The Reaction of *p*-Phenylenebisdiazonium Ion with Alcohols[1]

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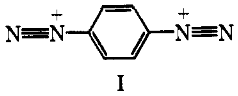
Abstract: In acidic aqueous solution, *p*-phenylenebisdiazonium ion (I, tetrazotized *p*-phenylenediamine) reacts with alcohols more rapidly than it does with water. A first-order course for the disappearance of the uv absorption of I describes only about the first half of the reaction. Deviations are ascribed to both chemical and analytical problems. The initial rate with 2-propanol and ethanol is $-d[I]/dt = k[I][ROH]/[H^+]$; the identified products were benzene and a smaller amount of benzenediazonium ion. The products are different and not identified in the presence of oxygen. Benzenediazonium ion is reduced extensively by this system. When 2-propanol-*d* is used, $k_H/k_D = 6$. A free-radical chain, initiated by the electron transfer from diazotate to diazonium ion or homolysis of a diazoanhydride, is proposed. With allyl alcohol, the product appears to be a *p*-alkylbenzenediazonium ion, the rate law is $-d[I]/dt = k[I][C_3H_5OH]/[H^+]^{1/2}$, and there is an inverse isotope effect using $CH_2{=}CH{-}CD_2OH$. Different initiation and chain-carrying steps are proposed. As predicted earlier, the iodide ion promoted conversion of I to *p*-hydroxybenzenediazonium ion involves oxygen; when oxygen is carefully excluded, this reaction is not observed.

The reactions of diazonium salts are conveniently understood in terms of the very large influence of substituents on the rates and equilibria of diazonium salt reactions[2,3] and the very large effect of the diazonium ion as a substituent on reactions elsewhere in the molecule.[4] This very large influence and susceptibility to influence are manifested in the unusual reactions of *p*-phenylenebisdiazonium ion (I) such as its acidity dependent hydrolysis[5] and its susceptibility to nucleophilic attack.[6] Unlike most diazonium salts, I does not show the "unimolecular"[7] mode of decomposition in water, yet it is unstable in the presence of most organic solvents,[5] and the reaction with dilute aqueous alcohols seemed therefore to be of interest.


I

Most diazonium salts show two types of reactions with alcohols. First, there is a reaction producing the aryl alkyl ether, which has about the same rate as the hydrolysis,[8] and follows the SN1 mechanism.[7] Secondly, there is a reaction producing the arane and an aldehyde or ketone, which is important either at high pH[9] or with electron-withdrawing substituents.[10] Since the rate is hard to reproduce and there is a pronounced sensitivity to oxygen, a free-radical chain has been proposed.[9]

Recently, conditions have been found in which the rates by the two processes are very similar, and strong evidence for a common intermediate in the two reactions has been presented.[11] No such relation between ionic and free-radical processes appears to contribute to the present problem.

The proposed chain-carrying steps are eq 1 and 2, with the possibility that eq 1 can be the two-step process 1a and 1b.

$$C_6H_5N_2^+ + R_2\dot{C}OH \longrightarrow C_6H_5\cdot + N_2 + R_2\overset{+}{C}OH \qquad (1)$$

$$C_6H_5\cdot + R_2CHOH \longrightarrow C_6H_6 + R_2\dot{C}OH \qquad (2)$$

$$C_6H_5N_2^+ + R_2\dot{C}OH \longrightarrow C_6H_5N_2\cdot + R_2COH^+ \qquad (1a)$$

$$C_6H_5N_2\cdot \longrightarrow C_6H_5\cdot + N_2 \qquad (1b)$$

Reaction 1a is an electron-transfer process, known to be fast and efficient, not only from a host of indirect evidence, but especially the rather direct results of Beckwith and Norman,[12] showing that esr signals of the radicals $\cdot CH_2OH$ and $CH_3\dot{C}HOH$ disappeared completely very shortly after mixing with diazonium salt solutions. These authors also presented evidence on reaction 1b, for on reduction of benzenediazonium salts with dithionite, a radical believed to be $C_6H_5N_2\cdot$ was observed, in agreement with earlier observations.[13] It thus appears that the reaction 1b is not essentially instantaneous, and perhaps is similar in nature to the reaction 3, which appears to be much faster with aliphatic R than with aromatic R. The perceptible stability of $ArN_2\cdot$ could have been guessed from the initial rather confusing polarographic data on the aqueous phase reduction of diazonium salts,[14] in which an apparent one-electron process is followed by further reduction to the arylhydrazine with the CN bond still intact, and is more clearly shown by the demonstrations that the first one-electron wave is well behaved in sul-

$$RCO_2\cdot \longrightarrow R\cdot + CO_2 \qquad (3)$$

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(1) Reaction of Diazonium Salts with Nucleophiles. XVII. Paper XVI in this series: E. S. Lewis and P. G. Kotcher, *Tetrahedron*, 4873 (1969). Supported by a grant from the Robert A. Welch Foundation.

(2) H. Zollinger, *Helv. Chim. Acta*, **36**, 1730 (1953).

(3) C. D. Ritchie, J. Saltiel, and E. S. Lewis, *J. Amer. Chem. Soc.*, **83**, 4601 (1961).

(4) E. S. Lewis and M. D. Johnson, *ibid.*, **81**, 2070 (1959).

(5) E. S. Lewis and M. D. Johnson, *ibid.*, **82**, 5399 (1960).

(6) E. S. Lewis and M. D. Johnson, *ibid.*, **82**, 5408 (1960).

(7) Although recently it has been shown that the unimolecular reaction *via* the aryl cation is more likely a concerted bimolecular substitution (E. S. Lewis, L. D. Hartung, and B. M. McKay, *ibid.*, **91**, 419 (1969)), the aryl cation is still a very good approximation for the transition state and the mechanism should not be abandoned, except when great detail is necessary.

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folane solutions.[15] The demonstration that eq 1b occurs readily is also apparent from the observation that the electrolysis of benzenediazonium ion in sulfolane leads to radical phenylations.[16] This free-radical chain is reminiscent of that in the hypophosphorous acid reduction of diazonium salts[17] in which the presence of inhibition and of initiation helped demonstrate the free-radical chain, and as confirmation bearing on both propagation and initiating steps, it was shown that *p*-nitrobenzenediazonium ion acted as an initiator for the reduction of *p*-toluenediazonium ion.

The mechanism of the reduction of diazonium salts by alcohols in a basic medium has been extensively restudied recently,[18] and two mechanisms were identified, one a presumed free-radical chain in which the hydrogen on the arane came from the carbon-bound hydrogen of the alcohol, and one, presumed ionic, in which the arane hydrogen came from the oxygen-bound hydrogen of the alcohol. For the free-radical reaction they prefer a chain using the radical $\cdot CH_2O^-$ instead of the $\cdot CH_2OH$ radical in De Tar's chain (eq 1 and 2). It is reasonable to suppose that either chain-carrying species may exist, depending on the acidity.

The problem of initiation of these free-radical reactions in aqueous media has been difficult. Perhaps the most satisfactory current solution has been that proposed by Rüchardt involving the homolysis of a reversibly formed diazoanhydride as in reactions 4 and 5.

$$2C_6H_5N_2^+ + H_2O \rightleftarrows C_6H_5N_2ON_2C_6H_5 \qquad (4)$$

$$C_6H_5N_2ON_2C_6H_5 \longrightarrow C_6H_5\cdot + N_2 + \cdot ON_2C_6H_5 \qquad (5)$$

This was originally proposed on the basis of kinetics of the Gomberg arylation[19] and found to be applicable with minor modification to arylation with substituted nitrosoacetanilides.[20] In this latter reaction an esr spectrum was reported, which was originally attributed to the $ArN_2O\cdot$ radical, but was later shown, quite convincingly, to be that of a more complex nitroxide radical,[21] but a second weaker, more general, resonance has been found and provisionally attributed to the $C_6H_5N_2O\cdot$ radical again.[22] Thus, we are not compelled to abandon the Rüchardt mechanism, in spite of the existence of another radical. Bunnett and Takagama[18] consider the Rüchardt mechanism unlikely in their anhydrous medium; if so, another initiation mechanism must exist.

In this paper we study the reactions of the tetrazonium ion I with isopropyl alcohol, ethanol, and allyl alcohol, and we also report one experiment confirming the participation of oxygen in the iodide ion promoted conversion of I to *p*-hydroxybenzenediazonium ion.[6]

Results

Kinetic measurements and product analysis were based almost exclusively on ultraviolet absorption spectra. The rate measurements were carried out by following the disappearance of absorption at 254 nm, the absorption maximum of I. The pseudo-first-order rate constants were obtained from the initial slope of a plot of $\ln(A - A_\infty)$ *vs.* time, where A_∞ is the absorbance after there was no perceptible further decrease. These plots were only linear for the first 40–50% of the reaction, and this is to be expected for reasons to be discussed later.

The reaction in the presence of 2-propanol and ethanol and in the absence of oxygen yielded primarily benzene as the product (identified by its characteristic fine structure in the uv absorption spectrum, both in the reaction mixture and in a pentane extract of a steam distillate of the reaction product, and also by its gas chromatographic retention time). In a larger scale run, the yield of benzene (measured gas chromatographically against an ethylbenzene internal standard) was 69%. A second product identified was benzenediazonium ion, qualitatively identified by the uv absorption of the reaction (λ_{max} 260 nm[23]) mixture and further identified by coupling with 2-naphthol 3,6-disulfonate to give a red solution λ_{max} 495 nm, in satisfactory agreement considering the purity and breadth of the peak with the value λ_{max} 490 nm previously reported.[24] The yield (based on the azo compound absorption) was 20%.

In the presence of oxygen, benzene and benzenediazonium ion were not important products. The product solution showed an ill-defined but generally strong absorbance. The products were not identified. The rate of disappearance of I was not very different from that with carefully degassed solutions.

The product using allyl alcohol (in the absence of oxygen) was a solution with λ_{max} 275 nm, very close to that of *p*-toluenediazonium ion (λ_{max} 277 nm[17]). The solution coupled with 2-naphthol 3,6-disulfonate to give a red solution. We propose tentatively that the major product is a *p*-alkylbenzenediazonium ion.

Table I shows kinetic results with 2-propanol at 30°. Runs 1–3 show the dependence on initial concentration of I, runs 4–7 show that the salt effect is small, runs 8–13 show the effect of changing alcohol concentration, runs 14–22 that of acidity, and runs 23–26 illustrate the isotope effect using 2-propanol-*2-d*. It can be seen from Table I that the reaction is first order in diazonium salt (runs 1–3), first order in 2-propanol (runs 8–13, in which the alcohol concentration varies by a factor of 5, but pseudo-second-order constant k_2 varies only randomly with a maximum range of 30%), and minus first order in acid (runs 14–21) as shown by the near constancy of *k* in the last column covering a range of perchloric acid concentrations of a factor of six. It can also be seen that the reproducibility is low (compare runs 12 and 13, 1–3 and 18, 4 and 14, and also the large, but apparently random scatter in the last column, excluding runs 25 and 26). The average value of *k* is 0.84×10^{-3} sec^{-1}, with a standard deviation of 0.12×10^{-3}. Finally, there is an isotope effect of about 6 (5.8 at 0.13 *M* alcohol and 6.3 at 0.33 *M* alcohol, not significantly different). In summary, the data are consistent with the rate law, eq 6, in which *k* includes a rate constant for attack on the alcohol α-hydrogen. In this

$$-d[ArN_2^+]/dt = k[ArN_2^+][(CH_3)_2CHOH]/[H^+] \qquad (6)$$

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Table Rate of Reaction of *p*-Phenylenebisdiazonium Ion with - ropanol in Water at 30°

Run no.	$[HClO_4]$, M	[ROH], M[a]	$k_\psi \times 10^3$, sec^{-1} [b]	$k_2 \times 10^3$, M^{-1} sec^{-1} [c]	$k \times 10^3$, sec^{-1} [d]
1	0.765[e]			1.25	0.95
2	0.765[f]			1.5	1.15
3	0.765[g]			1.2	0.92
4	0.26 (μ = 0.26)[h]			3.2	0.83
5	0.26 (μ = 0.64)[h]			3.6	0.94
6	0.26 (μ = 0.83)[h]			3.4	0.88
7	0.26 (μ = 1.28)[h]			3.4	0.88
8	0.765	0.525	0.65	1.25	0.96
9	0.765	1.05	1.08	1.05	0.80
10	0.765	1.78	1.98	1.10	0.84
11	0.765	2.10	2.10	1.00	0.77
12	0.765	2.63	3.2	1.20	0.92
13	0.765	2.63	3.4	1.30	0.99
14	0.26[i]			3.4	0.87
15	0.29[i]			3.7	1.07
16	0.48[i]			1.5	0.72
17	0.68[i]			0.9	0.62
18	0.765			1.15	0.88
19	1.07[i]			0.77	0.82
20	1.26[i]			0.67	0.84
21	1.65[i]			0.49	0.81
22	1.6[j]			0.54	0.86
23	0.44	0.13		1.7	0.75
24	0.44	0.33		2.3	1.01
25	0.44	0.13[k]		0.29	0.13
26	0.44	0.36[k]		0.36	0.16

[a] [ROH] is only shown when the variation is large. All runs fall within the range between 0.13 and 2.7 *M*. [b] The pseudo-first-order constant for disappearance of I. [c] Pseudo-second-order constant = k_ψ/[ROH]. [d] $k = k_2[H^+]$. [e] $[ArN_2^+]_0 = 1.6 \times 10^{-4}$ *M*. [f] $[ArN_2^+]_0 = 0.8 \times 10^{-4}$ *M*. [g] $[ArN_2^+]_0 = 0.4 \times 10^{-4}$ *M*. [h] Ionic strength μ made up to the value shown (in *M*) with sodium perchlorate. See Caution in Experimental Section. [i] Solutions made up to μ = 1.65 *M* with sodium perchlorate; see Caution. [j] The solution was 1.6 *M* H_2SO_4 instead of perchloric acid. The second ionization was neglected in calculating *k*. [k] The alcohol was 2-propanol-*2-d*.

Table II. Rate of Reaction of *p*-Phenylenebisdiazonium Ion with Ethanol in 0.753 *M* Perchloric Acid at 30°

[EtOH], M	$[ArN_2^+]$,[a] $M \times 10^4$	$k_\psi \times 10^4$ [b]	k_2[b] $\times 10^4$, M^{-1} sec^{-1}
0.66		2.3	3.5
1.98		7.7	3.9
2.64		10.3	3.8
3.30		10.8	3.3
1.98	1.45		3.9
1.98	0.72		3.7
1.98	0.37		3.5
		Av	3.7

[a] Roughly 1×10^{-4} *M* but not controlled with precision except where shown. [b] k_ψ and k_2 defined as in Table I.

equation and hereafter, Ar represents only the group $p\text{-}N_2^+C_6H_4^-$.

Table II shows some rather more limited results with ethanol, in which the order with respect to diazonium salt and alcohol is established, but not that with respect to acid. If the rate law is the same as eq 6, the value of *k* for ethanol is 2.7×10^{-4} sec^{-1}, about a third of that for isopropyl alcohol.

Three experiments measured the yield of benzenediazonium ion by coupling when the tetrazonium salt was all gone, and in two of these, benzenediazonium ion was deliberately added before reaction. The ionic decomposition of benzenediazonium ion in these solutions is insensitive to the presence of isopropyl alcohol and would amount to somewhat less than 10% of the total in the time of the experiments. The yields shown, therefore, are too low by substantially less than 10% of the value given. Table III presents these results. It is clear that substantial amounts of benzenediazonium ion disappear in this system; in the last entry the major reaction is the reduction of benzenediazonium ion.

Table III. Reduction of Benzenediazonium Ion by 2-Propanol in the Presence of *p*-Phenylenebisdiazonium Ion[a]

Initial $[ArN_2^+]$ (I), $M \times 10^5$	Initial $[C_6H_5N_2^+]$, $M \times 10^5$	Final $[C_6H_5N_2^+]$, $M \times 10^5$
7.75	0	1.52
7.75	4.8	1.85
3.88	9.6	3.8

[a] All solutions 0.765 *M* perchloric acid and 0.525 *M* 2-propanol.

The reaction with allyl alcohol not only gives different products, as described above, but also gives a different isotope effect. Table IV shows the kinetic results.

Table IV. Rates of Reaction of *p*-Phenylenebisdiazonium Ion with Allyl Alcohol at 30°

$[C_3H_5OH]$, M	$[HClO_4]$, M	k_2[a] $\times 10^3$ M^{-1} sec^{-1}	$k_{3/2}$[b] $\times 10^4$ $M^{-1/2}$ sec^{-1}
1.35	0.76	1.0	8.7
1.35	1.14	0.71[c]	7.6[c]
1.35	1.14	0.74[d]	7.9[d]
0.55	1.14	0.71	7.6
1.10	1.14	0.74	7.9
2.2	1.14	0.76	8.1
2.75	1.14	0.70	7.5
1.39	0.19	1.71	7.5
1.39	0.38	1.27	7.9
1.39	0.57	1.15	8.7
1.39	0.76	1.01	8.9
1.39	0.95	0.88	8.5
1.39	1.14	0.74	7.9
1.39	1.52	0.69	8.5
1.39	1.71	0.65	8.5
1.39	2.09	0.58	8.4
1.39	2.09	0.58	8.4
1.39	2.09[e]	0.79[e]	11.4[e]

[a] k_2 defined as in Table I, *i.e.*, the observed first-order constant divided by the alcohol concentration. [b] $k_{3/2} = k_2 \times [H^+]^{1/2}$. It is the constant of eq 6. The initial $[ArN_2^+]$ was of the order of 10^{-4}*M*, but not usually measured. [c] $[ArN_2^+]_{initial} = 1.1 \times 10^{-4}$ *M*. [d] $[ArN_2^+]_{initial} = 1.1 \times 10^{-4}$ *M*. [d] $[ArN_2^+]_{initial} = 0.51 \times 10^{-4}$ *M*. [e] The alcohol was $CH_2{=}CHCD_2OH$.

First-order rate plots were somewhat better than with the other alcohols; they did not deviate from linearity until more than half of the tetrazonium salt had disappeared. The last column, $k_{3/2}$, is the calculated rate law for eq 7, and the constancy (within reasonable

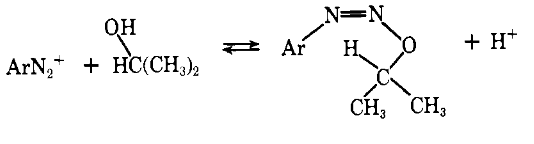
$$-d[ArN_2^+]/dt = k_{3/2}[ArN_2^+][C_3H_5OH]/[H^+]^{1/2} \quad (7)$$

limits) of $^3/_2$ supports the law. This equation gives $k_{3/2} = 0.81 \times 10^{-3}$ $M^{-1/2}$ sec^{-1} with a standard deviation of less than 0.02×10^{-3} $M^{-1/2}$ sec^{-1}, whereas *k* calculated using eq 5 varies by a factor of more than four. The isotope effect using propenol-*1-d*$_2$ is k_H/k_D = 0.76, which is probably significantly less than unity but is a little confused by an uncertainty described in the Experimental Section.

An earlier study of the reaction of I with iodide ion disclosed that there was a reaction in which iodide ion was consumed, but I was converted to *p*-hydroxybenzenediazonium ion.[6] A free-radical reaction involving oxygen was proposed tentatively. We have now repeated this observation, but when oxygen was removed and excluded by the same techniques used to study the alcohol reactions, we could find no perceptible absorption at 310 nm, the maximum of *p*-hydroxybenzenediazonium ion. The product was not otherwise identified, but the earlier radical mechanism is confirmed.

Discussion

The rate law with isopropyl alcohol can be fit by several mechanisms, one of which is the sequence of eq 8 and 9, with eq 8 rapid and reversible. This sequence is also compatible with the presence of a substantial isotope effect, the greater reactivity of the tetrazonium salt than benzenediazonium salt, and the observation that rapidly formed covalent diazo compounds usually have the syn geometry. The scheme is incompatible with the oxygen sensitivity, the reduction all the way to benzene, and the induced reduction of benzenediazonium ion. All of these are more consistent with a free-radical chain reaction, in agreement with earlier work on these reductions. The nature of the chain steps being reasonably well understood, the remaining question is the nature of initiation and termination steps.



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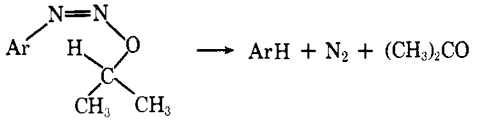


(9)

Three initiation steps may be first considered: (1) $ArN_2OH \rightarrow Ar\cdot + N_2 + \cdot OH$; (2) $ArN_2OR \rightarrow Ar\cdot + N_2 + \cdot OR$; (3) $ArN_2ON_2Ar \rightarrow Ar\cdot + N_2 + \cdot ON_2Ar$. Each of the initiating molecules may be assumed to be in rapid equilibrium with diazonium salt, at least in aqueous media. We shall also consider three termination steps, $Ar\cdot + Ar\cdot$, $Ar\cdot + R\cdot$, $R\cdot + R\cdot$, and we can then find the consequences of these in various combinations. Table V shows the predicted order with respect to ArN_2^+, alcohol, and acid for each combination. The acidity dependence arises from the equilibrium formation of initiator alone. All entries are based upon the unstable intermediate method and the assumption of long kinetic chains.

Table V. Kinetic Order with Respect to ArN_2^+, Alcohol, and Acid, Respectively, for Various Initiations and Terminations

	Termination		
Initiator	$R\cdot + R\cdot$	$R\cdot + Ar\cdot$	$Ar\cdot + Ar\cdot$
ArN_2OH	$^3/_2$, 0, $-^1/_2$	1, $^1/_2$, $-^1/_2$	$^1/_2$, 1, $-^1/_2$
ArN_2OR	$^3/_2$, $^1/_2$, $-^1/_2$	1, 1, $-^1/_2$	$^1/_2$, $^3/_2$, $-^1/_2$
ArN_2ON_2Ar	2, 0, -1	$^3/_2$, $^1/_2$, -1[a]	1, 1, -1[b]

[a] This also applies to the termination $R\cdot + ArN_2O\cdot$, if $[R] \gg [Ar\cdot]$. [b] Also for $Ar\cdot + ArN_2O\cdot$, if $[Ar\cdot] \gg [R\cdot]$.

In the first two cases of initiation, it is assumed that the radical $\cdot OH$ or $\cdot OR$ also initiates chains (by hydrogen abstraction from the alcohol), or (less likely) is inert. In the third, $ArN_2O\cdot$ can be conceivably inert, can terminate as shown in the footnotes, or can itself abstract hydrogen. It is clear that the lower right-hand entry fits the experimental results and we present below the scheme which we propose to explain the results. Equations with a letter as well as a number are alternatives which we may consider. Throughout, Ar is to be taken as p-$N_2^+C_6H_4$

$$2ArN_2^+ + H_2O \overset{K_{10}}{\rightleftharpoons} ArN_2ON_2Ar + 2H^+ \qquad (10)$$

$$ArN_2ON_2Ar \xrightarrow{k_{11}} Ar\cdot + N_2\cdot ON_2Ar \qquad (11)$$

$$ArN_2^+ + H_2O \overset{K_{10a}}{\rightleftharpoons} ArN_2O^- + 2H^+ \qquad (10a)$$

$$ArN_2^+ + ArN_2O^- \xrightarrow{k_{11a}} Ar\cdot + N_2 + \cdot ON_2Ar \qquad (11a)$$

$$Ar\cdot + HC(CH_3)_2OH \xrightarrow{k_{12}} ArH + \cdot C(CH_3)_2OH \qquad (12)$$

$$Ar\cdot + HC(CH_3)_2OH \longrightarrow \overline{ArH + \cdot C(CH_3)_2OH} \qquad (12a)$$

$$ArN_2O\cdot + HC(CH_3)_2OH \longrightarrow ArN_2^+ + OH + C(CH_3)_2OH \qquad (12b)$$

$$\cdot C(CH_3)_2OH + ArN_2^+ \xrightarrow{k_{13}} (CH_3)_2CO + H^+ + N_2 + Ar\cdot \qquad (13)$$

$$\cdot C(CH_3)_2OH + C_6H_5N_2^+ \longrightarrow (CH_3)_2CO + H^+ + N_2 + C_6H_5\cdot \qquad (14)$$

$$\overline{\cdot C(CH_3)_2OH + C_6H_5N_2^+} \longrightarrow (CH_3)_2CO + H^+ + N_2 + C_6H_5\cdot \qquad (14a)$$

$$C_6H_5\cdot + HC(CH_3)_2OH \longrightarrow C_6H_6 + \cdot C(CH_3)_2OH \qquad (15)$$

$$Ar\cdot + Ar\cdot \xrightarrow{k_{16}} \text{products} \qquad (16)$$

$$Ar\cdot + ArN_2O\cdot \longrightarrow \text{products} \qquad (16a)$$

$$C_6H_5\cdot + Ar\cdot \longrightarrow \text{products} \qquad (17a)$$

$$C_6H_5\cdot + C_6H_5\cdot \longrightarrow \text{products} \qquad (17b)$$

$$C_6H_5\cdot + ArN_2O \longrightarrow \text{products} \qquad (17c)$$

In the initial stages of the reaction when $[C_6H_5N_2^+]$ is small, we can consider only the series 10, 11, 12, 13, and 16, and the steady-state equation is eq 18. The kinetic law is in agreement with that observed, and the failure to give good kinetics over larger extents of completion is certainly to be expected from the neglect of reactions involving phenyl radicals and benzenediazonium ions, especially since many of the products absorb at the wavelength of measurement. The fact that k_{12} appears to be the first power explains the substantial isotope effect. A substantial isotope effect ($k_H/k_T = 7$) in the product-determining step in the reduction of *p*-nitrobenzenediazonium ion by ethanol has been observed,[25] but this may not bear on the rate-determining process. It is, therefore, not profitable to compare the magnitudes of the isotope effects.

$$-d[ArN_2^+]/dt = k_{12}\left(\frac{k_{11}k_{10}}{k_{16}}\right)^{1/2}\frac{[ArN_2^+][ROH]}{[H^+]} \qquad (18)$$

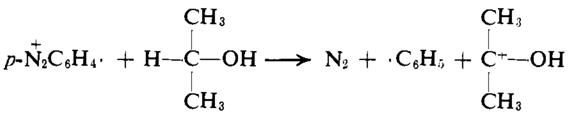
(25) L. Melander, *Ark. Kemi*, 3, 525 (1951); the experimental result is undisputed although the reaction was then thought to be a hydride transfer.

The reduction of benzenediazonium ion in methanol is also slowed by acid.[9] Oxygen was reported to have a marked influence on the rates as well as the products, but this report is now open to question.[11] Nevertheless, the similarity of the two situations is great, and we can consider the possibility that both have the same initiation steps. In anhydrous methanol, the diazoanhydride cannot be so easily formed,[18] but it is nevertheless possible if we recognize that the diazo acetates are acylating agents, as suggested by Rüchardt.[20] At least the diazoanhydride initiation is as good as any initiation suggested and recognized as inadequate by DeTar and Turetzky.[9]

Reactions 10a and 11a are kinetically acceptable and initiatively attractive alternatives here (and in Rüchardt's cases) to the homolysis of the diazoanhydride, reactions 10 and 11. Reaction 11a is another electron transfer reaction, possibly quite fast. If we attempt to guess k_{11}, the rate of homolysis of the diazoanhydride, no precise result can be obtained, but from related equilibria,[3,5,26] one would guess that the fraction of diazonium salt in the form of diazoanhydride under the conditions used would be between 10^{-6} and 10^{-10}, and if we further make the arbitrary guess that the kinetic chain length is 100, we find that k_{11} probably lies between 10 and 10^5. At 10° lower temperature, the half-life for the decomposition of 4,4′-dichlorodiphenyldiazoanhydride is 400 min,[27] corresponding to a rate constant of about 3×10^{-5} sec^{-1}. The extraordinary sensitivity to substituents might argue against both reactions being the same process, but it is also reported[27] that 4,4′-dinitrodiphenyldiazoanhydride is very unstable at 0° and not isolable. It does seem that the mode of decomposition of the diazoanhydrides is to give free radicals, either by reaction 11 or by heterolysis followed by 11a, rather than the one-step cis elimination proposed. It is of course possible that the cis–cis geometry proposed for the isolable diazoanhydrides is incorrect, since the evidence is somewhat ambiguous; an anhydride in mobile equilibrium with diazonium salt probably would have this cis–cis structure.

Equations 12a and 14a recognize that the products of 12 are the same as the reagents of 14, and hence if the reaction is fast enough, there may be a cage reaction. The fact that benzenediazonium ion is produced shows that there must be at least some leakage from the cage reaction 12a.

The possibility might be considered that, in fact, a portion of the reaction going from Ar· to C_6H_5 does not go through steps 12 and 14 or even 12a and 14a but instead through the one-step reaction 19. It is an



$$p\text{-}\overset{+}{N}_2C_6H_4\cdot + H{-}\underset{CH_3}{\overset{CH_3}{C}}{-}OH \longrightarrow N_2 + \cdot C_6H_5 + \underset{CH_3}{\overset{CH_3}{C^+}}{-}OH \quad (19)$$

amusing exercise to attempt to write this reaction with "curved arrows"; the difficulty is related to the fact that the π orbital system is orthogonal to the orbitals in which the odd electron probably resides. We do not consider this one-step process likely.

The scheme accounts for the formation of the products and predicts that benzenediazonium ion would be reduced by 2-propanol if a source of 2-hydroxy-2-propyl radicals were available. In fact, the radiolysis of water produces radicals which can attack 2-propanol to give these radicals, and benzenediazonium ion is reduced in a reaction of long chain length.[28]

The various alternative terminations are reasonable only if the two aryl radicals are the predominant ones, and this requires that reaction 12 be substantially slower than reaction 14. Electron-transfer reactions such as 14 can be very fast,[11] and may not have any barrier. Similarly, the electron transfer from hydroxyalkyl radicals to nitrobenzene is essentially complete in dilute solution in *ca.* 0.02 sec,[29] and diazonium salts should be even better electron acceptors. The hydrogen atom transfer 12 must be well below the diffusion-controlled rate in order to show a substantial isotope effect and by analogy with other abstraction reactions is many orders of magnitude below the diffusion-controlled limit. It is then reasonable to call upon reactions 16 or 16a for termination. The above discussion of diazoanhydride decomposition rates would suggest that in the absence of other reagents, reaction 10 would be followed by 16a, and the observation[27] of diazo ether p-$ClC_6H_4N_2OC_6H_4Cl$ as the reaction product from the diazoanhydride is entirely consistent with these views.

The reaction of the tetrazonium salt with allyl alcohol is quite different. The product appears to be a p-alkyldiazonium salt, the order with respect to acid is $-{}^1/_2$, and the isotope effect is different. The kinetics fit the central entry in Table V, and suggest a chain initiated by ArN_2OR, but the chain must be different. The inverse isotope effect suggests that loss of hydrogen from the α-hydrogen is involved in a termination step rather than propagation or initiation steps.[30] The following chain is tentatively suggested (eq 20–26). This

$$ArN_2^+ + HOCH_2CH{=}CH_2 \rightleftarrows ArN_2OCH_2CH{=}CH_2 + H^+ \quad (20)$$

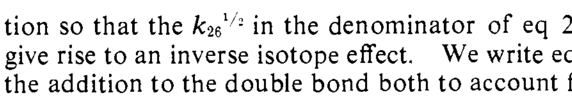
$$ArN_2OCH_2CH{=}CH_2 \longrightarrow ArN_2O\cdot + \cdot CH_2CH{=}CH \quad (21)$$

$$H_2O + \cdot CH_2CH{=}CH_2 + ArN_2^+ \longrightarrow HOCH_2CH{=}CH_2 + H^+ + N_2 + Ar\cdot \quad (22)$$

$$Ar\cdot + CH_2{=}CHCH_2OH \longrightarrow ArCH_2\dot{C}HCH_2OH\ (R\cdot) \quad (23)$$

$$R\cdot + CH_2{=}CHCH_2OH \longrightarrow R\cdot \quad (24)$$

$$H_2O + R\cdot + ArN_2^+ \longrightarrow H^+ + ROH + \cdot Ar + N_2 \quad (25)$$



$$R\cdot + ArN_2O\cdot \longrightarrow ArN_2OH + Ar(CH_2\underset{CH_2OH}{CH})_nCH_2CH{=}CHOH \quad (26)$$

series (if the chain is long, and if $[Ar\cdot] > [R\cdot]$) gives the rate law, eq 27. We write eq 26 as a hydrogen abstraction so that the $k_{26}^{1/2}$ in the denominator of eq 27 will give rise to an inverse isotope effect. We write eq 23 as the addition to the double bond both to account for the presumed product, p-alkylbenzenediazonium ion, and to agree with the known behavior of allyl compounds,

$$-d[ArN_2^+]/dt = k_{25}[ArN_2^+][C_3H_5OH]\left[\frac{k_{21}K_{20}}{k_{23}k_{26}[H^+]}\right]^{1/2} \quad (27)$$

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(26) E. S. Lewis, *Texas J. Sci.*, 11, 275 (1959).

(27) T. Kauffmann, H. O. Friestad, and H. Henkler, *Justus Liebigs Ann. Chem.*, **634**, 64 (1960).

(28) D. Schulte-Frohlinde and H. Blume, *Z. Phys. Chem.*, **59**, 282 (1968).

(29) A. L. Buley and R. O. C. Norman, *Proc. Chem. Soc.*, 225 (1964).

(30) See, for such an example, the polymerization of allyl acetate; P. D. Bartlett and F. A. Tate, *J. Amer. Chem. Soc.*, 75, 91 (1953).

which do polymerize (although not very well).[31] The initiation is novel but not unreasonable, and probably more reasonable than a reaction giving an alkoxy radical.

This chain, in spite of its success in accounting for the products, can hardly be taken to be more than an informed speculation, and we do not present it as more than this.

Experimental Section

Materials. The preparation of p'-phenylenebisdiazonium tetrafluoroborate was as described before.[5] The alcohols were commercial materials; 2-propanol-2-*d* was prepared by the lithium aluminum hydride reduction of acetone by standard procedures; it was gas chromatographically homogeneous. The deuterated allyl alcohol was made from acryloyl chloride and lithium aluminum deuteride,[32] but the product showed an impurity absorbing significantly at 254 mμ. This alcohol showed a fast reaction with the tetrazonium salt. On preparative scale gas chromatography (30% Ucon 50HB260 on 45–60 Chromosorb P) the absorbing material was removed and the rate was apparently normal. The sensitivity of the uv, the efficiency of the gas chromatography, and the rather modest rate acceleration with the impurity present lead us to believe that the reported k_D is correct, but there is a small chance that the inverse isotope effect may be due to an accelerating impurity in the deuterated species.

Kinetic Runs. A typical run describes the procedure which is straightforward except for the necessity for removing oxygen and the cautions described below. Separate solutions containing, respectively, 5.15 M sodium perchlorate, 5.15 M perchloric acid, and 6×10^{-5} M p-phenylenebisdiazonium tetrafluoroborate in 5.15 M perchloric acid were prepared. Prepurified nitrogen was bubbled first through water and then through each of the solutions for 4 hr. Nitrogen was also passed through 2-propanol for the same period. All solutions were kept in a water bath at 30° while the oxygen was being removed.

A 1-cm cylindrical quartz cell was fitted with a serum stopper through which two small glass tubes were passed. One was used to pass nitrogen into the cell, the other accommodated a thin Teflon tube attached to an all-glass syringe. Necessary amounts of the reagents were then withdrawn from the previously prepared solutions and added to the cell with a constant nitrogen stream flowing both during withdrawal and addition. After all the reagents were added, the glass tubes were removed from the stopper, the contents were mixed, and the cell was placed in the beam of a Cary 14 spectrophotometer in a thermostatted cell jacket. The instrument then gave a record of the absorbance at 254 nm *vs.* time.

Caution. The use of diazonium salts with perchlorates introduces a significant hazard. All diazonium perchlorates have a very limited solubility and the solids, if precipitated, are extremely sensitive, even when suspended in solution, and quite small amounts detonate with enough violence to break glassware. The amounts needed for spectrophotometric work are not hazardous, but attempts to increase the scale must be done with great caution. The solubility product of benzenediazonium perchlorate is of the order of 10^{-4} M^2, and others appear to be comparable. Thus, solid can be precipitated with even rather modest concentrations of both ions.

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A New Polymer-Support Method for the Synthesis of Ribooligonucleotide[1]

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Abstract: The ribooligonucleotide triuridine diphosphate (UpUpU) has been synthesized on a new polymer system of isotactic succinylated polystyrene. 2′-*O*-Benzoylpropionyl-3′-*O*-methoxyacetyluridine was linked to the polymer *via* a 5′ ester group and served as the first nucleoside unit. After repeated demethoxyacetylation and condensation with 2′-*O*-benzoylpropionyl-3′-*O*-methoxyacetyluridine 5′-phosphate, the trinucleotide was obtained. The yields were about 50% in each condensation step. The preparation of the suitably protected nucleosides and nucleotides used in the experiment is also described.

The synthesis of ribooligonucleotides of known sequence is important for the cytochemical study of the function of ribonucleic acid. While deoxyoligonucleotides have been prepared stepwise on a polymer support,[2–6] no successful solid-phase support procedure for the synthesis of ribooligonucleotide has so far been developed. The difficulties arise from (1) lack of suitable solid-phase support which can be used with ease and speed, and (2) the presence of the 2′-hydroxyl group in the ribofuranose moiety makes the 3′ nucleotide labile under extreme alkaline and acid conditions. We have recently found that high molecular weight isotactic polystyrene[7] can be used as a polymer support. Previously, soluble polystyrene or cross-linking polystyrene was used. The isotactic polymer possesses high crystallinity which makes it insoluble and reduces swelling in organic solvents. Therefore, this polymer should be superior for oligonucleotide synthesis since it contains less inner space when compared with the cross-linked polystyrene. In addition, the isotactic polymer can be

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