mechanism very similar to that under N_2, and that inhibition by O_2 is not totally efficient.

Registry No.—**1a,** 673-40-5; **1b,** 459-64-3; **2a,** 108-86-1; **2b,** 100-66-3; **3a,** 104-92-7; **3b,** 150-78-7; *p*-toluenesulfonic acid, 104-15-4; sulfuric acid, 7664-93-9; methanol, 67-56-1.

Supplementary Material Available. Tables IV and V give detail for all experiments similar to that given for a few in Table I (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Research supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society.
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Thermolysis of Arenediazonium Salts in Acidic Methanol. Effects of Substituents, Atmospheres, and Added Substances on the Competition between Ionic and Radical Mechanisms[1]

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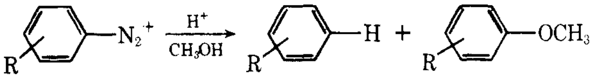
Thermolysis of benzenediazonium ions in acidic methanol gives either protodediazoniation or methoxydediazoniation. Several types of evidence, including the identity of minor by-products, experiments to trap radical intermediates, and the effects of added substances on product compositions, indicate competition between independent radical (giving protodediazoniation) and ionic (giving methoxydediazoniation) mechanisms. The radical mechanism is repressed by O_2 and certain other radical scavengers. For the *m*-Br, *p*-Br, *m*-Cl, *p*-Cl, and *p*-OCH_3 substituted benzenediazonium salts the radical mechanism predominates under a N_2 atmosphere and the ionic mechanism predominates under O_2. For the H, *p*-CH_3, *m*-CH_3, and *m*-OCH_3 compounds the ionic mechanism predominates under both atmospheres while for the *p*-NO_2 compound the radical mechanism predominates under both.

The main products from the thermolysis of diazonium salts in acidic methanol (at pH 1–3) are benzene derivatives (**2**) resulting from protodediazoniation and aryl methyl ethers (**3**) that represent methoxydediazoniation (eq 1).



(1)

1 **2** **3**

a, R = H
b, R = *m*-Br
c, R = *p*-Br
d, R = *m*-Cl
e, R = *p*-Cl
f, R = *m*-CH_3
g, R = *p*-CH_3
h, R = *m*-OCH_3
i, R = *p*-OCH_3
j, R = *p*-NO_2

DeTar and Kosuge[2] made the striking observation that for two diazonium salts (**1c** and **1i** bisulfates) the former type of product (**2**) predominates when the atmosphere above the reacting solution is nitrogen but that under oxygen principally the aryl methyl ether is formed. Arguing mainly from that evidence, they suggested that methoxydediazoniation occurs by an ionic mechanism, via aryl cation intermediates, and that protodediazoniation occurs for the most part by a radical mechanism. However, for the rather small component of protodediazoniation observed under O_2, where a radical mechanism was expected to be suppressed, they suggested an ionic mechanism involving abstraction of hydride ion from the α position of the alcohol by aryl cations.[3]

We have reinvestigated these phenomena, partly to extend description of them, partly to apply various tests of mechanism, and for the most part the evidence we have obtained supports the mechanistic suggestions of DeTar and Kosuge. However, we find no support for their suggestion of a minor ionic protodediazoniation pathway. We have given a preliminary account[4] of some of our work, but in one respect our present interpretation differs from that offered earlier.

Certain other studies bear directly on our work. Melander[5] investigated the dediazoniation of *o*- and *m*-nitrobenzenediazonium sulfates in acidic tritium-labeled methanol and ethanol, and found that the hydrogen atom that takes the place vacated by the diazonio group comes from the α position of the alcohol, not from the hydroxy group. Horner and Stöhr[6] found that thermolysis of unsubstituted benzenediazonium sulfate in methanol gave mainly anisole under either N_2 or O_2 and that benzene, formed in small amount (4%) under N_2, did not appear under O_2. The kinetics of protodediazoniation of benzene-1,4-bisdiazonium ion in aqueous 2-propanol were studied by Lewis and Chalmers.[7] The photolytic and radiolytic decomposition of *p*-toluenediazonium ion in water solutions of methanol and other alcohols was studied by Packer and co-workers;[8] the chief product is toluene, quantum yields as high as 8 have been measured for photolysis, and inhibition by O_2 is strong, all consistent with a radical chain mechanism.

Zollinger and associates[9] studied the thermolysis of benzenediazonium ion in 2,2,2-trifluoroethanol solutions; they found evidence of an ionic mechanism via phenyl cation except when a radical pathway was catalyzed by a substance

Table I. pH Effects on Rates and Products from Thermolysis of Benzenediazonium and p-Bromobenzenediazonium Fluoroborates in Methanol

					Products, %	
Substituent	Temp, °C	Acid[a] or base	Atmosphere	$10^4 k_\psi$, s^{-1}	2	3
H	29.8	TsOH, 0.01 M	N_2	2.0		
	65	TsOH, 0.1 M	N_2		0	88
	29.8	TsOH, 0.01 M	O_2	2.0[b]		
	65	TsOH, 0.1 M	O_2		0	92
	30	Nil	N_2	2.0	3	66
	30.1	CH_3ONa, 0.1 M	N_2	200		
	30	CH_3ONa, 1.1 M	N_2		64	0
p-Br	65.2	TsOH, 0.01 M	N_2	3.6–8.6[c]		
	65	TsOH, 0.1 M	N_2		73[d]	19[d]
	65.2	TsOH, 0.01 M	O_2	2.2[e]		
	65	TsOH, 0.1 M	O_2		4[d]	72[d]
	30	Nil	N_2	0.15	82	5
	30	CH_3ONa, 0.1 M	N_2	69		
	30	CH_3ONa, 0.01 M	N_2		66	0

[a] TsOH is p-toluenesulfonic acid. [b] Extrapolated from higher temperatures. [c] Extremes of the range of 18 observations are given; from measurements at 65.2 °C and other temperatures, the extrapolated k_ψ at 30 °C is 4.4×10^{-6} s^{-1}. [d] Average of determinations listed in Table II. [e] Average from three runs.

Table II. Product Compositions from Thermolysis of Substituted Benzenediazonium Fluoroborates under Nitrogen and under Oxygen at 65 °C

		Under N_2		Under O_2	
Registry no.	Substituent	2, %[a]	3, %[a]	2, %[a]	3, %[a]
369-57-3	H	0[b]	88, 89[c]	0,[b] 3	92,[c] 94
500-25-4	m-Br	38, 36, 39,[c] 68[c]	59, 52, 61,[c] 21[c]	4,[c] 0[d]	84,[c] 89[d]
673-40-5	p-Br[e]	68, 74, 63, 84, 78,[c] 85,[f] 94[g]	16, 20, 23, 16, 18,[c] 3,[f] 4[g]	3, 3, 4, 6[c]	69, 81, 70, 70[c]
456-39-3	m-Cl	44, 51, 55, 92, 84[c]	40, 36, 38, 9, 13[c]	6,[c] 0[d]	86,[c] 92[d]
673-41-6	p-Cl	71, 94, 84,[c] 90[c]	14, 8, 8,[c] 11[c]	5,[c] 13[c]	54,[c] 57[c]
1422-76-0	m-CH_3	0[b]	94, 95, 100[c]	0[b]	100,[c] 90[d]
459-44-9	p-CH_3	0[b]	93, 93, 90[c]	0	95[c]
17569-84-5	m-OCH_3	6, 6, 6[c]	85, 86, 90[c]	6,[c] 0[d]	86,[c] 91[d]
459-64-3	p-OCH_3[e]	80,[c] 76[c]	18,[c] 24[c]	22,[c] 8	62,[c] 78
456-27-9	p-NO_2	86, 92	0[b]	35, 40	7, 0.4

[a] Each entry in a column represents a different experiment, or the average of two concordant experiments; experiments are entered in the same order in the columns for % **2** and % **3**. [b] Only traces if any detected in any experiment. [c] Average of two concordant experiments utilizing the same batch of reacting solutions. [d] At 50.6 °C, with 0.01 M p-toluenesulfonic acid. [e] For more extensive data, see ref 12. [f] 30 °C. [g] 27 °C.

such as pyridine. Indeed, the discovery of isotopic exchange with added N_2 and of capture of added carbon monoxide ultimately to form trifluoroethyl benzoate point definitively to the intermediacy of phenyl cation.[10] In this connection, Swain, Sheats, and Harbison[11] adduced several types of evidence showing that aryl cation intermediates are intermediates in the thermal hydroxydediazoniation of diazonium salts in water.

Bunnett and Yijima[12] determined rates and products of the thermolysis of p-bromo- and p-methoxybenzenediazonium fluoroborates in acidic methanol under N_2 and under O_2. Their data show variation of product composition with atmosphere much as reported by DeTar and Kosuge,[2] and that the rate of methoxydediazoniation is independent of the atmosphere. An oxygen atmosphere specifically represses the rate of protodediazoniation.

Results

Gross pH Effects on Rates and Products. Some representative data are set forth in Table I. Unsubstituted benzenediazonium ion undergoes mainly methoxydediazoniation in acidic methanol under either O_2 or N_2 and its proclivity to this mode of reaction is such that anisole is the main product even in initially neutral methanol under N_2. The rate also is the same under these three sets of conditions. However, with methanolic sodium methoxide the rate is much greater and the product is mainly benzene,[13] no anisole being detectable. Indeed, in experiments with several diazonium salts (mostly not reported here) we have never observed any methoxydediazoniation to occur in methanol containing methoxide ion in substantial concentration (0.001 M or higher).

The rate–product pattern with p-bromobenzenediazonium ion is different; in acidic methanol the product composition and total thermolysis rate change sharply as the atmosphere is changed from N_2 to O_2. As with benzenediazonium ion itself, the rate of thermolysis in strongly basic methanol is much greater than in the absence of sodium methoxide and only protodediazoniation is observed.

Variation of Product Composition with Atmosphere. We determined the percentages of protodediazoniation (**2**) and methoxydediazoniation (**3**) products formed from several diazonium salts in acidic methanol under N_2 or under O_2. Our results are summarized in Table II. In the cases of the p-bromo- and p-methoxybenzenediazonium ions, Bunnett and Yijima[12] have performed this type of experiment more extensively and their data are qualitatively similar to those now reported.

Three diazonium salts, benzenediazonium fluoroborate (**1a**) and its *m*-methyl (**1f**) and *p*-methyl (**1g**) derivatives, undergo virtually exclusive methoxydediazoniation under either atmosphere, only traces of benzene or toluene being detectable as products. The behavior of the *m*-methoxy substrate (**1h**) is similar, only about 6% of protodediazoniation product being detectable even under N_2. At the other extreme is *p*-nitrobenzenediazonium fluoroborate (**1j**), which gave no methoxydediazoniation product (**3j**) under N_2 and very little of it under O_2.

The product compositions from the other diazonium salts are strongly dependent on the atmosphere, mainly protodediazoniation occurring under N_2 and mainly methoxydediazoniation under O_2.

We call attention to the variability of the product compositions observed from thermolysis of the *m*-bromo and *m*-chloro substrates under N_2. Although in some experiments protodediazoniation predominated just as for their para isomers, in others the two modes of reaction occurred in rather similar amounts. Essentially the same technique was used in all these cases.

Our results for the *p*-bromo and *p*-methoxy substrates are qualitatively similar to those of DeTar and Kosuge.[2] However, they differ appreciably in the case of *p*-nitrobenzenediazonium ion; the earlier workers reported about 40% of *p*-nitroanisole to be formed under either atmosphere. They also differ for *p*-toluenediazonium ion; the earlier report was that substantial amounts of toluene were formed under N_2, more at 25 °C than at 65 °C. In this case we also examined the thermolysis reaction under N_2 at 25 °C and at 46 °C and obtained results nearly the same as listed in Table II for 65 °C. DeTar and Kosuge determined product compositions by UV spectrophotometric analysis; the apparent errors in their determinations may be attributed to limitations of that method.

Formaldehyde as a By-Product. *p*-Bromobenzenediazonium fluoroborate (**1c**) was allowed to decompose completely in acidic methanol under N_2, and the resulting solution was treated with tetrahydrophthalazine; the expected product of condensation with formaldehyde[14] was obtained. However, by the same method no formaldehyde could be found as a product of thermolysis of **1c** in acidic methanol under O_2.

Minor Products from *p*-Bromobenzenediazonium Fluoroborate. Large-scale thermolysis reactions of this substrate (0.01 M) in methanol 0.1 M in H_2SO_4 were conducted under N_2 and O_2 atmospheres in order to provide substantial amounts of minor by-products for ease of determination and identification. Under N_2, besides 70.6% of bromobenzene and 14.5% of *p*-bromoanisole, we obtained 0.6% of *p*-bromobenzyl alcohol, 0.4% of *p*-bromophenol, 0.3% of 4,4′-dibromobiphenyl, and indications of traces of 4,4′-dibromoazobenzene. Under O_2, in addition to 4.2% of bromobenzene and 71.9% of *p*-bromoanisole, we got 6.4% of *p*-bromophenol and 0.3% of 4,4′-dibromobiphenyl. Although these product yields sum to less than 90% in both cases, we were unable despite assiduous search to find tangible amounts of other products.

Experiments to Trap Intermediates. Benzenediazonium fluoroborate was subjected to thermolysis under N_2 in methanol-*O-d* containing 0.1 M D_2SO_4 and also in initially neutral CH_3OD; the benzene obtained was virtually deuterium free in both cases. *p*-Bromobenzenediazonium fluoroborate thermolysis under the same two sets of conditions likewise furnished bromobenzene containing 1.5 mol % or less of deuterium. Thus the hydrogen atom that takes the place of the diazonio group in protodediazoniation comes from the methyl group of the methanol solvent, not from the hydroxy group.

Inasmuch as aryl radicals readily abstract iodine atoms from aryl iodides,[15] the obtaining of ArI from thermolysis of ArN_2^+ in the presence of Ar′I would constitute evidence for the intermediacy of Ar· radicals. We observed that thermolysis (at 65 °C) of *p*-bromobenzenediazonium fluoroborate in acidic methanol under N_2 in the presence of iodobenzene (0.24 M) afforded 40% of *p*-bromoiodobenzene. However, a similar reaction under O_2 gave no detectable amount of *p*-bromoiodobenzene. Thermolysis of benzenediazonium fluoroborate (at 30 °C) in acidic methanol under N_2 in the presence of *m*-chloroiodobenzene (0.21 M) yielded only 4% of iodobenzene. This criterion indicates that *p*-bromophenyl radicals are formed abundantly in the thermolysis of **1c** under N_2 but not under O_2, and that few phenyl radicals are generated during thermolysis of **1a** under N_2.

Thermolysis of *p*-bromobenzenediazonium fluoroborate in acidic methanol containing I_2 (0.009 M) under O_2 afforded 11% of bromobenzene, 5% of *p*-bromoanisole, and 37% of *p*-bromoiodobenzene.

Product Effects of Diverse Substances. Table III summarizes the effects of several substances on product yields, mainly from *p*-bromobenzenediazonium ion (**1c**). For each substrate and atmosphere, the average product composition in the absence of added substances (from Table II) is also shown.

For thermolysis of **1c** under N_2, sharply increased proportions of **3c**, at the expense of **2c**, were obtained when 2-methyl-2-nitrosopropane (*t*-BuNO), ferrous sulfate, or nitrous acid was present. Phenylazotriphenylmethane (PAT) and galvinoxyl had the opposite effect. Anthraquinone-2-sulfonic acid had, within experimental error, no effect. The effects of cuprous chloride and 2,2′-dipyridyl were slight and similar, being to increase somewhat the proportion of **2c** formed. It is noteworthy that at 35.2 °C **2c** remains the preferred product rather than **3c** despite the presence of 0.01 M nitrous acid; in the absence of nitrous acid the predominance of **2c** is also greater at the lower temperature, as may be seen in Table II.

For thermolysis of **1c** under O_2, added substances have qualitatively similar effects but they appear more subtly in the data. Certainly *t*-BuNO and perhaps nitrous acid operate further to repress formation of **2c**. Azobisisobutyronitrile (AIBN) causes the yield of **2c** actually to surpass that of **3c** under O_2 but the sum of the yields of the two products is only about 50%. The other added substances have effects indistinguishable from experimental error.

Considering now the other diazonium salts in Table III, we see that the effects of PAT and *t*-BuNO are qualitatively similar to those on thermolysis of **1c**. Especially to be noted is the cooperativity of the effects of O_2 and *t*-BuNO on thermolysis of *p*-nitrobenzenediazonium ion (**1j**); whereas this substrate forms no **3j** under N_2 and very little under O_2, the combination of O_2 and *t*-BuNO enables **3j** to become the predominant product, although the yields of **2j** and **3j** total only 37%.

Product Effect of Illumination. A few experiments were conducted in a Rayonet photochemical reactor equipped with "300-nm" (broad band) fluorescent lamps, the temperature of the reacting solution being 28 °C. Photolysis of **1c** under N_2 gave 77% of **2c** but no **3c**; under O_2 14% of **2c** and 25% of **3c** were formed, and it is unclear what happened to the rest of the **1c** under O_2. Comparison with thermolysis experiments at about the same temperature suggests that product patterns from the two modes of decomposition are rather similar.

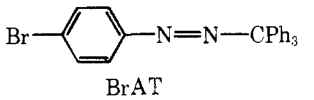
Atmosphere Effects on the Thermolysis of *p*-Bromophenylazotriphenylmethane (BrAT). These experiments have been performed to test the possibility that O_2 might affect product formation from **1c** by oxidizing *p*-bromophenylazo or *p*-bromophenyl radical to some precursor of **3c**.

Table III. Effects of Diverse Substances on Product Composition in Thermolysis of Substituted Benzenediazonium Fluoroborates in Acidic Methanol

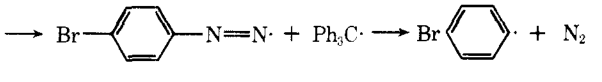
Substituent	Added substance	Temp, °C	Atmosphere	Products, %	
				2[a]	**3**[a]
p-Br		65	N_2	74[b]	18[b]
	t-BuNO,[c] 0.005 M	65	N_2	12, 9, 33	45, 67, 45
	$FeSO_4$, 0.00125 M	65.8	N_2	20[d]	70[d]
	HNO_2, 0.01 M	78.4	N_2	14	63
	HNO_2, 0.001 M	55.6	N_2	13	67
	HNO_2, 0.005 M	55.6	N_2	19, 32,[d] 20	56, 44,[d] 42
	HNO_2, 0.01 M	55.6	N_2	9, 23	63, 60
	HNO_2, 0.01 M	35.2	N_2	56, 49	26, 13
	Galv,[e] 0.005 M	65.8	N_2	94[d]	2[d]
	Anq,[f] 0.002 M	55.6	N_2	66	16
	Anq, 0.004 M	55.6	N_2	78	10
	PAT,[g] 0.005 M	65.4	N_2	99	0
	Dipy,[h] 0.001 M	65	N_2	74	7
	CuCl, 2×10^{-5} M	65.2	N_2	77	6
	CuCl, 0.001 M	65.2	N_2	76[d]	4[d]
p-Br		65	O_2	4[b]	72[b]
	t-BuNO, 0.005 M	65	O_2	1[d]	68[d]
	$FeSO_4$, 0.00125 M	65.8	O_2	6[d]	74[d]
	HNO_2, 0.01 M	78.4	O_2	4	78
	HNO_2, 0.001 M	55.6	O_2	0	68
	HNO_2, 0.005 M	55.6	O_2	4[i]	73[i]
	HNO_2, 0.01 M	55.6	O_2	3	73
	HNO_2, 0.01 M	35.2	O_2	15, 8	47, 41
	Galv, 0.005 M	65.8	O_2	18	40
	Anq, 0.002 M	55.6	O_2	5	67
	Anq, 0.004 M	55.6	O_2	4	67
	Dipy, 0.001 M	65	O_2	4	73
	CuCl, 2×10^{-5} M	65.2	O_2	9	54
	CuCl, 0.001 M	65.2	O_2	5	54
	AIBN,[j] 0.04 M[k]	70	O_2	32	20
	AIBN, 0.06 M[k]	70	O_2	31	16
p-Cl		65	N_2	86[b]	10[b]
	PAT, 0.005 M	65.4	N_2	95[d]	0[d]
p-OCH_3		65	N_2	78[b]	21[b]
	t-BuNO, 0.005 M	65.5	N_2	24	49
		65	O_2	17[b]	67[b]
	t-BuNO, 0.005 M	65.5	O_2	3	62
	t-BuNO, 0.01 M	65.5	O_2	11	60
p-NO_2		65	N_2	89[b]	0[b]
	t-BuNO, 0.01 M	65.5	N_2	43	16
		65	O_2	38[b]	4[b]
	t-BuNO, 0.01 M	65.5	O_2	6	31

[a] Each entry in a column represents a different experiment, or the average of two or more concordant experiments; experiments are entered in the same order in the columns for % **2** and % **3**. [b] Average value from Table II. [c] "*t*-BuNO" is 2-methyl-2-nitrosopropane. [d] Average of two concordant experiments. [e] "Galv" is galvinoxyl. [f] "Anq" is anthraquinone-2-sulfonic acid. [g] "PAT" is phenylazotriphenylmethane. [h] "Dipy" is 2,2′-dipyridyl. [i] Average of four concordant runs. [j] "AIBN" is azobisisobutyronitrile. [k] *p*-Toluenesulfonic acid, 0.01 M.

Thermolysis of BrAT under N_2 afforded **2c** in 70% yield. Under O_2 the same product was formed in 46% yield. In neither case was any **3c** obtained. Other products were not sought.



BrAT



(2)

The thermolysis of BrAT was also carried out in methanol containing 0.24 M iodobenzene. Under N_2 14% of **2c** and 29% of *p*-bromoiodobenzene were formed; under O_2 these yields sank to 10 and 18%, respectively. The formation of *p*-bromoiodobenzene is attributed to iodine atom abstraction from iodobenzene by the *p*-bromophenyl radical, formed as in eq 2.[16]

Discussion

The primary question to which this research was addressed was why changing the atmosphere from N_2 to O_2 should cause the course of thermolysis of several diazonium salts in acidic methanol to switch from mainly protodediazoniation to mainly methoxydediazoniation. The present results, together with the kinetic data of Bunnett and Yijima,[12] provide a clear answer: there are competing radical chain and ionic mechanisms of thermolysis; in some cases the balance of rates is such that the radical chain mechanism predominates under N_2 but is suppressed under O_2 sufficiently so that the slower ionic mechanism prevails. The radical mechanism leads principally to protodediazoniation products (**2**) and the ionic mechanism to aryl methyl ethers (**3**).

The present work also provides information about the effects of substituents on the relative rates of the two reaction pathways.

Evidence That Protodediazoniation Occurs by a Rad-

ical Mechanism. Most of the evidence relates to experiments with *p*-bromobenzenediazonium ion (**1c**).

Protodediazoniation is stimulated by the addition of good radical sources. Whereas thermolysis of **1c** under N_2 gives a mixture of mainly **2c** and some **3c**, thermolysis in the presence of PAT affords **2c** without **3c**. A parallel observation was made in respect to thermolysis of **1e** (Table III). PAT is known to undergo homolysis, in the manner of eq 2, to form phenyl radicals.[16,17] The phenyl radicals so formed initiate a radical chain mechanism which leads to **2c**, and the rate of initiation is so great that the slow ionic mechanism can no longer noticeably compete.

AIBN is also a familiar radical source.[18] Its effect, observed for thermolysis under O_2 (Table III), is qualitatively similar to that of PAT. Whereas thermolysis of **1c** under O_2 normally leads mainly to **3c**, with AIBN more of **2c** than of **3c** is formed. The yields of **2c** and **3c** total only about 50%; it is not surprising that a great deal of the reaction was diverted to other products, for a radical chain reaction occurring under O_2 would often be intercepted to form other products.

The minor products found from thermolysis of **1c** under N_2 indicate the intermediacy of *p*-bromophenyl radicals. 4,4′-Dibromobiphenyl is presumably obtained by dimerization of *p*-bromophenyl radical; we note that biphenyl was earlier observed[19] as a product from the thermolysis of **1a** in acetate-buffered methanol. *p*-Bromobenzyl alcohol formation can be ascribed to colligation of a *p*-bromophenyl and a hydroxymethyl radical. Under O_2, the chief minor product is *p*-bromophenol, the genesis of which is doubtless combination of *p*-bromophenyl radical with O_2 to form the *p*-bromophenylperoxy radical, *p*-$BrC_6H_4O_2\cdot$, followed by further steps not entirely clear.

The fact that thermolysis of **1c** under N_2 in the presence of iodobenzene forms a substantial amount of *p*-bromoiodobenzene further indicates the intermediacy of *p*-bromophenyl radicals, for aryl radicals are known to abstract iodine atoms from aryl iodides.[15]

Our finding that protodediazoniation in acidic CH_3OD affords products virtually deuterium free recalls Melander's similar observations for tritium-labeled methanol of a quarter century ago,[5] and is consistent with the intermediacy of aryl radicals. Aryl radicals are known to abstract hydrogen from the α carbon of methanol much faster than the hydroxy group.[20,21]

The fact that protodediazoniation is suppressed under an O_2 atmosphere is likewise consistent with a radical chain mechanism, for O_2 is a prominent scavenger of radicals.[22] Another scavenger that has qualitatively the same effect, as may be seen in Table III, is 2-methyl-2-nitrosopropane (*t*-BuNO).[23,24] Moreover, *t*-BuNO reinforces the effect of O_2; see especially in Table III the cooperative effects of *t*-BuNO and O_2 on the thermolysis of the *p*-bromo and *p*-nitro substrates.

Nature of the Radical Mechanism. Our observations are consistent with the propagation and termination steps of a radical chain mechanism for protodediazoniation proposed by DeTar and Turetzky.[19] The propagation cycle, slightly modified in view of evidence that arylazo radicals may have independent existence,[25] is sketched in Scheme I. Several

Scheme I

$$Ar\cdot + CH_3OH \rightarrow ArH + \cdot CH_2OH \qquad (3)$$

$$\cdot CH_2OH + ArN_2^+ \rightarrow ArN{=}N\cdot + CH_2OH^+ \qquad (4)$$

$$ArN{=}N\cdot \rightarrow Ar\cdot + N_2 \qquad (5)$$

features of this mechanism are substantiated by studies of Beckwith and Norman[26] in which reactive intermediates or spin-trapped derivatives thereof were observed by means of their ESR spectra.

The minor products of thermolysis of **1c** under N_2 are indicative of termination steps, namely, dimerization of aryl radicals and colligation of aryl with hydroxymethyl radicals.

The nature of initiation is, however, unclear. Bunnett and Yijima[12] have discussed the problem; they favor initiation by electron transfer directly from methanol to the diazonium ion, forming thereby an arylazo radical which enters the propagation cycle at step 5.

Nature of the Ionic Mechanism. With attention to evidence that the thermolysis of diazonium ions in water occurs via aryl cation intermediates,[10,11,27] we suggest that methoxydediazoniation occurs by heterolysis of the diazonium ion to generate an aryl cation, followed by its coordination with methanol and finally expulsion of a proton, as sketched in eq 6.

$$ArN_2^+ \longrightarrow N_2 + Ar^+ \xrightarrow{CH_3OH} ArOCH_3 + H^+ \qquad (6)$$

Effects of Other Additives. Nitrous acid under N_2 has an effect qualitatively similar to that of *t*-BuNO: it changes the products of **1c** thermolysis from mainly **2c** to mainly **3c**. It appears to suppress the radical chain mechanism. Nitrous acid is known to decompose on heating to release nitric oxide, NO,[28] which is an odd electron species and an effective scavenger of reactive radicals.[29]

It is noteworthy that under other circumstances nitrite ion acts to catalyze the formation of aryl radicals from diazonium salts. Addition of sodium nitrite to solutions of benzenediazonium fluoroborate and a monosubstituted benzene in dimethyl sulfoxide causes instantaneous reaction with evolution of N_2 and formation of biaryls of isomer ratio indicating the intermediacy of phenyl radicals.[30] In this situation nitrite ion acts to generate radicals and any inhibiting effect of the byproduct NO_2 molecules is of secondary significance.

Galvinoxyl operates, surprisingly, somewhat to increase the proportion of **2c** formed from **1c** under either N_2 or O_2. It is often employed as a radical scavenger,[31] but in the present system if anything it appears to have a mildly beneficial effect on the radical chain mechanism, perhaps by assisting initiation in some fashion that is not immediately obvious.

Ferrous sulfate under N_2 strongly represses protodediazoniation, changing the product composition approximately to that found under O_2. The probable agent of repression is ferric ion present as a contaminant or formed in the course of the reaction. Investigations by Norman and West[32] and by Walling[33] indicate that ferric ion effectively oxidizes hydroxymethyl radicals, thereby terminating radical chain reactions involving them. We did not investigate the effect of ferric ion as such, but are struck by the fact that under O_2, where one would anticipate a greater extent of oxidation of ferrous to ferric ion, the product ratio in the presence of added ferrous sulfate was much the same as in its absence. Years ago Waters[34] explained that the redox potential of the ferrous/ferric ion couple is such that ferrous salts cannot directly transfer an electron to diazonium ions.

Effect of Temperature. In Table II one can see that *p*-bromobenzenediazonium ion under N_2 gives an enhanced proportion of **2c** at 27 or 30 °C as compared to 65 °C. In Table III it is reported that under either N_2 or O_2 the proportion of protodediazoniation in the presence of 0.01 M nitrous acid is greater at 35 °C than at 55.6 °C. All these data indicate that the enthalpy of activation for the ionic mechanism leading to **3c** is greater than for the radical mechanism leading to **2c**.

Alternative Mechanistic Hypotheses. In 1970 we suggested the possibility that the radical and ionic pathways leading, say, from **1c** to **2c** and **3c**, respectively, might proceed via a common intermediate.[4] That tentative hypothesis arose from consideration of product data in comparison with kinetic data, as they varied from N_2 to O_2 atmosphere. The kinetic/product study of Bunnett and Yijima,[12] which utilizes a different experimental design that enables a more straightforward interpretation, affords data that can be interpreted simply in terms of competing radical and ionic mechanisms without need to invoke the hypothesis of a common intermediate. The present product study likewise provides no cause to invoke that unusual hypothesis.

In view of the rich chemistry of copper-catalyzed diazonium salt reactions[35] and the profound effects that traces of copper ions can have in other systems,[36] we studied the effect of adding cuprous chloride. It had no appreciable effect on product composition under either N_2 or O_2 atmosphere. We also probed the effect of adding 2,2′-bipyridyl, which complexes ferrous ion strongly in acidic solution and certain other metal ions considerably.[37] It also had no effect under either atmosphere. These experiments indicate that transition metal ions are not centrally involved in the phenomena which are our present interest.

DeTar and Kosuge[2] suggested that the formation of protodediazoniation products under O_2 occurred via an ionic mechanism in which aryl cations abstracted hydride ions from the methyl group of methanol. They were inclined to believe that the radical mechanism was suppressed almost completely under O_2. Our finding, for diazonium salts **1c**, **1i** and **1j** that *t*-BuNO reinforces O_2 in suppressing protodediazoniation indicates that the radical mechanism is not entirely blocked by the O_2 atmosphere, and that what remains is further retarded by a second radical scavenger. Although we do not feel that the ionic mechanism of protodediazoniation can be totally dismissed, we find no support for it.

Substituent Effects. The product compositions listed in Table II represent the outcome of competition between radical and ionic mechanisms. The rates of both in principle may be influenced by substituents. Except for *p*-nitrobenzenediazonium ion, methoxydediazoniation strongly predominates under O_2, and the rates under O_2 for the most part report substituent effects on the ionic mechanism. These rates correlate very well with rates of hydroxydediazoniation in water,[4] but they do not correlate with Hammett σ values.[1b] Thus, reaction is fast with certain substituents (e.g., *m*-CH_3 and *m*-OCH_3) that have positive or negative σ values of small magnitude, and slow with others (e.g., *p*-NO_2 and *p*-OCH_3) that have positive or negative σ values of larger magnitude. (For the *p*-nitro substrate, rates were not measured in methanol under O_2; the statement is based on measurements in water solution.[38])

Substituent effects on the competition between mechanisms appear to be determined in large part by the strong substituent dependence of the rate of the ionic mechanism. In methanol under O_2, the *m*-methoxy substrate (the fastest) reacts more than 11 000 times faster than its para isomer (the slowest).[1b] Those diazonium salts that give mainly or entirely methoxydediazoniation even under N_2 (**1a**, **1f**, **1g**, and **1h**) are the four that react fastest under O_2.

However, there is more to it than that. Under O_2 the *p*-methyl, *m*-bromo, and *m*-chloro substrates react at nearly the same rate but under N_2 the first undergoes only methoxydediazoniation whereas the latter two give mainly protodediazoniation products. It follows that the *m*-bromo and *m*-chloro substituents are more favorable to the radical mechanism than is *p*-methyl. Furthermore, although the ionic mechanism in water goes about 80 times faster for the *p*-nitro than for the *p*-methoxy substrate, the radical mechanism in methanol is nevertheless more pronounced for the former. Clearly the *p*-nitro substituent has an especially beneficial influence on the radical mechanism. In general, electron-withdrawing substituents appear to assist it.

From gross rate data for a radical chain mechanism it is hard to say why substituent effects are as they are. The overall reaction rate is composite, and in principle substituents may differently affect initiation, propagation, and termination rates.

The fact (Table II) that for the *m*-bromo and *m*-chloro substrates under N_2 product compositions varied widely between intended replicate determinations suggests a great sensitivity of the radical mechanism to inhibition by O_2. We surmise that minor contamination by O_2 occurred in some experiments, despite careful flushing with N_2, and considerably suppressed reaction by the radical pathway.

Experimental Section

Diazonium Salts. *m*-Bromo-, *m*-chloro-, *m*-methoxy-, and *m*-methylanilines, as well as aniline itself, were commercial products repurified by distillation at reduced pressure. *p*-Bromo-, *p*-chloro-, *p*-methoxy-, *p*-methyl-, and *p*-nitroanilines were reagent grade materials used without further purification. To 30 ml of 48% HBF_4 and 30 ml of water in a 200-ml polyethylene beaker, 0.1 mol of aromatic primary amine was slowly added. The mixture was cooled to below 5 °C by external cooling with an ice–NaCl mixture. With mechanical stirring, a solution of 0.1 mol of $NaNO_2$ in 30 ml of water was added slowly so that the temperature did not exceed 5 °C, and stirring was continued 5 min after completion of addition. The solid diazonium fluoroborate was collected and purified by three cycles of solution in a minimum amount of acetone and then flocculation by addition of diethyl ether, and then air dried. All were white except *m*-methoxybenzenediazonium fluoroborate, which was light yellow. Decomposition points were as follows: H, 108–110 °C; *m*-Br, 139–140 °C; *p*-Br, 137–138 °C; *m*-Cl, 146–148 °C; *p*-Cl, 136–137 °C; *m*-CH_3, 97–101 °C; *p*-CH_3, 109–111 °C; *m*-OCH_3, 87–88 °C; *p*-OCH_3, 142 °C; and *p*-NO_2, 157–158 °C. These are mostly very close to those reported by Schulte-Frohlinde and Blume.[38]

Methanol. Reagent grade methanol was repurified by the magnesium method.

Nitrogen. Commercial nitrogen gas was deoxygenated by passing it through columns packed with activated copper metal on an inert support (BASF Catalyst R 3-11).

2-Methyl-2-nitrosopropane (*t*-BuNO). *tert*-Butylamine was oxidized to 2-methyl-2-nitropropane after Kornblum and Clutter;[39] the latter was reduced to *tert*-butylhydroxylamine after Kamm;[40] and the last was oxidized to *t*-BuNO after Emmons.[41]

***p*-Bromophenylazotriphenylmethane (BrAT).** The procedure of Cohen and Wang[42] was used; the product had mp 109–110 °C dec.

General Procedure for Product Determinations Summarized in Tables II and III. The diazonium fluoroborate (2.50×10^{-4} mol) was dissolved in 25 ml of methanol 0.1 M in *p*-toluenesulfonic acid (or in a few cases 0.5 M); the resulting solution was 0.01 M in diazonium salt. By pipet, 10 ml was transferred to a thin-walled, flat-bottomed glass ampule rated as "10 ml" but having total volume to the seal-off point about 14.0 ml. The solution in the ampule was bubbled gently with a stream of O_2 or of deoxygenated N_2, the bubbling tube was removed, a small piece of plastic film (Parafilm) was placed temporarily over the open end, and the ampule was sealed with a torch. In the case of O_2 ampules, the methanol solution was frozen by cooling with liquid nitrogen before sealing. The ampule was placed in a thermostat bath and left there for 10 or more half-lives as estimated from kinetic studies carried on concurrently.[1b]

Ampules removed from the thermostat were cooled, rinsed externally, and opened, and their contents were transferred to a 25-ml volumetric flask. To each flask, 5 ml of an 0.02 M solution of either iodobenzene or *m*-dichlorobenzene in methanol was added, and finally methanol to the mark. GLC analysis was conducted by means of an Aerograph Model 200 gas chromatograph equipped with flame ionization detector and disk integrator. The column was 3.2 mm i.d. by 183 cm long, packed either with 10% Carbowax 20M on Chromosorb P or with 4% Carbowax 20M on Chromosorb G. Molar response factors for products of type **2** and **3** against iodobenzene or *m*-dichlorobenzene as internal standard were redetermined in connection with each set of determinations and used in evaluating the GLC data.

Minor Products from *p*-Bromobenzenediazonium Fluoroborate. In 1 l. of 0.1 M sulfuric acid in methanol contained in a 2-l. single-neck flask, 2.71 g (0.01 mol) of the substrate was dissolved. The solution was bubbled for 2 h with either O_2 or deoxygenated N_2, the space above the liquid was flushed with the relevant gas, and a condenser was installed with an arrangement at the top to provide a small positive pressure of the relevant gas. The solution was heated in a thermostat bath at 65.4 °C for about 40 h, cooled, and equipped for distillation and the volume reduced to about 300 ml by slow distillation. Water saturated with NaCl (100 or 150 ml) was added and the mixture was thrice extracted with diethyl ether. The combined ether layers were dried over anhydrous sodium sulfate and concentrated by distillation, heat being provided by an oil bath at 45 °C. The resulting product mixture was yellow for the reaction under N_2 and red for that under O_2.

Product yields were determined by GLC, with *m*-dichlorobenzene and *p*-bromobiphenyl being used as internal standards, and molar response factors being evaluated with use of authentic samples except for *p*-bromobenzyl alcohol (for which the same factor as for *p*-bromophenol was assumed) and for 4,4′-dibromoazobenzene (which was not detectable in quantitative GLC). By means of elution chromatography from silica gel, the crude product mixtures were separated into fractions eluted with petroleum ether and with diethyl ether–acetone. Each of these fractions was further fractionated by preparative GLC, and components were identified by the following evidence: bromobenzene, GLC t_R* (retention time) and IR* (the asterisk means spectrum identical with that of an authentic sample); *p*-bromoanisole, GLC t_R,* IR,* and NMR;* 4,4′-dibromobiphenyl, GLC t_R,* MS, and IR;* *p*-bromophenol, GLC t_R,* MS, and IR;* *p*-bromobenzyl alcohol, MS and IR (in agreement with the published spectrum[43]); and 4,4′-dibromoazobenzene, MS and mp 202–205 °C (lit.[44] mp 202–204 °C).

Experiments in Methanol-*O-d*. About 0.2 g of benzenediazonium fluoroborate or its *p*-bromo derivative was dissolved in 10 ml of CH_3OD[45] and (for runs in acidic CH_3OD) one drop of D_2SO_4 was added. For the bromo compound, the solution was placed in an ampule and bubbled with N_2. The ampule was sealed and heated in a thermostat at 65 °C overnight. The ampule was cooled, its contents added to 20 ml of cold water, and the mixture extracted with 30 ml of pentane. The pentane extract was washed with water, dried over anhydrous magnesium sulfate, and concentrated to about 1 ml. The mass spectrum was obtained by means of an Hitachi RMU-6E mass spectrometer. Deuterium content was judged from the relative magnitudes of the M + 1 and M peaks, after correction for normal isotopic abundance of carbon-13 and deuterium. For benzenediazonium fluoroborate, the method was the same except that the reaction was carried out in a 10-ml volumetric flask kept overnight in a thermostat at 30 °C.

Reactions in the Presence of Aryl Iodides. Reactions were conducted as indicated in the text in the presence of 0.01 M *p*-toluenesulfonic acid for a time sufficient to ensure complete decomposition of the diazonium salt, as indicated by kinetic measurements. Products were determined by GLC, the method being calibrated both as to retention times and molar response factors with use of authentic samples.

Detection of Formaldehyde. A solution of *p*-bromobenzenediazonium fluoroborate (0.098 M) in methanol 0.1 M in *p*-toluenesulfonic acid was bubbled with N_2, sealed in an ampule, and heated at 65 °C for 19 h. The ampule was opened and 2 ml of its contents combined with 1 ml of aqueous acetate buffer and a solution of 0.07 g of tetrahydrophthalazine[14] in 2 ml of water. A precipitate formed; after 10 min, it was collected and dried; weight 0.0077 g (27%). A similar run was conducted under O_2, but no precipitate formed after addition of tetrahydrophthalazine. However, upon addition of a small amount of authentic formaldehyde, a precipitate formed.

Kinetic Determinations. In a 100-ml volumetric flask, a solution of ca. 1×10^{-4} mol of diazonium salt in methanol sometimes containing acid or base (as indicated in Table I) was prepared. For runs at ca. 30 °C, the solution was prepared at thermostat temperature with use of solvent or reagent solutions previously flushed with the indicated gas, and samples were taken at recorded times by means of a 5-ml pipet. For runs at 65 °C, 5-ml aliquots of the reaction solution were transferred to ampules which were bubbled with the indicated gas and then sealed; for runs under O_2 the contents of each ampule were frozen by external cooling with liquid nitrogen before sealing. The sealed ampules for a run at 65 °C were all placed at once in the thermostat, and single ampules were removed at recorded times and plunged into ice-cold water. The pipetted samples from 30 °C runs or the entire contents of ampules for 65 °C runs were discharged into 100-ml volumetric flasks containing 5 ml of an 0.02 M solution of α-naphthylamine in methanol and (for the neutral and $NaOCH_3$ reactions) 1 ml of concentrated hydrochloric acid. The flasks were filled to the mark with methanol and after 15 min the absorbance of the resulting azo dye was measured at 525 nm for **1a** and 540 nm for **1c**. Plots of ln A_t vs. time were linear for reactions in acidic solution under O_2 and at least approximately so in other cases.

Experiments with *p*-Bromophenylazotriphenylmethane (BrAT). Solutions of 10 ml volume, containing 0.01 M BrAT and 0.1 M *p*-toluenesulfonic acid and in some cases 0.24 M iodobenzene, were placed in ampules and bubbled with the gas indicated in the text. The ampules were sealed and heated overnight or longer at 65 °C. They were opened, a measured volume of a standard solution of *m*-dichlorobenzene was added to serve as internal standard, and GLC analysis was conducted. Retention times and molar response factors were independently determined with use of authentic samples.

Registry No.—BrAT, 53034-21-2; *p*-toluenesulfonic acid, 104-15-4; methanol, 67-56-1.

References and Notes

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