions*, 1944, **2**, 262.

[3] N. Kornblum, G. D. Cooper, and J. E. Taylor, *J. Amer. Chem. Soc.*, 1950, **72**, 3013.

[4] N. Kornblum, A. E. Kelley, and G. D. Cooper, *J. Amer. Chem. Soc.*, 1952, **74**, 3074.

[5] A. L. J. Beckwith, *Austral. J. Chem.*, 1972, **25**, 1887.

[6] D. F. De Tar and M. N. Turetzky, *J. Amer. Chem. Soc.*, 1955, **77**, 1745; D. F. De Tar and T. Kosugi, *ibid.*, 1958, **80**, 6072.

[7] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 403.

[8] E. S. Lewis and D. J. Chalmers, *J. Amer. Chem. Soc.*, 1971, **93**, 3267.

[9] K. M. Bansal and G. R. Freeman, *Radiation Res. Rev.*, 1971, **3**, 209.

and $G(-\mathrm{ArN_2^+})$ values were calculated from the initial slope of the absorbance–dose plot. Extinction coefficients and wavelengths were: toluene-*p*-diazonium ion, 16,300 l mol^{-1} cm^{-1} at 278 nm; and anisole-*p*-diazonium ion, 22,000 l mol^{-1} cm^{-1} at 314 nm.

Pulse Radiolysis and Dosimetry.—Techniques were as described in Part I.

RESULTS AND DISCUSSION

The general reaction for the reduction of the diazonium ion to the parent aromatic hydrocarbon may be written as (vi), where $\mathrm{RH_2}$ is a two-electron reducing agent. For

$$\mathrm{ArN_2^+ + RH_2 \longrightarrow ArH + R + N_2 + H^+} \qquad \text{(vi)}$$

the radiation-induced reaction in aqueous solution the initiation, propagation, and termination steps shown in reactions (1)—(11) can be postulated. All three radical

$$\mathrm{H_2O \rightsquigarrow HO\cdot + H\cdot + e_{aq}^-} \quad \mathrm{(+H_2 + H_2O_2)} \qquad (1)$$

$$\mathrm{e_{aq}^- + H^+ \longrightarrow H\cdot} \qquad (2)$$

$$\left.\begin{array}{ll} \mathrm{e_{aq}^- + ArN_2^+ \longrightarrow Ar\cdot + N_2} & (3) \\ \mathrm{H\cdot + RH_2 \longrightarrow H_2 + \dot{R}H} & (4) \\ \mathrm{HO\cdot + RH_2 \longrightarrow H_2O + \dot{R}H} & (5) \end{array}\right\}\text{initiation}$$

$$\left.\begin{array}{ll} \mathrm{Ar\cdot + RH_2 \longrightarrow ArH + \dot{R}H} & (6) \\ \mathrm{ArN_2^+ + \dot{R}H \longrightarrow Ar\cdot + N_2 + R + H^+} & (7) \end{array}\right\}\text{propagation}$$

$$\left.\begin{array}{ll} \mathrm{Ar\cdot + ArN_2^+ \longrightarrow products} & (8) \\ \mathrm{2\dot{R}H \longrightarrow products} & (9) \\ \mathrm{2Ar\cdot \longrightarrow ArAr} & (10) \\ \mathrm{Ar\cdot + \dot{R}H \longrightarrow ArH + R} & (11) \end{array}\right\}\text{termination}$$

species from water radiolysis can initiate a chain reaction, and the initiation yield should not be affected by pH as reaction of $\mathrm{e_{aq}^-}$ with hydrogen ions produces hydrogen atoms.

If termination takes place by reaction (8) alone, a stationary state analysis of this mechanism gives equation (A).

$$G(-\mathrm{ArN_2^+}) = G_r(2 + k_6[\mathrm{RH_2}]/k_8[\mathrm{ArN_2^+}]) \qquad \text{(A)}$$

where $G_r = G_{\mathrm{OH}} + G_{\mathrm{H}} + G_{\mathrm{e^-_{aq}}} \simeq 6$.

We call this class A kinetics, and our previously reported results with methanol fall into this class. Plots of $G(-\mathrm{ArN_2^+})$ against $[\mathrm{RH_2}]/[\mathrm{ArN_2^+}]$ give values of k_6/k_8, and this was found to be 1/30 for methanol and toluene-*p*-diazonium ions.

Formate and Formic Acid with Toluene-p-*diazonium Ions.*—Figures 1 and 2 show the effect of $[\mathrm{ArN_2^+}]$, $[\mathrm{HCO_2^-}]$, and pH on $G(-\mathrm{ArN_2^+})$ for the toluene-*p*-diazonium ion–sodium formate system at a dose rate of 1·1 × 10^{16} eV l^{-1} s^{-1}. A ten-fold decrease in dose rate did not alter the yields. The kinetics of the reaction in the absence of added acid are clearly of the same class as for methanol, but the chain length is much greater. Recently Beckwith and Norman, using the e.s.r. flow technique,[7] showed that the $\dot{\mathrm{C}}\mathrm{O_2^-}$ radical reduces diazonium ions. Thus the propagation steps are (6a) and (7a). From a

$$\mathrm{Ar\cdot + HCO_2^- \longrightarrow ArH + \dot{C}O_2^-} \qquad \text{(6a)}$$

$$\mathrm{ArN_2^+ + CO_2^- \longrightarrow Ar\cdot + N_2 + CO_2} \qquad \text{(7a)}$$

plot of $G(-\mathrm{ArN_2^+})$ against $[\mathrm{HCO_2^-}]/[\mathrm{ArN_2^+}]$, the k_6/k_8 value for this system is 1·8. Combining this with the k_6/k_8 value for methanol leads to the expression (vii).

$$\frac{k(p\text{-}\mathrm{MeC_6H_4\cdot + HCO_2^-})}{k(p\text{-}\mathrm{MeC_6H_4\cdot + MeOH})} = 54 \qquad \text{(vii)}$$

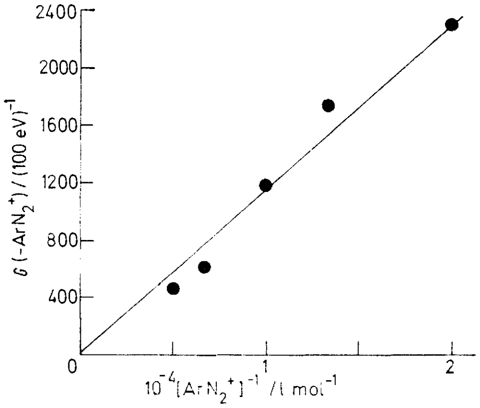

FIGURE 1 $G(-\mathrm{ArN_2^+})$ as a function of $[\mathrm{ArN_2^+}]$ for toluene-*p*-diazonium ions and 1·0 × 10^{-2}M-sodium formate; dose rate, 1·1 × 10^{16} eV l^{-1} s^{-1}

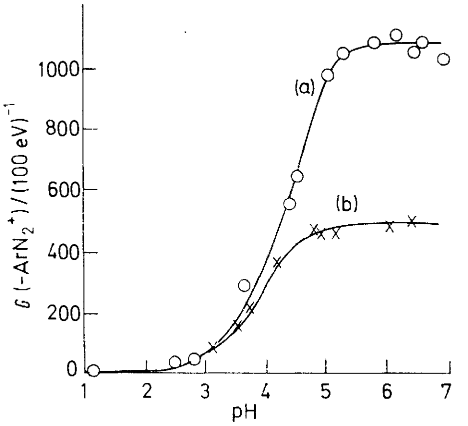

FIGURE 2 $G(-\mathrm{ArN_2^+})$ as a function of pH for toluene-*p*-diazonium ions (10^{-4} mol l^{-1}) and sodium formate; dose rate, 1·1 × 10^{16} eV l^{-1} s^{-1}; (a) $[\mathrm{HCO_2^-}]$ = 1·0 × 10^{-2} mol l^{-1}, (b) $[\mathrm{HCO_2^-}]$ = 0·5 × 10^{-2} mol l^{-1}

The corresponding ratios for hydrogen abstraction from these two substrates by HO· and H· are 5 and 130, respectively.[10] Thus the *p*-tolyl radical falls between HO· and H· in its selectivity and therefore probably in its reactivity.

As shown in Figure 2, $G(-\mathrm{ArN_2^+})$ falls off with pH in a way implying that the conjugate acid of a reactive species is much less reactive. In principle this could be because k_6 for formic acid is much less than for formate anion, or k_7 for $\dot{\mathrm{C}}\mathrm{O_2H}$ is much less than for $\dot{\mathrm{C}}\mathrm{O_2^-}$. It has been shown that $\dot{\mathrm{C}}\mathrm{O_2H}$ reduces aryl halides less readily

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[10] M. Anbar and P. Neta, *Internat. J. Appl. Radiation Isotopes*, 1967, **18**, 493.

than does $\dot{C}O_2^-$.[11] However the pH at the mid-point of the plot in Figure 2 is very close to the pK_a value of formic acid, suggesting that the effect is caused by aryl radicals abstracting hydrogen from formic acid much more slowly than from formate. Earlier work gives the pK_a of $\dot{C}O_2H$ as about the same as that for HCO_2H,[12] but a more recent paper[13] gives a value of 1·4. Further evidence for the pH effect operating through reaction (6) comes from Beckwith and Norman's observation that $\dot{C}O_2^-$ or $\dot{C}O_2H$ reacts readily with diazonium ions at pH 1—2.[11] If Buxton's value of pK_a($\dot{C}O_2H$) is correct, this work would not be proof that $\dot{C}O_2H$ does reduce diazonium ions, as at pH 1—2 reduction could occur *via* $\dot{C}O_2^-$ and reaction (12).

$$\dot{C}O_2H \rightleftharpoons \dot{C}O_2^- + H^+ \qquad (12)$$

That $\dot{C}O_2H$ does in fact react rapidly with toluene-*p*-diazonium ions can be deduced from our results shown in Figure 3. On reducing the pH to zero and increasing the formic acid concentration a chain reaction of appreciable length occurred, with $G(-ArN_2^+)$ still inversely proportional to $[ArN_2^+]$. Here the contribution of formate ions to $G(-ArN_2^+)$ calculated from equation (A) is only about 16, showing that formic acid, in sufficiently high concentration for reaction (6) to compete with reaction (8), can reduce diazonium ions by a class (A) mechanism. The increase in $G(-ArN_2^+)$ with pH shown in Figure 3 is caused by increase in concentration of formate ion. As a class (A) mechanism operates at pH 0, reaction (7) for $\dot{C}O_2H$ must be relatively fast. If it were not the system would show class (B) kinetics (see later). It has been shown[14] that $\dot{C}O_2H$ reacts with formic acid to give the adduct $HO_2C-\dot{C}(OH)_2$. Our results do not differentiate between this and $\dot{C}O_2H$ as the reducing agent.

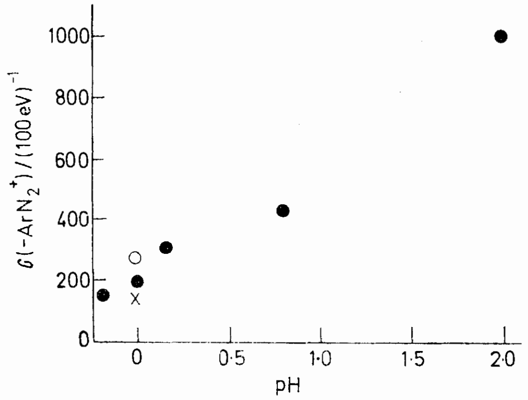

FIGURE 3 $G(-ArN_2^+)$ dependence on $[ArN_2^+]$ and pH for toluene-*p*-diazonium ions and M-formic acid; $[ArN_2^+]$/mol l^{-1}: ○ $0·5 \times 10^{-4}$, ● $1·0 \times 10^{-4}$, × $1·5 \times 10^{-4}$

From the values of $G(-ArN_2^+)$ at pH 0 a value of k_6/k_8 of 3×10^{-3} for the formic acid–toluene-*p*-diazonium ion system is found. This leads to expression (viii).

$$\frac{k(p\text{-}MeC_6H_4\cdot + HCO_2^-)}{k(p\text{-}MeC_6H_4\cdot + HCO_2H)} \simeq 6 \times 10^2 \qquad \text{(viii)}$$

The corresponding ratios for HO· and H· are 5 and 2×10^2, respectively,[10] and thus in this case a change in the ionisation state of the substrate has the greatest effect on the aryl radical.

When the concentration of sodium formate in the absence of added acid was increased above 2×10^{-2} mol l^{-1} we found considerable thermal reaction to occur on deaeration, but not in the presence of air. This suggests that the thermal reaction also proceeds by the same free-radical chain mechanism, ion pairs or arenediazo formate molecules giving rise to Ar· and probably $\dot{C}O_2^-$.

Cysteine Hydrochloride with Toluene-p-*diazonium Ions*.—A report[15] on the induced decomposition of arenediazo thiolates prompted us to investigate the use of a thiol (cysteine) as a reducing agent. Figure 4 shows the effect of dose rate for the toluene-*p*-diazonium ion–cysteine hydrochloride system at the natural pH of the reactants (2—3). $G(-ArN_2^+)$ was insensitive to cysteine hydrochloride concentration over the measured range ($1—4 \times 10^{-2}$ mol l^{-1}) and was directly proportional to $[ArN_2^+]$ in the measured range ($0·25—1·5 \times 10^{-4}$ mol l^{-1}). Lowering the pH to 1 with $HClO_4$ or raising it to above 4 with NaOH inhibited the reaction completely.

The dose rate effect implies radical–radical termination and the yield dependence on $[ArN_2^+]$ suggests competition for a radical between ArN_2^+ and a radical, the former propagating the chain and the latter terminating it. Should reaction (6) be fast so that reaction (8) becomes insignificant, and reaction (7) sufficiently slow for the $\dot{R}H$ concentration to build up to allow termination by reaction (9), stationary state analysis of the mechanism gives equation (B), where N is Avagadro's constant and D is

$$G(-ArN_2^+) = k_7(100NG_r/2k_9D)^{\frac{1}{2}}[ArN_2^+] \qquad \text{(B)}$$

the dose-rate in eV l^{-1} s^{-1}. We call this class B kinetics, and this is the type of kinetics reported for the radiation-

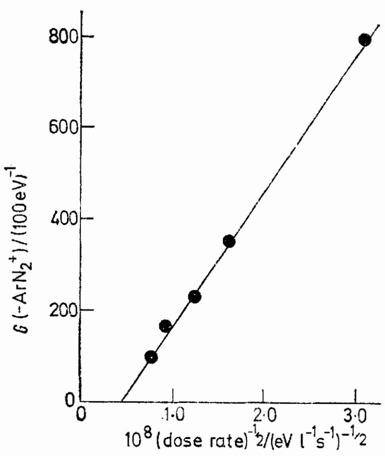

FIGURE 4 $G(-ArN_2^+)$ as a function of dose rate for toluene-*p*-diazonium ions (10^{-4} mol l^{-1}) and 0·01M-cysteine hydrochloride

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[11] A. L. J. Beckwith and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1969, 400.

[12] A. Fojtic, G. Czapski, and A. Henglein, *J. Chem. Phys.*, 1970, **74**, 3204.

[13] G. V. Buxton and R. M. Sellers, *J.C.S. Faraday I*, 1973, **69**, 555.

[14] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389.

[15] H. Van Swet, J. Reiding, and E. C. Kooyman, *Rec. Trav. chim.*, 1971, **90**, 21.

induced oxidation of alcohols by electron scavengers in alkaline solution,[9] and of methanol by hydrogen peroxide in neutral solution,[16] and corresponds to the common rate equation for chain reactions terminated by radical–radical reaction.[17]

Abstractions from thiols by many radicals are known to be fast, this being one of the reasons for thiols acting as radiation protecting agents.[18] Thus we suggest reactions (6), (7), and (9) can be written as (6b), (7b), and (9b),

$$\mathrm{Ar\cdot + CySH \longrightarrow ArH + CyS\cdot} \qquad (6b)$$

$$\mathrm{CyS\cdot + ArN_2^+ \xrightarrow{CySH} Ar\cdot + N_2 + CySSCy + H^+} \qquad (7b)$$

$$\mathrm{2CyS\cdot \longrightarrow CySSCy} \qquad (9b)$$

respectively. As $G(-\mathrm{ArN_2^+})$ was independent of cysteine concentration, the rate of reaction (7b) must also be independent of it. If $2k_{9b}$ is known, the value of k_{7b} can be calculated from equation (B). Hoffman and Hayon[19] give $2k_{9b}$ at pH 1 as $1{\cdot}0 \times 10^{10}$ l mol^{-1} s^{-1}. However their value for the corresponding radicals from cysteamine ($1{\cdot}4 \times 10^{10}$ l mol^{-1} s^{-1}) is a factor of 10 greater than that given by Adams and his co-workers,[20] and thus their figure may be high. By using a figure of 10^{10}—10^9 l mol^{-1} s^{-1} for k_{9b}, we obtain 11×10^5 l mol^{-1} s^{-1} $\geqslant k_{7b} \geqslant$ $3{\cdot}5 \times 10^5$ l mol^{-1} s^{-1}.

We offer a possible explanation of the inhibiting effect of lowering the pH of the solution. At the natural pH of the cysteine hydrochloride solution the radical CyS· will probably exist, at least partially, in the zwitterion form $\mathrm{NH_3^+CH(CO_2^-)CH_2S\cdot}$, but on addition of acid this might be converted into its positively charged conjugate acid. The rate of reaction of this positively charged thiyl radical with the positively charged diazonium ion is probably much less than that of the overall neutral zwitterion, making k_{7b} too low to propagate the chain. We have no explanation of the inhibition on increasing pH. At higher pH one would expect some of the CyS· radical to exist in the form of $\mathrm{Cy\dot{S}\bar{S}Cy}$, and to be an efficient reducing agent in view of the fact that it reduces molecular oxygen.[21] Neither do we know why the plot of $G(-\mathrm{ArN_2^+})$ against (dose rate)$^{\frac{1}{2}}$ has an apparent negative intercept.

Methanol with Anisole-p-*diazonium Ions*.—Class A kinetics were found for this system for $[p\text{-}\mathrm{MeOC_6H_4N_2^+}]$ $\geqslant 1 \times 10^{-4}$ mol l^{-1}, but the plot of $G(-\mathrm{ArN_2^+})$ against $[\mathrm{MeOH}]/[\mathrm{ArN_2^+}]$ was steeper than for the toluene-*p*-diazonium ion system, the value of k_6/k_8 being 0·064. The reasons for the increase will be discussed in a later paper.

Relationship between Class A and Class B Kinetics.—Class A and class B kinetics are extremes of an overall mechanism, the kinetic form depending on the relative rates of reactions (6)—(9). If the diazonium ion concentration is raised in a system showing class B kinetics the steady-state concentration of aryl radicals $[\mathrm{Ar\cdot}]_{\mathrm{SS}}$ increases and the fraction of Ar· reacting *via* reaction (8) rather than reaction (6) increases, and although $[\dot{\mathrm{R}}\mathrm{H}]_{\mathrm{SS}}$ is not affected the fraction of $\dot{\mathrm{R}}\mathrm{H}$ reacting by reaction (7) rather than reaction (9) increases. Thus as the $\mathrm{ArN_2^+}$ concentration is increased the relative importance of reactions (8) and (9) as terminating steps increases and decreases respectively, and one might expect to see an inverse diazonium ion concentration effect being superimposed on the direct proportionality of class B. We will suggest that this accounts for the departure of linearity of the $G(-\mathrm{ArN_2^+})$ *vs*. $[\mathrm{ArN_2^+}]$ plots for hypophosphorous acid (see later).

In a system exhibiting class A kinetics,

$$[\dot{\mathrm{R}}\mathrm{H}]_{\mathrm{SS}} \propto \frac{k_6[\mathrm{RH_2}]}{k_7k_8[\mathrm{ArN_2^+}]^2}\cdot D \text{ and } [\mathrm{Ar\cdot}]_{\mathrm{SS}} \propto \frac{D}{k_8[\mathrm{ArN_2^+}]}$$

Thus decreasing $[\mathrm{ArN_2^+}]$ raises $[\dot{\mathrm{R}}\mathrm{H}]_{\mathrm{SS}}$ significantly and increases the likelihood of reaction (9) becoming important in chain termination while at the same time lowering the fraction of aryl radicals undergoing chain-terminating reaction (8). Thus as $[\mathrm{ArN_2^+}]$ is lowered in a class A system one might expect to see a change in the effect of $[\mathrm{ArN_2^+}]$ and the onset of a dose-rate effect. Comparing two diazonium ions having different values of k_6/k_8 for the same reducing agent, one would expect the change to class B kinetics to start at higher diazonium concentration for the system with the higher value of k_6/k_8.

The data shown in Figure 5 were obtained from experiments undertaken to test this theory. The change from a negative to a positive dependence on $[\mathrm{ArN_2^+}]$ with decreasing $[\mathrm{ArN_2^+}]$ and the onset of a dose-rate effect for both diazonium ions is clearly seen. Further the onset of this effect occurs at higher concentration for anisole-*p*-diazonium ions than for toluene-*p*-diazonium ions, as predicted. Also the change in diazonium ion concentration dependence occurs at higher diazonium ion concentration for both ions at the higher dose rate, consistent with $[\dot{\mathrm{C}}\mathrm{H_2OH}]_{\mathrm{SS}}$ being proportional to dose rate.

Hypophosphite and Phosphite as Reducing Agents.—As mentioned in the introduction, Kornblum and his co-workers showed that both phosphorous acid[4] and hypophosphorous acid[3] could be used as reducing agents for diazonium ions. In their comparison they did not isolate their diazonium ion, but added $\mathrm{H_3PO_3}$ or $\mathrm{H_3PO_2}$ so that the concentration ratio $\mathrm{ArN_2^+ : H^+ : H_3PO_3}$ (or $\mathrm{H_3PO_2}$) was 1 : 6 : 15. They obtained yields in the range 56—71% with phosphorous acid[4] and 65—81% with hypophosphorous acid.[3] Hypophosphorous acid reductions occurred faster and peroxide catalysis was required with phosphorous acid. Beckwith[5] showed that each of the radicals $\mathrm{H\dot{P}O_3^-}$ (pH $\geqslant$ 2), $\mathrm{\dot{P}O_3^{2-}}$ (pH 8), and $\mathrm{H\dot{P}O_2^-}$ (pH 2) reduced diazonium ions. Thus it was hoped that

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[16] C. E. Burchill and I. S. Ginns, *Canad. J. Chem.*, 1970, **68**, 2628.

[17] C. Walling, 'Free Radicals in Solution,' Wiley, New York, 1957, p. 67.

[18] J. E. Packer, 'The Chemistry of the Thiols,' ed. S. Patai, Interscience, London, 1974, ch. 11, p. 510.

[19] M. Z. Hoffman and E. Hayon, *J. Amer. Chem. Soc.*, 1972, **84**, 7950.

[20] G. E. Adams, R. C. Armstrong, A. Charlesby, B. D. Michael, and R. L. Wilson, *Trans. Faraday Soc.*, 1969, **65**, 732.

[21] J. P. Barton and J. E. Packer, *Internat. J. Radiation Phys. Chem.*, 1970, **2**, 159.

a kinetic study of the system initiated by radiation would show essential differences between the two systems.

A pH effect was anticipated in that RH_2 can be H_3PO_3, $H_2PO_3^-$, or HPO_3^{2-} and $\dot{R}H$ $H_2\dot{P}O_3$, $H\dot{P}O_3^-$, or $\dot{P}O_3^{2-}$ in the case of the phosphite system, while with hypophosphite RH_2 can be H_3PO_2 or $H_2PO_2^-$ and $\dot{R}H$ $H_2\dot{P}O_2$ or $H\dot{P}O_2^-$. In the light of the formate work, H abstraction [reaction (6)] from an anion is likely to be faster than from the neutral molecule, and, as the diazonium ion is positively charged, reaction (7) would be expected to be faster for an anion than for a neutral species. Further, reaction (9) will be faster for uncharged radicals. Thus one would expect yields decreasing with decreasing pH, and possibly changes in kinetic form depending on the changes in rates of reactions (6), (7), and (9).

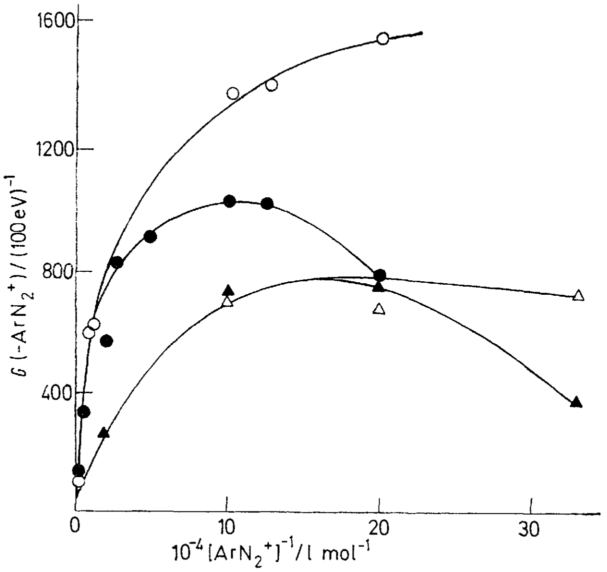

FIGURE 5 $G(-ArN_2^+)$ as a function of $[ArN_2^+]$ and dose rate for anisole-*p*-diazonium ions and toluene-*p*-diazonium ions with 0·10M-methanol; ○● *p*-$MeOC_6H_4N_2^+$; △▲ *p*-$MeC_6H_4N_2^+$; dose rate ($eV\ l^{-1}\ s^{-1}$): ●▲ $1{\cdot}03 \times 10^{16}$; ○△ $1{\cdot}23 \times 10^{15}$

We have had great difficulty in obtaining reproducible results with these reducing agents, yields differing by factors of up to four on different days or with different workers, all of whom can reproduce yields in the methanol system. In spite of this some information and trends have been found.

First, larger yields were obtained with 10^{-2} mol l^{-1} NaH_2PO_2 and Na_2HPO_3 than with formate: for 10^{-4} mol l^{-1} *p*-$MeC_6H_4N_2^+$, values of 5620 and 2420, respectively, in two experiments. The irreproducible nature of the results suggest that impurity scavenging may be the main source of termination, and therefore the true yields are probably higher. Impurity scavenging has frequently been invoked to explain the lack of dose-rate effect in radiation-induced chain reactions.[9] Recently the rate constants for reaction (9) for $H\dot{P}O_2^-$ and $\dot{P}O_3^{2-}$ have been measured as $9{\cdot}4 \times 10^8$ and $3{\cdot}0 \times 10^7$ l mol^{-1} s^{-1}, respectively.[22] On the assumption that our chains are terminated by these reactions, *i.e.* class B kinetics, we can calculate values of k_7 from equation (B). At our dose-rates these are $2{\cdot}5 \times 10^6$ and 2×10^5 l mol^{-1} s^{-1} for $H\dot{P}O_2^-$ and $\dot{P}O_3^{2-}$, respectively. If the true yields are higher, and/or class B kinetics do not prevail, then these rate constants must be larger. Thus we can quote these figures as lower limits.

Experiments designed to study the effect of pH showed that $G(-ArN_2^+)$ decreased markedly on addition of perchloric acid. Thus in a series of consecutive experiments the following results were obtained:

10^{-4} mol l^{-1} *p*-$MeC_6H_4N_2^+$ with 10^{-2} mol l^{-1} NaH_2PO_2:

$[HClO_4]$:	0	0·1	1·0	mol l^{-1}
$G(-ArN_2^+)$:	5620	650	800	

10^{-4} mol l^{-1} *p*-$MeC_6H_4N_2^+$ with 10^{-2} mol l^{-1} Na_2HPO_3:

$[HClO_4]$:	0	0·1	1·0	2·0	mol l^{-1}
$G(-ArN_2^+)$:	2420	568	207	108	

Irreproducibility made studies of the concentration effects of ArN_2^+ and RH_2 difficult. However the phosphite system appeared to show class A characteristics,

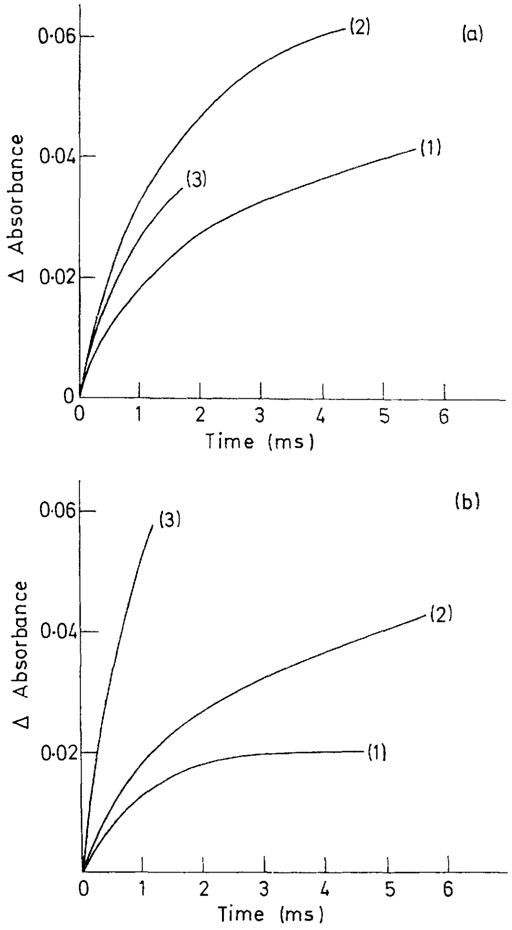

FIGURE 6 Increase in transmission at 318 nm of argonated toluene-*p*-diazonium tetrafluoroborate solutions following a 5 ns pulse of radiation as a function of time; (a) 10^{-4}M-ArN_2^+: (1) 0·1M-H_3PO_2, (2) 0·01M- and 0·05M-H_3PO_2, (3) 0·01M-H_3PO_2; (b) 0·1M-H_3PO_2: (1) $0{\cdot}5 \times 10^{-4}$M-ArN_2^+, (2) $1{\cdot}0 \times 10^{-4}$M-ArN_2^+, (3) $2{\cdot}0 \times 10^{-4}$M-ArN_2^+

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[22] D. Behar and R. W. Fessenden, *J. Phys. Chem.*, 1972, **76**, 1706.

with increasing $G(-\mathrm{ArN_2}^+)$ values on raising the phosphite and lowering the diazonium ion concentrations. Most absorbance–dose plots showed increasing $G(-\mathrm{ArN_2}^+)$ with increasing dose. On the other hand in acidic solution hypophosphorous acid systems showed class B characteristics in that increasing the diazonium ion concentration increased $G(-\mathrm{ArN_2}^+)$, and there appeared little effect on changing the hypophosphorus acid concentration, although higher concentrations of H_3PO_2 led to some decrease in $G(-\mathrm{ArN_2}^+)$ probably because of impurity scavenging. The increase in $G(-\mathrm{ArN_2}^+)$ with increasing $[\mathrm{ArN_2}^+]$ fell away as the toluene-*p*-diazonium ion concentration was increased from 10^{-4} to 10^{-3} mol l^{-1}. This may be due to the onset of reaction (8) at the higher diazonium ion concentrations. Absorbance–dose plots usually showed a decrease in $G(-\mathrm{ArN_2}^+)$ as the reaction proceeded.

Early in the investigation some pulse radiolysis experiments were carried out with H_3PO_2 as reducing agent and results are shown in Figure 6. The effects of $[\mathrm{ArN_2}^+]$ and $[H_3PO_2]$ on $G(-\mathrm{ArN_2}^+)$ found in the γ radiolysis work are seen to be qualitatively the same under pulse conditions. The effect of changing $[\mathrm{ArN_2}^+]$ and $[\mathrm{RH_2}]$ on the initial rate of loss of diazonium ions immediately after a pulse of fast electrons was different from that in the methanol system.[1] With H_3PO_2 the rate increased with increasing $[\mathrm{ArN_2}^+]$ and was independent of $[H_3PO_2]$, whereas with methanol it increased with methanol concentration and was independent of $[\mathrm{ArN_2}^+]$. This is consistent with class B type kinetics for hypophosphorous acid, with reaction (7) being rate-controlling. Although $G(-\mathrm{ArN_2}^+)$ was much larger for H_3PO_2 than for MeOH with the same concentrations of $\mathrm{ArN_2}^+$ and $\mathrm{RH_2}$, the initial rate of loss of $\mathrm{ArN_2}^+$ after similar pulses was slightly less with hypophosphorous acid. This confirms that reaction (6) is faster for H_3PO_2 than for MeOH, and shows that the rate of reduction of $\mathrm{ArN_2}^+$ by $H_2\dot{P}O_2$ (or $H\dot{P}O_2^-$, depending on the pK_a of $H_2\dot{P}O_2$) is less than for $\dot{C}H_2OH$.

In Kornblum's experiments the ratios $[\mathrm{ArN_2}^+] : [\mathrm{RH_2}]$ were much higher than in our work, and the lower product yields may be attributed to reaction (8). Although no firm conclusions can be drawn, this work suggests that the superiority of H_3PO_2 to H_3PO_3 as a reducing reagent may be attributed to hydrogen abstraction from H_3PO_2 occurring more readily than from H_3PO_3, rather than to the relative reducing efficiencies of $H_2\dot{P}O_2$ and $H_2\dot{P}O_3$ or their conjugate bases. This is consistent with Kornblum's finding that a catalyst was required to initiate the phosphorous acid but not the hypophosphorous acid reductions.

We found that thermal reactions between the diazonium ions and both hypophosphite and phosphite occurred when the concentration of the reducing agent was increased above 10^{-2} mol l^{-1}, but as with the radiolysis the rates of these reactions were erratic. As these reactions only occurred on deaeration, a radical mechanism is probable.

[4/767 *Received*, 17*th April*, 1974]