Thermolysis of Arenediazonium Ions in Acidic Methanol. Evidence for Competing, Independent Ionic and Radical Mechanisms[1]

Joseph F. Bunnett* and Chino Yijima[2]
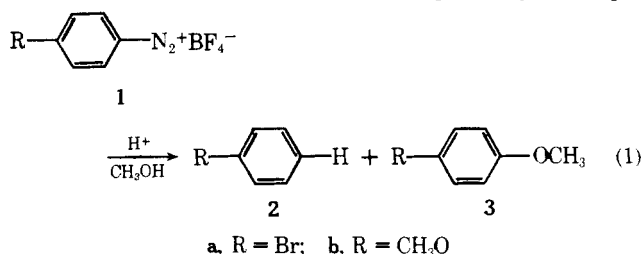
University of California, Santa Cruz, California 95064

Received July 29, 1976

Thermolysis of p-bromo- or p-methoxybenzenediazonium ions in acidic methanol affords products of protodediazoniation (ArH) and methoxydediazoniation (ArOCH$_3$), mainly the former under N$_2$, mainly the latter under O$_2$. In our experiments, both rates and products are determined from events within a single sealed ampule. Overall rate constants are dissected into components k_r and k_i in proportion to the yields of ArH and ArOCH$_3$, respectively. Changing the atmosphere from N$_2$ to O$_2$ depresses k_r by two orders of magnitude but has no significant effect on k_i. The results are intelligible in terms of competing, independent radical and ionic mechanisms, the former severely inhibited by O$_2$, the latter unaffected. There is no need to invoke an earlier hypothesis that the radical and ionic mechanisms involve a common intermediate.

In 1970, Broxton, Bunnett, and Paik[3] entitled a communication: Do Radical and Ionic Pathways of Decomposition of Arenediazonium Ions in Acidic Methanol proceed via a Common Intermediate? We have carefully restudied the matter, and our data provide an answer to that question. The answer is that in two representative cases rate and product data are entirely consistent with a model of competing, independent ionic and radical mechanisms. We find no need to invoke the unusual hypothesis earlier suggested.

The phenomenon of interest was first described by DeTar and Kosuge:[4] certain substituted benzenediazonium ions, such as those with p-bromo and p-methoxy substituents, decompose in acidic methanol *under nitrogen* to give mainly protodediazoniation products (bromobenzene and anisole, respectively), but in the same solutions *under oxygen* to afford principally products of methoxydediazoniation (p-bromoanisole and p-dimethoxybenzene, respectively); see eq 1.

R⎯⟨ ⟩⎯N$_2$$^+BF_4$$^-$

1

$$\xrightarrow[\text{CH}_3\text{OH}]{\text{H}^+}\quad \text{R}⎯⟨\ ⟩⎯\text{H}\ +\ \text{R}⎯⟨\ ⟩⎯\text{OCH}_3 \quad (1)$$

2   **3**

a, R = Br;   b, R = CH$_3$O

Broxton, Bunnett, and Paik[3] confirmed the essential observations of DeTar and Kosuge, and adduced evidence of several sorts that radical intermediates and a radical chain mechanism are involved in formation of protodediazoniation products **2a** and **2b**. However, they found no evidence for radical intermediates in the reactions leading to methoxydediazoniation products **3a** and **3b**.

The reason that Broxton, Bunnett, and Paik[3] suggested that the radical and ionic pathways might share a common first step was a striking confrontation of product with kinetic data. Although changing the atmosphere from N$_2$ to O$_2$ caused a drastic change in product composition, the measured diminution in rate was relatively modest, so that it was difficult to account for the change in product composition in terms merely of suppression by O$_2$ of a fast radical mechanism leading to **2a** or **2b** so as to allow a slow ionic process to prevail.

Subsequent observations by Ohmori[5] motivated our reexamination of the thermolysis of **1a** and **1b**. We noted that the rate and product determinations of Broxton, Bunnett, and Paik[3] were made in separate experiments under similar but not exactly identical conditions. For example, in Paik's experiments[6] each ampule in kinetic runs contained 5 ml of reaction solution while each ampule for product determination

contained 10 ml of similarly prepared solution. Conceivably the difference in sample volume or some other minor variation caused the kinetic and product data to be not quite strictly comparable.

An obvious way to avoid such doubts is to perform both rate and product determinations on portions of the very same solution which has undergone reaction in a single sealed ampule. That is what we have now done, but we hasten to point out that this straightforward approach is not simple in its execution. For an estimate of rate to be meaningful, reaction must have occurred only partially by the time of measurement, but the unreacted diazonium ion complicates determination of the yields of, say, bromobenzene and p-bromoanisole by GLC. Our response to this challenge was to combine the partially reacted solution with excess phenol in alkaline aqueous medium, allowing azo coupling to occur, and then to extract with ether to remove the bromobenzene and p-bromoanisole for GLC analysis.

Experimental Section

Materials. p-Bromo- and p-methoxybenzenediazonium fluoroborates were prepared by diazotization of the redistilled primary amines in 24% fluoroboric acid solution below 5 °C by addition of an equimolar amount of sodium nitrite. The crystalline diazonium salt was collected and purified by dissolving it in a minimum amount of acetone and reprecipitating by addition of diethyl ether. Before each set of experiments, each diazonium salt was repurified by three cycles of solution in acetone and precipitation by ether.

Commercial p-toluenesulfonic acid was recrystallized from 37% hydrochloric acid and the resulting hydrate was dehydrated by keeping it at reduced pressure over KOH and P$_2$O$_5$; the anhydrous acid was stored at reduced pressure over P$_2$O$_5$.

Methanol was purified by the magnesium method.[7] Bromobenzene, p-bromoanisole, anisole, p-dimethoxybenzene, and m-dichlorobenzene were purified by redistillation before use. α-Naphthylamine p-toluenesulfonate was prepared as described elsewhere.[8]

GLC Determinations. An Aerograph Model 200 instrument equipped with flame ionization detector and disk integrator was used. An aluminum column, 3.2 mm i.d. by 183 cm long, packed with 4% Carbowax 20M on Chromosorb G was used. The column temperature was 70 °C for analysis of bromobenzene, anisole, and m-dichlorobenzene, 120 °C for p-dimethoxybenzene, and 130 °C for p-bromoanisole. Molar response factors, relative to m-dichlorobenzene (the internal standard), were determined for all products by repeated analysis of standard mixtures.

General Experimental Procedure. A solution of the diazonium salt (**1a** or **1b**) and p-toluenesulfonic or sulfuric acid in dry methanol was prepared by mixing measured amounts of the ingredients at 0 °C. Aliquots (5 ml) were transferred to "5-ml" ampules (total volume to seal-off point about 7.6 ml) by pipet, the ampules were cooled to <-50 °C by partial immersion in a slurry of solid carbon dioxide in 2-propanol, and each ampule was gently bubbled for 15–20 min either with oxygen gas or with deoxygenated nitrogen or argon, the gas being passed through methanol at the same temperature before entering the solution in the ampule. Immediately after the bubbling treatment,

Table I. Thermolysis of p-Bromobenzenediazonium Fluoroborate in Acidic Methanol at 56 °C: Some Representative Experiments[a]

Expt no.	Atmosphere	Time, min	Reaction by GLC, %	$10^5 k_g$,[b] s^{-1}	Product ratio[c]	$10^5 k_r$, s^{-1}	$10^5 k_i$, s^{-1}	Reaction, photometric, %	$10^5 k_c$,[d] s^{-1}
89	N$_2$	15	60.6	103	28.8	100	3.47	62.0	108
90	N$_2$	15	67.1	124	35.6	120	3.38	68.9	130
91	N$_2$	20	66.5	91.2	29.4	88.2	3.00	65.8	89
92	N$_2$	20	84.3	154	45.2	151	3.34	82.3	144
93	N$_2$	25	81.9	114	24.2	110	4.53	88.6	145
94	N$_2$	25	80.1	108	31.1	104	3.35	80.3	108
95	N$_2$	400	95.8		36.8				
96	N$_2$	0						0.2	
105	O$_2$	200	37.5	3.92	1/5.13	0.64	3.28	46.2	5.17
106	O$_2$	200	41.4	4.46	1/5.54	0.68	3.78	44.5	4.90
107	O$_2$	230	45.9	4.46	1/7.31	0.54	3.92	49.0	4.88
108	O$_2$	230	44.9	4.31	1/7.51	0.51	3.80	49.7	4.98
109	O$_2$	260	51.4	4.63	1/10.1	0.42	4.21	55.0	5.12
110	O$_2$	260	55.3	5.16	1/8.62	0.54	4.62	55.0	5.12
111	O$_2$	3000	83.0		1/17.7				
112	O$_2$	0						0	

[a] In these experiments, $[H_2SO_4]$ = 0.108 M. [b] Pseudo-first-order rate constant from GLC product data. [c] Molar ratio of C_6H_5Br to p-bromoanisole. [d] Pseudo-first-order rate constant from photometric data.

Table II. Thermolysis of p-Bromobenzenediazonium Fluoroborate in Acidic Methanol at 56 °C: Resume of Kinetic Data

Expt no.	Atmosphere	[TsOH],[a] M	$10^5 \bar{k}_g$,[b] s^{-1}	10^5 s.d. in k_g, s^{-1}	Mean product ratio[c]	s.d. in product ratio	$10^5 \bar{k}_r$, s^{-1}	10^5 s.d. in $\bar{k}_r$, s^{-1}	$10^5 \bar{k}_i$, s^{-1}	10^5 s.d. in $\bar{k}_i$, s^{-1}	$10^5 \bar{k}_c$,[d] s^{-1}	10^5 s.d. in $\bar{k}_c$, s^{-1}
25–28	N$_2$	0.0098	120	8	28	3	116	8	4.13	0.28	116	10
33–36	N$_2$	0.0098	111	14	27	5	107	15	4.08	0.46	123	9
42–49	N$_2$	0.101	33	3	7.6	0.7	29	3	3.79	0.21	40	6
60–64	N$_2$	0.100	28	3	6.6	1.5	25	3	3.82	0.50	29	3
81–86	N$_2$	0.0010	81	7	23	3	77	7	3.45	0.42	89	12
89–94	N$_2$	0.108[e]	116	22	32	7	112	22	3.51	0.52	121	22
116–127	Degassed	0.100	48	9	9.8	2.4	43	9	4.50	0.71	38	12
134–137	Ar	0.100	24	1.7	4.4	0.4	19.5	1.5	4.45	0.34	34	6
Average of 49 expt under N$_2$, Ar, or degassed									4.00	0.61		
29–30	O$_2$	0.0098	5.80	0.32	1/8.9	0.9[f]	0.58	0.02	5.21	0.34	6.52	0.02
37–39	O$_2$	0.0098	5.99	0.68	1/7.2	1.0[f]	0.74	0.10	5.26	0.63	6.46	0.24
51–58	O$_2$	0.101	4.14	0.48	1/10.1	1.6[f]	0.38	0.03	3.76	0.48	4.77	0.09
67–72	O$_2$	0.100	5.32	0.51	1/4.4	0.7[f]	0.98	0.07	4.34	0.52	5.15	0.11
97–102	O$_2$	0.0010	4.01	0.39	1/2.9	0.2[f]	1.03	0.13	2.98	0.28	9.65	0.20
105–110	O$_2$	0.108[e]	4.49	0.41	1/7.4	1.9[f]	0.55	0.10	3.94	0.45	5.03	0.12
Average of 31 expt under O$_2$									3.99	0.82		

[a] p-Toluenesulfonic acid, except as otherwise indicated. [b] Average total rate constant, from GLC data. [c] Molar ratio of C_6H_5Br to p-bromoanisole. [d] Average total rate constant, from photometric data. [e] Sulfuric acid. [f] Standard deviation in the mean ratio of p-bromoanisole to C_6H_5Br.

each ampule was sealed with a torch and retained in the cold bath until a set of ampules could be placed all at once in the thermostat at 56 or 80 °C. Single ampules were removed from the thermostat at recorded times, thrust directly into an ice–water slurry to terminate thermolysis, and then stored in a solid CO_2-2-propanol slurry until analysis of the contents was undertaken.

Events in each ampule constitute a separately numbered experiment for tabulation purposes. Inasmuch as several ampules were supplied with aliquots from the same batch of reaction solution on a given day, some being bubbled with nitrogen, some with oxygen, our experiments occur in sets of common origin. These sets comprise experiments 17–24, 25–32, 33–41, 42–58, 60–74, 81–88 plus 97–104, 89–96 plus 105–112, 116–128, 130–139, M1–M21, M22–M42, M43–M53, and M54–M65. Between sets of experiments some days or weeks passed. Moreover, they were based on separate repurifications of diazonium salt and sometimes involved different tanks of sweep gases or different batches of methanol solvent.

In all experiments the diazonium salt concentration was 0.01 M. Hydrogen ions were provided by p-toluenesulfonic acid, for experiments with 1a at concentrations indicated in Table II, but 0.100 M for all experiments with 1b, except that sulfuric acid (0.108 M) was used for the experiments listed in Table I.

For analysis of the contents of ampules, somewhat different procedures were employed for 1a reactions than for 1b reactions. This was learned by experience; the cause is apparently a great difference in electrophilic reactivity between 1a and 1b.[9]

Ampules for 1a reactions were brought to 0 °C by immersion in an ice–water slurry, opened, and a measured volume (0.1 or 0.2 ml) was removed by pipet and discharged into 2 ml of a solution of α-naphthylamine p-toluenesulfonate (0.017 M) in methanol in a 25-ml volumetric flask at 0 °C. After swirling, the resulting solution of azo dye was allowed to stand for 20 min, then acidified by addition of 0.5 ml of 12 M HCl and diluted to the mark with methanol. The absorbance at 540 nm was measured by means of a Gilford spectrophotometer. This method for determination of unreacted diazonium salt was calibrated by analysis of a series of solutions of 1a of varying concentration, and it was shown that absorbance is linearly related to diazonium ion concentration.

Immediately following withdrawal of the aliquot for colorimetric determination of unreacted diazonium salt, another aliquot (1.0 ml) was withdrawn by pipet and discharged into 1 ml of an aqueous solution of phenol, adjusted to pH 10 by external spotting of pH indicator paper, contained in a 10-ml test tube and held at 0 °C. After 2 or 3 h at that temperature, 1 ml of 0.5 M NaOH in water and 0.1 ml

Table III. Thermolysis of *p*-Methoxybenzenediazonium Fluoroborate in Acidic Methanol at 80 °C. Resume of Kinetic Data[a]

Expt no.	Atmo-sphere	$10^5 \bar{k}_g$, s⁻¹	10^5 s.d. in $\bar{k}_g$, s⁻¹	Mean product ratio[b]	s.d. in product ratio	$10^5 \bar{k}_r$, s⁻¹	10^5 s.d. in $\bar{k}_r$, s⁻¹	$10^5 \bar{k}_i$, s⁻¹	10^5 s.d. in $\bar{k}_i$, s⁻¹	$10^5 \bar{k}_c$, s⁻¹	10^5 s.d. in $\bar{k}_c$, s⁻¹
M1–M8	N_2	34	10	8.4	1.1	30	8	3.77	1.41	33	10
M23–M28	N_2	112	37	53	8	110	36	2.05	0.52	140	70
M43–M51	N_2	26	2.5	7.6	1.2	23	2.5	3.10	0.29	27	2.4
Average of 23 expt under N_2								3.06	1.09		
M12–M20	O_2	4.34	0.30	1/3.5	0.5[c]	0.99	0.15	3.35	0.20	4.22	0.24
M33–M40	O_2	3.67	0.37	1/3.9	1.0[c]	0.80	0.26	2.87	0.18	4.48	0.19
M54–M63	O_2	3.20	0.36	1/16	2.0[c]	0.19	0.03	3.01	0.34	3.71	0.15
Average of 27 expt under O_2								3.08	0.32		

[a] *p*-Toluenesulfonic acid, 0.100 M, present in all experiments; rate constant symbols as in Table II. [b] Molar ratio of anisole to *p*-dimethoxybenzene. [c] Standard deviation in the mean ratio of *p*-dimethoxybenzene to anisole.

of a standard solution of *m*-dichlorobenzene in methanol were added. The resulting solution was extracted six times with 6-ml portions of diethyl ether and the combined ether extracts were dried over anhydrous $CaCl_2$ overnight. The extract was passed through a small column (7 mm diameter, 60 mm long) packed with basic alumina to remove traces of azo dye, concentrated by distillation of the ether to a volume of about 1 ml, and analyzed by GLC as described above.

The procedure was similar for ampules for **1b** reactions. The chief differences were that the original 0.1- or 0.2-ml portion of an ampule's contents was discharged into 2 ml of a methanol solution 0.06 M in α-naphthylamine and 0.05 M in *p*-toluenesulfonic acid, that absorbance was measured at 570 nm, and that the subsequent coupling with phenol was conducted at pH 9.0 during 2 or 3 h at room temperature.

Calculation and Presentation of Results. This experimental procedure gave two measures of the extent of reaction: the amount of diazonium salt unreacted, and the amount of products **2a** and **3a** or **2b** and **3b** formed. From the amount of **1a** or **1b** unreacted and the relevant time of heating, a rate constant (symbolized k_c) for the total rate of thermolysis of the diazonium salt was reckoned, it being assumed that first-order kinetics prevailed and that the ampule attained thermostat temperature immediately upon immersion. Earlier work[3,6] showed that first-order kinetics are obeyed accurately by these reactions under oxygen and approximately by those under nitrogen. From the sum of the amounts of **2a** and **3a** or of **2b** and **3b** formed, a rate constant (symbolized k_g) for the total rate of thermolysis was calculated on the basis of the foregoing assumptions and the further assumption that **2a** and **3a** or **2b** and **3b** were the sole products formed. k_g values were then separated into parts relevant to the formation of **2a** or **2b** (symbolized k_r) and of **3a** or **3b** (symbolized k_i) in proportion to product yields. In Table I results are fully tabulated for a set of experiments with **1a** that happen to involve sulfuric acid as the source of protons but which are otherwise representative. For other sets of data, only mean values for sets are presented in print, in Tables II and III, but results are fully tabulated in Table IV and V, which appear in the supplementary material.

Several sets of experiments included ampules that were not heated or which were heated for a very long time in order to effect complete thermolysis of the diazonium salt. Those that were not heated were shown by photometric analysis to contain within experimental error all the diazonium salt originally present. Those heated until "infinity" contained no diazonium salt according to the photometric analysis but the combined yields of **2a** and **3a** or of **2b** and **3b** totaled less than 100%. Specifically, infinity total yields of **2a** plus **3a** totaled 95–98% for reactions under N_2 or Ar, and 83, 80, and 60% under O_2, while infinity total yields of **2b** plus **3b** totaled 85–92% under N_2 and 83–87% under O_2. These totals are similar to those observed by Paik.[6]

Inasmuch as infinity total yields of **2a** plus **3a** or **2b** plus **3b** are less than 100%, we infer that the summed yields of these products as measured for interrupted reactions (most of our experiments) underestimate the extent of reaction that had occurred. Indeed, most (but not all) of our k_g values are lower than the k_c values for the same experiments. However, our method for dividing k_g values into k_r and k_i components, which ignores miscellaneous by-products, considerably compensates for that underestimate. The extent of compensation is better the more nearly the summed yields of **2a** and **3a** or **2b** and **3b** approach the actual percent of thermolysis of the diazonium salt. It is also better the lower the percent of thermolysis at the time of interrupting the reaction. Sample calculations show that at 30%

thermolysis k_r or k_i is underestimated by 2.0% if the summed yields of the two products represent 90% of the actual thermolysis, or by 3.9% if they represent 80% of it. At 60% thermolysis, k_r or k_i is underestimated by 5.8 or 10.8%, respectively, if the summed yields of the two products represent 90 or 80% of the actual thermolysis. The shortfall in the summed yields of **2a** plus **3a** or **2b** plus **3b** was worse in our experiments under O_2 than under N_2, but the percent thermolysis at the time of interruption was in general lower for the experiments under O_2. With attention to the sample calculations mentioned, we judge that our estimates of k_i and k_r are low at most by about 10%. This is less than the random error in our measurements, but must be recognized as a systematic factor affecting experiments under all atmospheres.

For experiments 97–102, under O_2, the k_c values derived from our data are more than double the k_g values. Another extraordinary measurement in the same set is the very low percent of thermolysis at infinity (expt 103) as determined by GLC, namely, 60.2%. One might think the cause to be an erroneously low measurement of the amount of **1a** used, but that is unlikely to be the case because for experiments under N_2 in the same set, based on the same master batch of reaction solution, there is reasonably good agreement between k_c and k_g for expt 81–86, and the summed yields of **2a** and **3a** in expt 87 are 95.8%.

For each set of kinetic-product experiments, mean values of product ratios (**2a/3a** or **2b/3b**) and the several rate constants were reckoned, together with standard deviations, by means of a Texas Instruments SR-51A calculator preprogrammed for these calculations. The standard deviation (abbreviated s.d.) is calculated with $n - 1$ weighting:

$$\text{s.d.} = \left[\sum_{i=1}^{n} (x_i - \bar{x})^2 / (n - 1) \right]^{1/2}$$

These mean values and standard deviations are listed in Tables II and III. Product ratios for reactions under O_2 are listed as the reciprocals of the **3a/2a** or **3b/2b** ratios, and the standard deviations refer to mean values of the latter ratios. In Tables II and III also listed are mean values and standard deviations of k_i for all kinetic-product experiments under O_2 and for all those under N_2, Ar, or degassed.

Results

Each of our experiments involved determination of rate and product composition from events in a single ampule with a specified atmosphere heated for a measured period of time. Detailed data for a representative set of experiments are displayed in Table I, and averaged data for sets of experiments are set forth in Tables II and III. Each "set" of experiments utilized aliquots from a single master batch of reaction solution.

In all cases rates under N_2, Ar, or in degassed ampules were higher than under O_2. For experiments within a set, overall rates under N_2 are at least sixfold greater than under O_2, and at most 53-fold greater (in terms of k_g values). Within a set, under either atmosphere the standard deviation in the mean k_g value is about 10%, but between sets there are great variations of overall rates under N_2 while variations of overall rates under O_2 are moderate, at the level of ±20%.

For reactions of **1a**, the effect of changing hydrogen ion concentration was explored, but pH (within the range 1–3) had little bearing on rates or product compositions. Thus, for runs under N_2 hydrogen ion concentration was about 0.001 M in expt 81–86, 0.01 M in expt 25–28 and 33–36, and 0.1 M in expt 42–49, 60–64, and 89–94, and average k_g values bear no consistent relationship to acid concentration. It appears to matter little whether hydrogen ions are provided by sulfuric acid (expt 89–94 and 105–110) or *p*-toluenesulfonic acid (the rest).

Turning attention now to product ratios, we see immediately the gross difference first noted by DeTar and Kosuge,[4] namely, the preponderance of protodediazoniation leading to **2a** or **2b** under N_2, Ar, or degassed conditions but of methoxydediazoniation leading to **3a** or **3b** under O_2. Looking more closely, we see marked differences in product ratio between sets of experiments under the same atmosphere but lesser differences between experiments in the same set. Significant differences in the product ratio between sets are observed for reactions under O_2 as well as under N_2.

As to the k_r and k_i obtained by dissection of k_g values, the k_r differ enormously—by two orders of magnitude—between atmospheres, and substantially between sets of experiments under a given atmosphere, but the k_i show only moderate variation between sets of experiments or even between N_2 and O_2 atmospheres. *The average k_i value under N_2, Ar, or in degassed conditions is virtually identical with the average k_i under O_2.* As shown in Tables II and III, this important finding emerges from our studies either on **1a** or **1b**, spectacularly in either case.

Discussion

Broxton, Bunnett, and Paik[3,10] present evidence that radical intermediates are involved in the reaction of **1a** under N_2 that leads predominantly to protodediazoniation product **2a**. The reaction of **1a** under O_2 leading mainly to **3a** does not respond to tests for the intermediacy of radicals. The present results show that the rate of formation of methoxydediazoniation product **3a** is unaffected by the atmosphere. The rate of transformation of **1b** to **3b** is also independent of the atmosphere.

Methoxydediazoniation thus behaves as expected of an ionic mechanism. With attention to evidence concerning the mechanism of hydroxydediazoniation in water,[11-13] we propose that reaction occurs via aryl cation intermediates (eq 2). The huge depression in the rate of protodediazoniation as the atmosphere is changed from N_2 to O_2 is then attributed to scavenging by O_2 of radical intermediates in a radical chain mechanism.

$$ArN_2^+ \rightarrow N_2 + Ar^+ \xrightarrow{CH_3OH} ArOCH_3 + H^+ \quad (2)$$
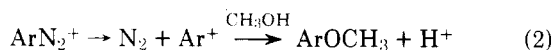
There is no need to invoke the hypothesis, tentatively advanced by Broxton, Bunnett, and Paik,[3] that the radical pathway to **2a** or **2b** and the ionic pathway to **3a** or **3b** involve a common intermediate.

How then did the data of Broxton, Bunnett, and Paik[3] cause them seriously to formulate that hypothesis? Their kinetic data (at 65 °C) are not directly comparable with ours, but the present total photometric rate constants (k_c) under O_2 are in good agreement with those extrapolated or interpolated from data of Paik[6] at other temperatures; in units of $s^{-1} \times 10^{-5}$, our average k_c for **1a** at 56 °C is 6.15 while 6.27 is extrapolated from Paik, and our average k_c for **1b** at 80 °C is 4.14 while 4.13 is interpolated from his measurements. The product ratios of Broxton, Bunnett, and Paik[3] fall within or very close to the range of our measurements. The chief difference between their data and ours lies in the rate measurements under N_2; whereas they reported ratios of k_c (N_2) to k_c (O_2) of about 2, we find

such ratios ranging from 5.6 to 24.0 for **1a** and from 7.3 to 31.2 for **1b**. We surmise that some feature of the experimental technique employed by Broxton, Bunnett, and Paik[3] allowed a significant amount of O_2 to be present in the ampules used in kinetic studies under N_2, causing substantial depression of the reaction rate.

As to the mechanism of the radical reaction that predominates under N_2, we find the propagation sequence postulated by DeTar and co-workers[4,14] to be attractive and compatible with the evidence available; it comprises steps 3, 4, and 5.

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

$$\cdot CH_2OH + ArN_2^+ \rightarrow ArN=N\cdot + CH_2OH^+ \quad (4)$$

$$ArN=N\cdot \rightarrow Ar\cdot + N_2 \quad (5)$$
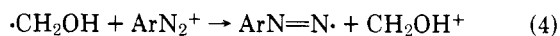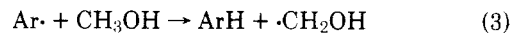
Actually, steps 4 and 5 were earlier[4,14] amalgamated as one, but subsequent work[15] indicates that the phenylazo radical can have discrete existence as such.

The nature of the initiation and termination steps is less clear. The very considerable variation of the observed k_r value between sets of our experiments based on different repurifications of diazonium salts and sometimes on different batches of solvent or different tanks of N_2 suggests that unidentified, adventitious impurities play significant roles either in initiation or in termination steps. Our experiments do, however, allow rejection of one conceivable initiation hypothesis, namely, that a neutral, covalent arylazo methyl ether (ArN=NOCH$_3$) initiates protodediazoniation by homolysis to arylazo (ArN=N·) and methoxyl radicals. The fact that arylazo methyl ethers are detectable in methanol solutions only if they are alkaline[16] indicates that the azo ether conjugate acids are prone to dissociate to diazonium ions and methanol molecules (eq 6). Because of this equilibrium and the acid–

$$ArN=N\!-\!\overset{\displaystyle O^+}{\underset{\displaystyle H}{|}}\!-\!CH_3 \;\rightleftharpoons\; ArN_2^+ + CH_3OH \quad (6)$$
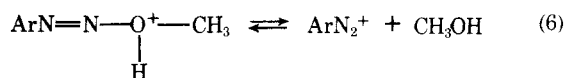
base equilibrium between arylazo methyl ethers and their conjugate acids, the concentrations of arylazo methyl ethers in acidic methanol solutions should be inversely proportional to the hydrogen ion concentration. Accordingly the rate of initiation via arylazo methyl ether homolysis should vary 100-fold between 0.1 and 0.001 M *p*-toluenesulfonic acid, but we find no correlation of k_r with hydrogen ion concentration within this range.

Initiation by homolysis of the conjugate acids of arylazo methyl ethers is not excluded by our data, nor is initiation by electron transfer from methanol to diazonium ion, forming directly arylazo radicals. Intuitively, we favor the latter possibility.

Protodediazoniation under Oxygen. Arguing that an atmosphere of O_2 should suppress radical mechanisms, DeTar and Kosuge[4] suggested that the formation of protodediazoniation products under O_2 may occur by a heterolytic mechanism, namely, by hydride ion abstraction from methanol by aryl cations (eq 7).

$$Ar^+ + CH_3OH \rightarrow ArH + CH_2OH^+ \quad (7)$$
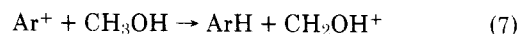
In our experiments we find substantial variation of k_r and the product ratio from one set of experiments to another, even under O_2 (see Tables II and III). It is unlikely that the rate of an ionic process, or the ratio of rates of two ionic processes, would vary so much between experiments set up to be identical or nearly identical. Moreover, Broxton, Bunnett, and Paik[3,10] have shown that the proportion of protodediazoniation under O_2 is further reduced, sometimes to the point of undetectability, by addition of 2-methyl-2-nitrosopropane as a supplementary radical scavenger. We judge, therefore, that protodediazoniation under O_2 occurs by a radical

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.
(2) On sabbatical leave from Meiji Pharmaceutical College, Tokyo, Japan, 1973–1974.
(3) T. J. Broxton, J. F. Bunnett, and C. H. Paik, *Chem. Commun.*, 1363 (1970).
(4) D. F. DeTar and T. Kosuge, *J. Am. Chem. Soc.*, **80**, 6072 (1958).
(5) H. Ohmori, unpublished work in this laboratory.
(6) C. H. Paik, Ph.D. Thesis, University of California, Santa Cruz, June 1972.
(7) J. A. Riddick and E. E. Toops, Jr., "Organic Solvents", 2d ed, Interscience, New York, N.Y., 1955, p 333.
(8) C. R. Noller and P. Liang, *J. Am. Chem. Soc.*, **54**, 670 (1932).
(9) Cf. H. Zollinger, *Helv. Chim. Acta*, **36**, 1730 (1953).
(10) T. J. Broxton, J. F. Bunnett, and C. H. Paik, *J. Org. Chem.*, following paper in this issue.
(11) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951).
(12) C. G. Swain, J. E. Sheats, and K. G. Harbison, *J. Am. Chem. Soc.*, **97**, 783 (1975).
(13) R. G. Bergstrom, C. H. Wahl, Jr., and H. Zollinger, *Tetrahedron Lett.*, 2975 (1974); R. G. Bergstrom, R. G. M. Landells, G. H. Wahl, Jr., and H. Zollinger, *J. Am. Chem. Soc.*, **98**, 3301 (1976).
(14) D. F. DeTar and M. N. Turetzky, *J. Am. Chem. Soc.*, **77**, 1745 (1955).
(15) N. A. Porter, L. J. Marnett, C. H. Lochmüller, G. L. Closs, and M. Shobataki, *J. Am. Chem. Soc.*, **94**, 3664 (1972).
(16) W. J. Boyle, Jr., T. J. Broxton, and J. F. Bunnett, *Chem. Commun.*, 1469 (1971), and unpublished observations.

Thermolysis of Arenediazonium Salts in Acidic Methanol. Effects of Substituents, Atmospheres, and Added Substances on the Competition between Ionic and Radical Mechanisms[1]

Trevor J. Broxton, Joseph F. Bunnett,* and Chang Hum Paik

University of California, Santa Cruz, California 95064

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).

$$R\text{—}N_2^+ \xrightarrow[\text{CH}_3\text{OH}]{\text{H}^+} R\text{—}H + R\text{—}OCH_3 \quad (1)$$

1	**2** **3**

a, R = H   f, R = m-CH$_3$
b, R = m-Br   g, R = p-CH$_3$
c, R = p-Br   h, R = m-OCH$_3$
d, R = m-Cl   i, R = p-OCH$_3$
e, R = p-Cl   j, R = p-NO$_2$
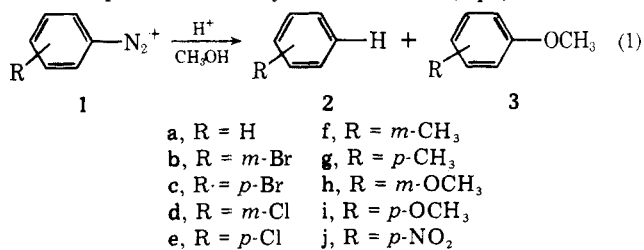
DeTar and Kosuge[2] made the striking observation that for two diazonium salts (1c and 1i bisulfates) the former type of product (**2**) predominates when the atmosphere above the reacting solution is nitrogen but that under oxygen principally the aryl methyl ether is formed. Arguing mainly from that 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 mecha-

nism, 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