Free-radical Reductions of Arenediazonium Ions in Aqueous Solution. Part III.[1] Kinetics of Reactions of Toluene-*p*-diazonium Ions with Ethanol, Propan-2-ol, and Acetaldehyde

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The kinetics of the radiation induced chain reaction between toluene-*p*-diazonium ions (ArN_2^+) and the reducing agents ethanol, propan-2-ol, and acetaldehyde (RH_2) is consistent with a mechanism involving both α- and β-hydrogen abstraction from RH_2 by the *p*-tolyl radical. The ratio k_α/k_β for these reactions has been determined for each of the reducing agents above. α-$\dot{R}H$ Radicals reduce diazonium ions and propagate the chain. β-$\dot{R}H$ Radicals react either with RH_2 to give α-$\dot{R}H$ radicals [reaction (11)] or with ArN_2^+ in a chain-terminating step [reaction (12)]. The rate constant ratios k_{11}/k_{12} have been determined and the ratio is larger for acetaldehyde than for the alcohols. The reasons for this and the nature of reaction (12) are discussed, and it is postulated that the β-$\dot{R}H$ radicals add to the terminal nitrogen of the diazonium ions.

FREE-RADICAL chain reactions between arenediazonium ions (ArN_2^+) and a number of reducing agents (RH_2) resulting in replacement of the N_2^+ group by hydrogen according to equation (1) can be initiated quantitatively

$$ArN_2^+ + RH_2 \longrightarrow ArH + N_2 + R + H^+ \quad (1)$$

with ^{60}Co γ-radiation. In Parts I[2] and II[1] we presented work with the reducing agents methanol, formate, cysteine, hypophosphite, and phosphite, and described two classes of kinetics labelled (A) and (B) which could be interpreted in terms of reactions (2)—(9). In class

$$H_2O \rightsquigarrow e_{aq}^-, \cdot OH, H\cdot, H_2, H_2O_2 \quad (2)$$

$$e_{aq}^- + ArN_2^+ \longrightarrow Ar\cdot + N_2 \quad (3)$$

$$HO\cdot + RH_2 \longrightarrow H_2O + \dot{R}H \quad (4)$$

$$H\cdot + RH_2 \longrightarrow H_2 + \dot{R}H \quad (5)$$

$$Ar\cdot + RH_2 \longrightarrow ArH + \dot{R}H \quad (6)$$

$$\dot{R}H + ArN_2^+ \longrightarrow Ar\cdot + N_2 + R + H^+ \quad (7)$$

$$Ar\cdot + ArN_2^+ \longrightarrow \text{Products} \quad (8)$$

$$\dot{R}H + \dot{R}H \longrightarrow \text{Products} \quad (9)$$

(A) $G(-ArN_2^+)$, the number of diazonium ions lost per 100 eV of radiation energy absorbed, is given by equation

$$G(-ArN_2^+) = G_r(2 + k_6[RH_2]/k_8[ArN_2^+]) \quad (A)$$

and in class (B) by

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

where $G_r = G_{e_{aq}^-} + G_{OH} + G_H \simeq 6(100\ eV)^{-1}$; $G_{e_{aq}^-} = G_{OH} = 2{\cdot}7(100\ eV)^{-1}$; $G_H = 0{\cdot}6(100\ eV^{-1})$, N is Avogadro's constant, and D the dose rate in eV $l^{-1}\ s^{-1}$. Chain termination is entirely by reaction (8) when the kinetics are class (A) and entirely by reaction (9) when the kinetics are class (B). It was shown that the kinetic class depended on the relative rates of reactions (6)—(8) and by lowering $[ArN_2^+]$ the kinetics could be changed from class (A) to class (B).

In Part I we suggested that the product of reaction (8) was the radical cation $Ar\dot{N}\overset{+}{N}Ar$, and recent CIDNP studies and MO calculations have confirmed this view.[3] Although we suggested that the intermediate would be reduced to the azo-compound by $\cdot CH_2OH$ or e_{aq}^- we incorrectly analysed the effect of this reaction on the

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[1] Part II, J. E. Packer, R. K. Richardson, P. J. Soole, and D. R. Webster, *J.C.S. Perkin II*, 1974, 1472.

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

[3] J. Bargon and K.-G. Seifert, *Tetrahedron Letters*, 1974, 2265.

kinetics. The termination steps for class (A) kinetics should be written as (8′) and (10) and a factor of two

$$\mathrm{ArN_2{}^+ + Ar\cdot \longrightarrow Ar\dot{N}\overset{+}{N}Ar} \qquad (8')$$

$$\mathrm{Ar\dot{N}\overset{+}{N}Ar + \dot{R}H \longrightarrow ArNNAr + R + H^+} \qquad (10)$$

should be introduced into equation (A) which becomes (A′).

$$G(-\mathrm{ArN_2{}^+}) = \tfrac{1}{2}G_\mathrm{r}(2 + k_6[\mathrm{RH_2}]/k_8[\mathrm{ArN_2{}^+}]) \qquad (\mathrm{A}')$$

In recent years there has been considerable interest in the formation and reactions of alcohol radicals. Studies include the relative rates of hydrogen abstraction from different positions by HO• radicals, [4,5] the redox potentials of the radicals,[6,7] the rates of reactions of α- and β-radicals,[8] and the relative importance of electron transfer and/or addition to various acceptor molecules.[9-11]

In this paper we report our studies of the reactions between toluene-*p*-diazonium ions with ethanol, propan-2-ol, and acetaldehyde, all of which have α- and β-hydrogens, and obtain information on (a) the relative rates of α- and β-hydrogen abstraction by *p*-tolyl radicals, and (b) the reactions of α- and β-radicals with toluene-*p*-diazonium ions.

EXPERIMENTAL

The techniques used were those described in Parts I and II. Ethanol (Merck), acetaldehyde (B.D.H.), and [1,1,1-3,3,3-$^2H_6$]propan-2-ol (Merck, Sharp and Dohme) were used as supplied. Propan-2-ol (B.D.H.) was distilled from acidified 2,4-dinitrophenylhydrazine. Acetaldehyde was analysed as a product from reductions with ethanol by the method of Sawicki using 3-methylbenzothiazolin-2-one hydrazone hydrochloride.[12]

RESULTS AND DISCUSSION

Figures 1—3 summarise our experimental data, showing the relationship between $G(-\mathrm{ArN_2{}^+})$ and the concentrations of toluene-*p*-diazonium ion and reducing agent for ethanol, propan-2-ol, and acetaldehyde respectively. There was no dose-rate effect. Acetaldehyde was produced quantitatively with ethanol as reducing agent.

The kinetics are similar to those of class (A) in that $G(-\mathrm{ArN_2{}^+})$ is proportional to $[\mathrm{RH_2}]/[\mathrm{ArN_2{}^+}]$ but differ in that there is an appreciable intercept when $G(-\mathrm{ArN_2{}^+})$ is extrapolated to zero value of $[\mathrm{RH_2}]/[\mathrm{ArN_2{}^+}]$. This latter feature is similar to that found by Burchill in his studies of the radiation-induced chain reactions between hydrogen peroxide and ethanol or propan-2-ol.[4,13] Plots of $G(\mathrm{CH_3CHO})$ or $G(\mathrm{CH_3COCH_3})$ against the respective alcohol concentration were linear and gave a finite value of G(product) at zero alcohol concentration. He found a dose-rate effect and interpreted his results in terms of

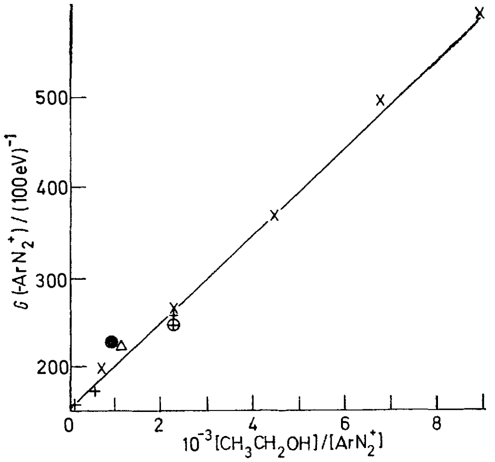

FIGURE 1 $G(-\mathrm{ArN_2{}^+})$ As a function of the concentrations of ethanol and toluene-*p*-diazonium ions in deaerated aqueous solution: ×, $1{\cdot}0 \times 10^{-4}$; +, $2{\cdot}0 \times 10^{-4}$; △, $4{\cdot}0 \times 10^{-4}$; ●, $5{\cdot}0 \times 10^{-4}$M-$\mathrm{ArN_2{}^+}$, dose rate, $1{\cdot}0 \times 10^{16}$ eV $\mathrm{l^{-1}\,s^{-1}}$: ○, $2{\cdot}0 \times 10^{-4}$M-$\mathrm{ArN_2{}^+}$, dose rate, $1{\cdot}2 \times 10^{15}$ eV $\mathrm{l^{-1}\,s^{-1}}$

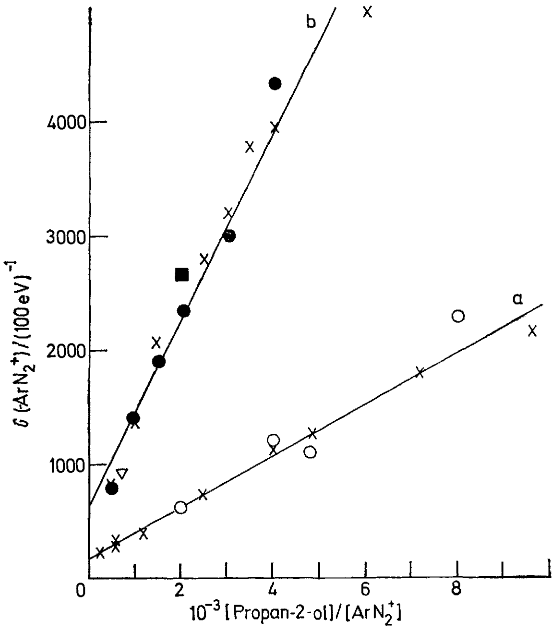

FIGURE 2 $G(-\mathrm{ArN_2{}^+})$ As a function of the concentrations of propan-2-ol and toluene-*p*-diazonium ions in deaerated aqueous solution: a, $\mathrm{(CH_3)_2CHOH}$, $1{\cdot}0 \times 10^{-4}$M-$\mathrm{ArN_2{}^+}$, dose rate: ×, $9{\cdot}5 \times 10^{15}$; ○, $1{\cdot}2 \times 10^{15}$ eV $\mathrm{l^{-1}\,s^{-1}}$: b, $\mathrm{(CD_3)_2CHOH}$, ●, $0{\cdot}5 \times 10^{-4}$; ▽, $0{\cdot}75 \times 10^{-4}$; × $1{\cdot}0 \times 10^{-4}$M$\mathrm{ArN_2{}^+}$, dose rate, $9{\cdot}5 \times 10^{15}$ eV $\mathrm{l^{-1}\,s^{-1}}$: ×, $0{\cdot}5 \times 10^{-4}$M-$\mathrm{ArN_2{}^+}$, dose rate, $1{\cdot}2 \times 10^{15}$ eV $\mathrm{l^{-1}\,s^{-1}}$

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[4] C. E. Burchill and G. F. Thompson, *Canad. J. Chem.*, 1971, **49**, 1305.

[5] K. D. Asmus, H. Makel, and A. Henglein, *J. Phys. Chem.*, 1973, **77**, 1218.

[6] J. Lilie, G. Beck, and A. Henglein, *Ber. Bunsengesellschaft Phys. Chem.*, 1971, **75**, 458; M. Grätzel, A. Henglein, J. Lilie, and M. Scheffler, *ibid.*, 1972, **76**, 67.

[7] P. S. Rao and E. Hayon, *J. Amer. Chem. Soc.*, 1974, **96**, 1287.

[8] G. E. Adams and R. L. Willson, *Trans. Faraday Soc.*, 1969, **65**, 2981.

[9] M. McMillan and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 590.

[10] G. E. Adams and R. L. Willson, *J.C.S. Faraday I*, 1973, 719.

[11] C. L. Greenstock and I. Dunlop, *J. Amer. Chem. Soc.*, 1973, **95**, 6917.

[12] E. Sawicki, T. R. Hauser, T. W. Stanley, and W. Elbert, *Analyt. Chem.*, 1961, **33**, 93.

[13] C. E. Burchill and I. S. Ginns, *Canad. J. Chem.*, 1970, **48** (*a*) 1232; (*b*) 2628.

competing α- and β-hydrogen abstraction from the alcohol by HO•. The α-radical could reduce hydrogen peroxide to hydroxyl radicals to propagate the chain, but the β-radical could not, either undergoing coupling or disproportionation resulting in chain termination, or reacting with a second alcohol molecule to give an α-radical.

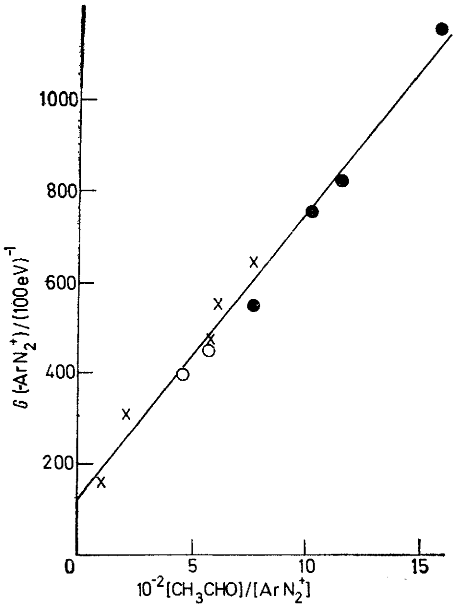

FIGURE 3 $G(-ArN_2^+)$ As a function of the concentrations of acetaldehyde and toluene-*p*-diazonium ions in deaerated aqueous solution: ●, 0·075M-CH_3CHO; dose rate, 9·35 × 10^{15} eV l^{-1} s^{-1}: ×, 1·0 × 10^{-4}M-ArN_2^+; dose rate, 9·35 × 10^{15} eV l^{-1} s^{-1}: ○, 1·0 × 10^{-4}M-ArN_2^+; dose rate, 1·12 × 10^{15} eV l^{-1} s^{-1}

We interpret our results in a somewhat similar way. The α-radicals from our reducing agents reduce the diazonium ion to aryl radicals, but the β-radicals do not,

$$\begin{array}{rll}
e_{aq}^- + ArN_2^+ & \longrightarrow Ar\cdot + N_2 & (3)\\
 & \nearrow \alpha\cdot + H_2O & (4\alpha)\\
HO\cdot + RH_2 & & \\
 & \searrow \beta\cdot + H_2O & (4\beta)\\
 & \nearrow \alpha\cdot + H_2 & (5\alpha)\\
H\cdot + RH_2 & & \\
 & \searrow \beta\cdot + H_2 & (5\beta)\\
 & \nearrow ArH + \alpha\cdot & (6\alpha)\\
Ar\cdot + RH_2 & & \\
 & \searrow ArH + \beta\cdot & (6\beta)\\
\alpha\cdot + ArN_2^+ & \longrightarrow Ar\cdot + N_2 + R + H^+ & (7)\\
\beta\cdot + RH_2 & \longrightarrow RH_2 + \alpha\cdot & (11)\\
\beta\cdot + ArN_2^+ & \longrightarrow Ar\dot{N}\overset{+}{N}\beta & (12)\\
Ar\dot{N}\overset{+}{N}\beta + \alpha\cdot & \longrightarrow ArNN\beta + R + H^+ & (13)
\end{array}$$

SCHEME

their fate being to react either with RH_2 to produce the corresponding α-radical or with the diazonium ion in a chain termination step. Our postulated mechanism in general terms is given in the Scheme where α• and β• are $CH_3\dot{C}HOH$ and $\cdot CH_2CH_2OH$ for ethanol, $(CH_3)_2\dot{C}OH$ and $\cdot CH_2CH(OH)CH_3$ for propan-2-ol, and $CH_3\dot{C}O$ and $\cdot CH_2CHO$ for acetaldehyde, although in the latter case the situation might be a little more complex because of possible hydration of the carbonyl group. The product R will be acetaldehyde, acetone, and acetic acid for ethanol, propan-2-ol, and acetaldehyde respectively.

A steady-state analysis of this scheme involving initiation by reactions (3)—(5), propagation by reactions (6), (7), and (11), and termination by reactions (12) and (13) gives expression (14). In a plot of $G(-ArN_2^+)$

$$G(-ArN_2^+) = \tfrac{1}{2}G_r + \tfrac{1}{2}\left(1 + \frac{k_{6\alpha}}{k_{6\beta}}\right)\left[G_{e_{aq}^-} + \left(\frac{k_{4\alpha}}{k_{4\alpha} + k_{4\beta}}\right)G_{OH} + \left(\frac{k_{5\alpha}}{k_{5\alpha} + k_{5\beta}}\right)G_H\right] + \tfrac{1}{2}G_r\left(1 + \frac{k_{6\alpha}}{k_{6\beta}}\right)\frac{k_{11}[RH_2]}{k_{12}[ArN_2^+]} \qquad (14)$$

against $[RH_2]/[ArN_2^+]$, the intercept measures the first two terms of the equation and represents the amount of ArN_2^+ destroyed *via* α-radicals only, whereas the third term, the yield in addition to that given by the intercept, represents the amount of ArN_2^+ destroyed in propagation steps involving β-radicals.

Our results, at the concentrations of ArN_2^+ and RH_2 used, are consistent with this expression, and to establish further the validity of this mechanism we planned experiments to test (a) that both α- and β-abstraction were occurring, and (b) that β-radicals do not reduce diazonium ions in a chain propagating step.

For (a) we used the technique of Burchill,[4] comparing $(CH_3)_2CHOH$ and $(CD_3)_2CHOH$ in the propan-2-ol system. Assuming a primary isotope effect, $k_{6\alpha}/k_{6\beta}$ should be higher for the deuteriated alcohol, and as a result both the intercept and slope of the plot of $G(-ArN_2^+)$ against $[PrOH]/[ArN_2^+]$ should be greater for $(CD_3)_2CHOH$. Figure 2 shows clearly that this is the case.

β-Alcohol radicals have been shown to be weaker reducing agents than their α-alcohol counterparts by Henglein who found only the α-radicals reduce tetranitromethane,[5] by Adams who found that $\cdot CH_2CH_2OH$ reduced ferricyanide 100 times more slowly than $CH_3\dot{C}HOH$,[8] and by Greenstock who showed that the β-radicals formed by addition of HO• to allyl and crotyl alcohols add to nitrobenzene rather than reduce it.[11] We tested (b) by two methods.

(1) We were unable to induce a chain reaction by irradiating deaerated aqueous toluene-*p*-diazonium ions and allyl alcohol. (2) By irradiating toluene-*p*-diazonium ions with ethylene glycol in neutral and acidic (1M-$HClO_4$) solution we were able to show that $\cdot CH_2CHO$ does not reduce the diazonium ion. Whereas in neutral solution we get an appreciable chain reaction, presumably *via* reactions (15) and (16) the addition of perchloric acid completely inhibits this reaction. It has been shown [14,15]

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[14] A. C. Buley, R. O. C. Norman, and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1966, 349.

[15] S. Steenken and D. Schulte-Frohlinde, *Tetrahedron Letters*, 1973, 653.

that the ethylene glycol radical formed by hydrogen

$$\mathrm{Ar^{\bullet} + CH_2OHCH_2OH \longrightarrow ArH + HO\dot{C}HCH_2OH} \quad (15)$$

$$\mathrm{HO\dot{C}HCH_2OH + ArN_2^+ \longrightarrow Ar^{\bullet} + N_2 + OCHCH_2OH + H^+} \quad (16)$$

abstraction with $\mathrm{HO^{\bullet}}$ undergoes heterolytic elimination of water in acidic solution [reaction (17)]. Henglein[16]

$$\mathrm{HO\dot{C}HCH_2OH + H^+ \longrightarrow H^+ + O\dot{C}HCH_2 + H_2O} \quad (17)$$

has shown that the protonated form of $\mathrm{HO\dot{C}HCH_2OH}$ has $\mathrm{p}K_\mathrm{a}$ 0·74 and decays with a first-order rate constant of $8{\cdot}6 \times 10^5\ \mathrm{s^{-1}}$. He has also shown that dehydration of $\mathrm{HO\dot{C}HCH_2OH}$ is catalysed by hydroxide ions, and by pulse radiolytic polarography has found $\mathrm{OCH\dot{C}H_2}$ in alkaline solution to be a poorer reducing agent than $\mathrm{HO\dot{C}HCH_2OH}$ in neutral solution by 0·7 V. Calculations using Henglein's rate data show that under our conditions reaction (16) would need a rate constant $>10^{10}\ \mathrm{l\ mol^{-1}\ s^{-1}}$ to compete with reaction (17). Thus inhibition of the $\mathrm{ArN_2^+}$–ethylene glycol reaction by perchloric acid provides good evidence for the failure of the β-radical $\mathrm{{}^{\bullet}CH_2CHO}$ to reduce diazonium ions and provides chemical evidence for the lowered reducing power of $\mathrm{{}^{\bullet}CH_2CHO}$ compared with $\mathrm{HO\dot{C}HCH_2OH}$ as measured polarographically by Henglein. This together with the similarity of the kinetics between acetaldehyde, ethanol, and propan-2-ol confirms that neither $\mathrm{{}^{\bullet}CH_2CH_2OH}$ nor $\mathrm{{}^{\bullet}CH_2CH(OH)CH_3}$ reduces $\mathrm{ArN_2^+}$.

If the rate constant ratios $k_{4\alpha}/k_{4\beta}$ and $k_{5\alpha}/k_{5\beta}$ are known, the values of $k_{6\alpha}/k_{6\beta}$ (the rate constant ratio for α- and β-abstraction by *p*-tolyl radicals) can be determined from the plots of $G(-\mathrm{ArN_2^+})$ against $[\mathrm{RH_2}]/[\mathrm{ArN_2^+}]$. Burchill gives $k_{4\alpha}/k_{4\beta} = 6$ for ethanol and 5·2 for propan-2-ol,[4] assuming $k_{5\alpha}/k_{5\beta}$ values of 10·5 for ethanol and 20 for propan-2-ol.[17] Using these figures we determine $k_{6\alpha}/k_{6\beta}$ as 55·4 for ethanol and 57·3 for propan-2-ol from the intercepts. Thus the *p*-tolyl radical shows greater selectivity than either $\mathrm{HO^{\bullet}}$ or $\mathrm{H^{\bullet}}$. On the basis of the number of hydrogens available the ratios for α : β abstraction become 83 : 1 for ethanol and 344 : 1 for propan-2-ol.

The values of $k_{4\alpha}/k_{4\beta}$ and $k_{5\alpha}/k_{5\beta}$ are not known for acetaldehyde. Using the figures for ethanol we obtain $k_{6\alpha}/k_{6\beta}$ as 40·6 from the intercept of Figure 3. Thus the *p*-tolyl radical is less selective towards acetaldehyde than ethanol. As the $\mathrm{HO^{\bullet}}$ radical is probably even less selective a value for $k_{4\alpha}/k_{4\beta}$ of <6 should probably be used. However the figures used are not critical as neither reaction (4) nor (5) are involved in chain propagation. Thus a value of $k_{4\alpha}/k_{4\beta}$ of 1 raises $k_{6\alpha}/k_{6\beta}$ to 52·4 while complete α-abstraction by $\mathrm{HO^{\bullet}}$ lowers it to 38·0. On the basis of the number of hydrogens the α : β abstraction ratio for acetaldehyde becomes 122 : 1.

From the experiments with $\mathrm{(CD_3)_2CHOH}$ the primary isotope effect for β-abstraction from propan-2-ol by *p*-tolyl radicals can be determined. From the intercept of the upper plot of Figure 2 $k_{6\alpha}(\mathrm{H})/k_{6\beta}(\mathrm{D})$ is 210 giving $k_{6\beta}(\mathrm{H})/k_{6\beta}(\mathrm{D})$ as 3·7. The corresponding ratio for $\mathrm{HO^{\bullet}}$ with propan-2-ol $k_{4\beta}(\mathrm{H})/k_{4\beta}(\mathrm{D})$ is 2·1,[4] again showing the greater selectivity of the *p*-tolyl radical with respect to hydrogen abstraction.

From the slopes of the lines in Figures 1—3 the values of k_{11}/k_{12} were found to be $2{\cdot}9 \times 10^{-4}$ for $\mathrm{CH_3CH_2OH}$, $1{\cdot}3 \times 10^{-3}$ for $\mathrm{(CH_3)_2CHOH}$, $1{\cdot}4 \times 10^{-3}$ for $\mathrm{(CD_3)_2CHOH}$, and $5{\cdot}1 \times 10^{-3}$ for $\mathrm{CH_3CHO}$. As only a secondary isotope effect is involved with the deuteriated propan-2-ol, the figures for this alcohol are in excellent agreement. Burchill has reported absolute values of k_{11} as 33 for ethanol and 51 l mol^{-1} s^{-1} for propan-2-ol from his alcohol–$\mathrm{H_2O_2}$ studies,[4] assuming $2k_9$ for both β-radicals to be $2 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$. Using his figures we calculate k_{12} as $1{\cdot}12 \times 10^4$ for ethanol and $3{\cdot}8 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$ for propan-2-ol. No value of k_{11} for acetaldehyde has been reported and therefore we cannot determine k_{12} for acetaldehyde.

Our values of k_{12} are *ca.* 10^2 smaller than the value of k_8 which we estimated from pulse radiolysis studies,[2] and this is consistent with reaction (12) involving addition of the β-radical to the terminal nitrogen of the diazonium ion as $\mathrm{Ar\dot{N}\overset{+}{N}X}$ will be less resonance stabilised when X is an alkyl group than when it is an aryl group. This work confirms the recent suggestion of Seifert that alkyl radicals might add to diazonium ions,[3] but is inconsistent with his suggestions concerning the fate of the intermediate arylazoalkane radical cations.[18]

Two other possible courses of reaction (12) are addition to the ring or abstraction of the methyl hydrogen. We think the first unlikely as the intermediate cyclohexadienyl radical should reduce a diazonium ion and propagate the chain, and we discount the second as we find replacement of the *p*-$\mathrm{CH_3}$ group by *p*-$\mathrm{CH_3O}$ or *p*-$\mathrm{NO_2}$ on $\mathrm{ArN_2^+}$ gives no change in the class of kinetics with ethanol as reducing agent.

The donor–acceptor theory of radicals[19] accounts for the fact that k_{11}/k_{12} is considerably greater for acetaldehyde than for the alcohols because $\mathrm{{}^{\bullet}CH_2CHO}$, unlike $\mathrm{{}^{\bullet}CH_2CH_2OH}$ and $\mathrm{{}^{\bullet}CH_2CH(OH)CH_3}$ is an acceptor radical, this enhancing hydrogen abstraction from the donor substrate acetaldehyde and retarding reaction at a positive centre.

Lewis and Chalmers have studied the reaction of *p*-phenylenebisdiazonium ions with propan-2-ol in aqueous acidic solutions[20] and found equation (18) applies.

$$-\mathrm{d}[\mathrm{N_2^+C_6H_4N_2^+}]/\mathrm{d}t = k[\mathrm{N_2^+C_6H_4N_2^+}][\mathrm{(CH_3)_2CHOH}]/[\mathrm{H^+}] \quad (18)$$

Using [2-^{2}H]propan-2-ol they found an isotope effect of

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[16] K. M. Bansal, M. Grätzel, A. Henglein, and E. Janata, *J. Phys. Chem.*, 1973, **77**, 16.

[17] I. G. Draganić, M. T. Nenadović, and Z. D. Draganić, *J. Phys. Chem.*, 1969, **73**, 2564.

[18] C. J. Heighway, J. E. Packer, and R. K. Richardson, *Tetrahedron Letters*, 1974, 4441.

[19] E. S. Huyser, 'Free-radical Chain Reactions,' Wiley–Interscience, New York, 1969, ch. 4.

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

ca. 6. As initiation was by thermal reactions their kinetic system was more complex than the one described in this work. However in discussing their mechanism they assumed or concluded (a) that termination was mainly by radical–radical combination of *p*-$N_2^+C_6H_4^\bullet$, and (b) that β-abstraction from propan-2-ol did not occur. The results of Part I and this study show that the likelihood of termination by aryl radical dimerisation is remote. The aryl radicals might react with diazonium ions [reaction (8)] or, as β-abstraction would almost certainly occur, termination by reaction (12) and (13) is more likely. Termination by both reactions (8) and (12) would require a $[N_2^+C_6H_4N_2^+]^{-1}$ term in their kinetics. If this is the case their conclusions on initiation become invalid. Further, interpretation of their kinetic isotope effect will be more complex than they suggested. Use of [2-^{2}H]propan-2-ol would lower the fraction of aryl radicals yielding α-alcohol radicals, and the lowered yields they observed would be caused through chain termination *via* β-radicals. Although this paper only shows that $k_{6\alpha}/k_{6\beta}$ increases when the β-hydrogens are replaced by deuterium, Burchill's work on the H_2O_2–propan-2-ol system clearly shows the reverse effect when C-2 is deuteriated.

In a recent review [21] Zollinger concludes that we do not completely understand the mechanisms of homolytic decomposition of diazonium ions and related diazo-compounds and expresses the expectation that spectroscopic and chain reaction kinetic studies will be instrumental in solving the problems involved. The above discussion of Lewis's paper illustrates the dangers of drawing conclusions on chain initiation steps from kinetic data when the propagation and termination steps are unknown, while this series of papers, involving quantitative initiation of chain reactions, shows that the chain reaction kinetics vary markedly with reducing agent, concentrations, and rate of initiation.

[4/2168 *Received*, 21*st October*, 1974]

[21] H. Zollinger, *Accounts Chem. Res.*, 1973, **6**, 335.