Similar coupling results can be obtained from the β-naphthalenediazonium fluoborate reactions. Since the coupling reaction is relatively unimportant with this salt, the coupling data are subject to large errors.

It is interesting to note that cupric sulfate seems to increase the coupling rate of α-naphthol, but not the rate of carbon–nitrogen bond cleavage (*cf.* nitrogen yields for runs 15, 18, 19, 20 as compared with runs 10, 16, 17). This effect did not show up with the β-naphthalenediazonium fluoborate and β-naphthol.

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COLUMBIA, S. C.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY OF CORNELL UNIVERSITY AND FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Mechanisms of Diazonium Salt Reactions. IV. A Kinetic Study of the Reactions of Benzenediazonium Fluoborate with Methanol in the Absence of Oxygen

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The thermal decomposition of benzenediazonium fluoborate in methanol in the presence of an acetate buffer and in the absence of oxygen has previously been shown to give benzene as the principal product. A free radical chain mechanism was proposed to account for this result. The present paper is a report of a preliminary investigation of the kinetics of the reaction. The kinetics are complex and not too reproducible; oxygen is a strong retarder. Reaction products are without effect on the kinetics within the limits of the present investigation. The latter part of the reaction can be fitted accurately by the function for a reaction of first plus half-order, a result consistent with the mechanism previously proposed. A brief investigation of the corresponding reactions in aqueous solution indicates that in the aqueous solvent the decomposition takes place largely by an ionic mechanism up to a *p*H of about 7.

The kinetics of the thermal decomposition of diazonium salts in aqueous solution have been investigated by many workers.[3–5] Fewer reliable studies have been made of the reaction in alcoholic solutions.[3a] In both the aqueous and in the non-aqueous solvents under acidic conditions the nitrogen evolution follows first-order kinetics, and there is a great deal of evidence that a heterolytic S_N cleavage of the C–N bond is occurring.[5] In acidic methanol anisole is the major product.[6]

We have been interested in those reactions of diazonium salts which lead to a homolytic cleavage of the C–N bond to give free radical intermediates. A study of the products of the reaction of benzenediazonium fluoborate in methanol in the presence of acetate buffers has given clear evidence that the thermal decomposition of the diazonium salt under these conditions is a free radical process since benzene (80–90%) is the main product with biphenyl (5%) and anisole (5–15%) the principal by-products.[6] In the presence of oxygen the product mixture is dark brown in color, while in the absence of oxygen the mixture is nearly colorless. Furthermore, the above listed products account for about 99% of the diazonium salt when oxygen is absent, but for only about 89% or less when oxygen is present.

Representative examples of the reactions carried out in outgassed methanol in the presence of acetate buffers are given in Figs. 1 and 2.[7] From 50–100 points were obtained for each reaction; the reaction was usually followed to more than 95% completion. The reactions were sensitive to traces of oxygen and were not accurately reproducible in spite of the care used in preparing the reaction mixtures. The curve for most of the reactions was noticeably S-shaped. The latter part of the reaction was somewhat less than first order.

A number of methods were investigated to summarize the data. The most generally useful criteria were found to be the initial rate, the nitrogen yield and the over-all shape of the per cent. reaction *vs.* time curves.

Twenty of the first 23 reactions given in Table IV of ref. 7 (excluding those in which oxygen or copper sulfate were present) were intended to be exact replicates. Comparison of the per cent. reaction *vs.* time plots showed that some reasonable match could be made for those reactions in the first group of runs (*cf.* runs 182, 242, 165 and 238 of Fig. 1) especially over the latter portions of the reactions. Those reactions in the second group had two features; no two gave a match, and all were slower (*cf.* run 236 of Fig. 1). The average initial rate of the second group of reactions is also significantly lower than the average initial rate for the first group, though the nitrogen yields do not differ significantly. It is clear from inspection of

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[3] Examples are (a) H. A. Pray, *J. Phys. Chem.*, **30**, 1417 (1926); (b) M. Crossley, R. Kienle and C. Benbrook, THIS JOURNAL, **62**, 1400 (1940); (c) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

[4] (a) Part II, D. F. DeTar and A. R. Ballentine, THIS JOURNAL, **78**, 3916 (1956); (b) Part III, D. F. DeTar and S. Kwong, *ibid.*, **78**, 3921 (1956).

[5] See *e.g.*, D. F. DeTar and D. I. Relyea, *ibid.*, **76**, 1680 (1954).

[6] D. F. DeTar and M. N. Turetzky, *ibid.*, **77**, 1745 (1955).

[7] Tables summarizing the rate data for the other diazonium salts reported in this paper and in papers II–III of this series have been deposited as Document number 4819 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. A copy may be secured by citing the Document number and by remitting in advance $2.50 for photoprints or $1.75 for 35 mm. microfilm by check or money order payable to Chief, Photoduplication Service, Library of Congress.

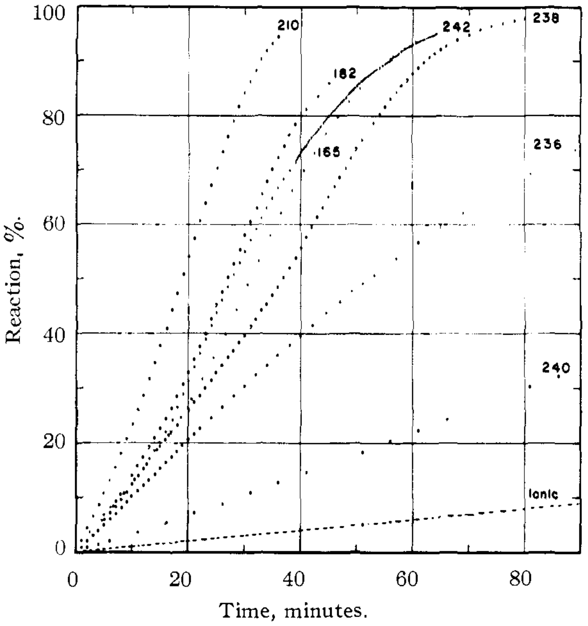

Fig. 1.—The thermal decomposition of benzenediazonium fluoborate in methanolic solution at 15°. The line labeled "ionic" is calculated from an estimated rate constant of 1.88 × 10^{-5} sec.$^{-1}$ for anisole formation (see Table I, Footnote *d*). The dots representing experimental points were taken at even time intervals; some initial points have been omitted. In all runs shown here the concentrations of diazonium salt and of buffer constituents was the same (*cf.* Table IV[7]). All reaction mixtures were outgassed on the vacuum train and were run under a nitrogen atmosphere. The limiting reactions of the first group in Table IV[7] are illustrated by runs 182, 242, 165 and 238. Run 210 is faster due to added cupric sulfate. Run 240 illustrates the marked influence of oxygen; in this run 1% of oxygen was admitted to the reaction flask. Run 236 is typical of those runs in the second group of Table IV.[7] The slower rate is probably due to traces of oxygen. The solid portion of the curve of run 242 is accurately fitted by the equation for a reaction of first-plus half-order; the equation: p = 371.63 − 936.60e^{ct} + 1592.02e^{2ct} with c = −0.0141979 reproduces the observed points with a standard deviation of 0.2 mm. (14 D.F.). For this reaction p_∞ = 513.1, $p_\infty - p_0$ = 454.5; the portion fitted lies between p = 383.6 and p = 490.4.

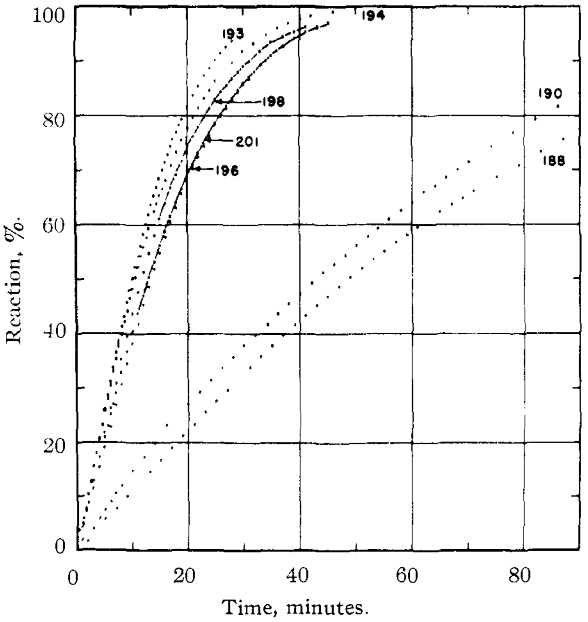

Fig. 2.—The thermal decomposition of benzenediazonium fluoborate in outgassed methanol in the presence of acetate buffers at 15°. These curves illustrate the relative insensitivity of the reactions to reaction products. Reactions 193 and 194, 198 and 201 were run at a diazonium salt concentration of 0.019 *M*; 194 was run in the reaction mixture of 193; 201 was run in the reaction mixture of 198. Reaction 196 (0.038 *M*) was run in the 193 plus 194 reaction mixture. Most of the decrease in rate can be attributed to a decrease in the pH of the medium in successive reactions. Runs 190 and 188 are less significant because they belong to the slow second group of Table IV.[7] Runs 198 and 201 are accurately fitted over the region connected by the dashed line by the equation of a reaction of the first plus half order. For 201 the expression: p = 176.02 + 710.02e^{ct} − 799.74e^{ct} with c = −0.014913 (min.)$^{-1}$ fitted from p = 202.7 to p = 330.1 (44-97% reaction) with a std. dev. of 0.1 mm. For 198 the expression: p = 285.78 + 161.55e^{ct} − 419.37e^{ct} with c = −0.0282106(min.)$^{-1}$ fitted from p = 212 to p = 295 (60-95% reaction) with a std. dev. of 0.11 mm.

runs 177, 240 and 157[7] that oxygen lowers the apparent nitrogen yield somewhat, and that it also has a very large effect on the rate of the reaction (*cf.* run 240 of Fig. 1). Since every effort was made to eliminate impurities by using various sources of methanol, various samples of diazonium salt, and various specimens of sodium acetate and of acetic acid, it seems probable that the residual variability between these two groups of runs is due to variable traces of oxygen. The results of product studies have been reported for several runs.[6] The product yields are not at all sensitive to those variables that lead to rate differences. The products of run 210 (trace of copper sulfate present, *cf.* Fig. 1) are nearly identical with those of 238 and 242, and those of even 240 are not greatly different. The main difference in products arises from a variation in the anisole yield, this depending on how long there is diazonium salt present to react by the ionic process. A curve to illustrate this much slower ionic reaction is also shown in Fig. 1 for purposes of comparison.

A number of runs were carried out to determine whether reaction products had either a retarding or an accelerating effect. The outcome was that no effect could be detected with certainty. *A priori* formaldehyde seemed to be the product most likely to have an effect. However, a comparison of the per cent. reaction *vs.* time curve of run 181 with that of 165 showed as good a correspondence as do any of the runs without formaldehyde.[7] Runs 173 and 174 did not show this correspondence, but the initial rates are similar. Benzene had no effect on the rate; run 242 matches 165 fairly well. The benzene was added primarily in order to determine its effect on the biphenyl yield.[6] A much more rigorous investigation of the effect of products was carried out in three series of experiments 188 and 190; 193, 194 and 196;

TABLE I

KINETICS OF THE THERMAL DECOMPOSITION OF BENZENEDIAZONIUM SALTS IN ACIDIC METHANOL AND IN AQUEOUS BUFFERS AT 25°

Salt (mmoles)	Solvent	Buffer [NaOAc]/[HOAc]	[NaOAc]	pH	k_{obsd}[a] $\times 10^5$, sec.$^{-1}$	k_1[b] $\times 10^5$, sec.$^{-1}$	Nitrogen yield,[c] %
$C_6H_5N_2Cl$ (0.86)	40 ml. CH_3OH	...	...	...	9.6[d]	...	...
$C_6H_5N_2Cl$ (0.75)	40 ml. CH_3OH	...	...	...	9.8	...	...
$C_6H_5N_2BF_4$ (1.00)	50 ml. H_2O	0.21	0.199	4.01-3.95	4.7	4.2	98.2
$C_6H_5N_2BF_4$ (1.00)	50 ml. H_2O	0.85	.095	4.60-4.33	5.3	4.6	88.4
$C_6H_5N_2BF_4$ (1.00)	50 ml. H_2O	10.3	.199	5.66-5.38	7.6	4.7	63.4
$C_6H_5N_2BF_4$ (1.00)	50 ml. H_2O	[e]	[e]	7.15-6.90	12.3	5.7	44.2

[a] First-order rate constant. Std. dev. probably about 3% relative for first two runs, 5% for rest. The last four rate constants were obtained from a plot of log $(p_\infty - p)$ *vs.* t and are based on $(p_\infty - p_0)_{obsd}$; $k_{obsd} = [1/(p_{\infty obsd} - p_0)](dp/dt)_0$. [b] Obtained from same initial (dp/dt) as k_{obsd} values, but based on the initial diazonium salt concentration assuming the salt to be 100% pure; $k_1 = (1/a_0vq)(dp/dt)_0$. k_1 is the rate constant for eq. 3. [c] Std. deviation about 1.5% relative based on a large number of runs. [d] Pray[3a] reports rates at 20, 30 and 40°; his data may be represented by the equation $\ln k = 36.9392 - 27.366/RT$. The rate constant for 25° is 9.57×10^{-5} sec.$^{-1}$ and for 15° is 1.88×10^{-5} sec.$^{-1}$ [e] Phosphate buffer containing 1.33 g. of $Na_2HPO_4 \cdot 7H_2O$ and 0.34 g. of $NaH_2PO_4 \cdot H_2O$. From this reaction a tan solid, m.p. 151-154°, was obtained; p-hydroxyazobenzene has a m.p. of 155-156°.

and 198, 201 and 202 (see Fig. 2). After an initial reaction had been carried out, the flask was returned to the vacuum train and the volatile contents distilled into a reservoir. A new sample of diazonium salt was introduced, and after purging with nitrogen the reaction mixture was distilled back into the reaction flask. As a result the new reaction was run in the presence of all the products of the preceding reaction, excepting possibly very volatile products (which are not very likely).

The mechanism suggested previously[6] for the reaction requires first-plus half-order kinetics in accordance with the equations

$$dp/dt = k_1(p_\infty - p) + k_{1/2}(p_\infty - p)^{1/2} \qquad (1)$$

$$100(dp/dt)_0/(p_\infty - p_0) = 100k_1 + 100k_{1/2}(p_\infty - p_0)^{-1/2} \qquad (2)$$

The left-side of eq. 2 is the initial reaction rate in per cent. per sec. as tabulated in Table IV.[7]

The preliminary runs have not embraced a sufficient range of concentrations to permit a test of eq. 2. The observed variation among runs 193, 194, 196, 198, 201 and 202 can be accounted for completely as pH variation. An attempt to utilize the integrated form of eq. 1 was partly successful.[8] The latter portions of several of the reactions were accommodated by this expression. Examples are given in Figs. 1 and 2. With the present runs the scatter of k and $k_{1/2}$ values was too large to permit a useful examination of these constants. The first-order and the half-order components make comparable contributions to the rate.

The effect of methoxide concentration and of acetate ion concentration was briefly investigated. It was assumed that the constants of eq. 2 can be approximated by the expression $k_{obsd} = k[OCH_3^-]^b$ or in other words that log (initial rate) $= a + b \log[NaOAc]/[HOAc]$. Such an expression ($a = -0.748$, $b = 1.462 \pm 0.043$) correlates the data moderately well, within a 10% error in k (0.04 in log k). Very few runs were carried out with variation in the acetate ion concentration, but since doubling the concentration in the series 158, 159, 160, 192 has no detectable effect on the rate, the effect is presumably small.

In considering possible mechanisms for the thermal decomposition of benzenediazonium salts in methanol in the presence of acetate buffers there is evidence from product studies[6] and from reactions carried out in the presence of air[9] as well as that of the present work.

The results obtained in the present study may be summarized briefly as follows. (1) The reaction order is less than unity, it is approximately first-plus half-order. (2) Reaction products do not affect the reaction rate. (3) The reaction is highly sensitive to retardation by oxygen. (4) The reaction rate is more sensitive to the buffer ratio (a measure of methoxide ion concentration) than it is to total acetate ion concentration. These results are all in agreement with the free radical chain mechanism previously suggested,[6] except that the reaction depends on a higher power of the buffer ratio than would be expected on the basis of that mechanism. This point deserves further investigation, but it may mean only that the initiation step requires modification.

Of the various termination steps involving phenyl radicals and hydroxymethyl radicals, the reaction of two phenyl radicals (eq. 6)[6] leads to a half-order chain process, of two hydroxymethyl radicals leads to a three-halves order chain process, and of one hydroxymethyl radical and one phenyl radical (eq. 7)[6] (to give benzyl alcohol or perhaps to give benzene and formaldehyde) leads to a first-order chain reaction. The rather large value of the first-order component of the reactions in outgassed methanol suggests that termination reactions involving hydroxymethyl radicals are of some importance.

A few experiments were carried out in aqueous buffers to see whether a free radical chain process was occurring in aqueous solution. It has frequently been observed that the thermal decomposition of diazonium salts in aqueous solution is accelerated by such buffer agents. The buffer results along with results of some runs carried out in acidic methanolic solutions are presented in Table I.

Since the nitrogen yield is not quantitative, $(p_\infty - p_0)$ is suspect as a measure of a_0, the initial diazonium ion concentration. The use of $(p_\infty - p_0)$ for this purpose would be valid if the diazonium solutions evolved a fraction of the

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(8) D. F. DeTar, THIS JOURNAL, **77**, 2013 (1955).

(9) D. F. DeTar and M. N. Turetzky, *ibid.*, **78**, 3928 (1956).

nitrogen that remained constant throughout the reaction. But since in some of the runs *p*-hydroxyazobenzene was formed, it is clear that some of the nitrogen deficit is due to coupling (eq. 3 and 4), a reaction that becomes increasingly important as

$$C_6H_5N_2^+ \xrightarrow{k_1} C_6H_5OH + N_2 + H^+ \qquad (3)$$

$$C_6H_5N_2^+ + C_6H_5OH \xrightarrow[k_2]{\text{buffer}} C_6H_5N_2C_6H_4OH + H^+ \qquad (4)$$

reaction proceeds. Thus the fraction of nitrogen evolved decreases throughout the reaction. Equations have been developed to allow for the coupling reaction,[4b] but these are not applicable to the last two runs in Table I because the extent of coupling exceeds that accommodated by the approximations used. The rate of the C–N cleavage step was therefore estimated by use of eq. 5 (*cf.* ref. 4b)

$$100(dp/dt)_0/a_0qv = \text{initial rate} \qquad (5)$$

in which a_0 is the initial diazonium salt concentration, q an apparatus constant, and v the solution volume in liters.[9] Since these initial rates are nearly independent of *p*H, the apparent acceleration in rate can largely be accounted for by the coupling reaction and is not evidence for a change of mechanism over to a homolytic one.

Acknowledgment.—The authors are indebted to the Rohm and Haas Company and to the U. S. Rubber Company for fellowships and to the Research Committee of the University of South Carolina for a grant for assistance in carrying out the extensive calculations involved.

Experimental

Rate Measurements.—The apparatus employed was the shaker equipment already described.[10] The reaction flask and the ballast flask each consisted of a 500-ml. 24/40 joint flask.

The diazonium salt was weighed out in a bucket constructed of Kel-F[11] with a platinum bail. These two materials seemed to be without effect on the reactions, although the point was not given a completely rigorous investigation. Glass buckets used initially caused rapid grinding of the flask interiors.

The oxygen-free reaction mixtures were prepared on a simple vacuum train consisting of vacuum feed, high purity nitrogen feed, reservoirs for distilled methanol, a sealed-on measuring tube and joints for attaching flasks. Spherical joints were less trouble than straight joints. The special head was a preliminary version of the type described before.[10] It consisted of a 24/40 inner joint with hook for the bucket to which was sealed a 2 mm. high-vacuum stopcock, on the other side of which was a joint for attaching the assembly to the vacuum train. To a side arm sealed to the flask side of the stopcock was attached a length of Tygon[12] tubing which was plugged when the flask was evacuated. The capillary tube and the second stopcock shown in Fig. 2 of ref. 10 were not used. Evacuation with the Tygon tubing in the system cannot be carried to less than about 10 μ. With the modified head (Fig. 2 of ref. 10) 0.01 μ is readily obtainable. In the reaction flask were placed acetic acid and sodium acetate, and the diazonium salt sample was placed in the basket. The assembly was attached to the vacuum train (side tube plugged), cooled with a Dry Ice bath, evacuated to 0.05 mm., then flushed with "high purity" grade tank nitrogen, the process being repeated twice more. Methanol was then distilled in from the measuring tube. The methanol had been outgassed by several trap to trap distillations. Nitrogen pressure was admitted to the loaded reaction flask, the flask disconnected from the train, allowed to warm almost to room temperature, then placed in the constant temperature bath. After an hour, the plug was removed from the Tygon line (the nitrogen pressure having been adjusted so that a little nitrogen escaped at this point) and the line was connected to the manometer.

Calculation of Initial Rates.—These were obtained from pressure *vs.* time graphs, from per cent. reaction *vs.* time graphs, and from log $(p_\infty - p)$ *vs.* time graphs. The analytical method[9] did not work out as conveniently because of the S-shaped nature of the initial part of the curves. The initial rates in per cent. per second are based on the equation

$$\text{initial rate } (\% \text{ per sec.}) = [100/(p_\infty - p_0)](dp/dt).$$

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[10] D. F. DeTar, This Journal, **78**, 3911 (1956).

[11] Trade Mark of the M. J. Kellogg Company for polychlorotrifluoroethylene.

[12] Polyvinyl chloride–polyvinyl acetate polymer.

[Contribution from the Baker Laboratory of Chemistry of Cornell University and from the Department of Chemistry of the University of South Carolina]

The Mechanisms of Diazonium Salt Reactions. V. A Kinetic Study of the Reactions of Benzenediazonium Fluoborate with Methanol in the Presence of Oxygen

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In methanol in the presence of oxygen and an acetate buffer the thermal decomposition of benzenediazonium salts is a complicated free radical reaction leading to dark brown reaction mixtures. Measurement of the initial rate under a variety of conditions has shown that the reaction is of mixed first plus half-order, and that the initial rate is approximately dependent on the square root of methoxide concentration and only slightly dependent on acetate ion concentration. Since there seems to be only one type of termination reaction which leads to a reaction of less than first order, namely, reaction of two phenyl radicals, the mechanism of the decomposition can be restricted to a small number of choices. The dependence on methoxide concentration rather than on acetate concentration indicates that the diazomethyl ether rather than the diazoacetate is the probable initiator.

In a continuation of work reported previously,[3] a preliminary study has been made of the kinetics of the reaction of benzenediazonium fluoborate with methanol in the presence of acetate buffers. The reaction is sufficiently complicated that even an extended investigation might not permit quantitative statements about its details. The present work, however, provides several indications about the reaction mechanism.

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[2] Rohm and Haas Research Assistant 1950–1951; U. S. Rubber Research Fellow 1952–1953 at Cornell University.

[3] Part IV, D. F. DeTar and M. N. Turetzky, This Journal, **78**, 3925 (1956).