[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTH CAROLINA]

The Mechanism of Diazonium Salt Reactions. III. The Kinetics of the Thermal Decomposition of α- and β-Naphthalenediazonium Fluoborates in Aqueous Solution[1]

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The thermal decomposition of the naphthalenediazonium salts in aqueous acidic solution to give the corresponding naphthols is complicated by the occurrence of a side reaction consisting of coupling of the diazonium ion with the naphthol. This side reaction amounts to 5% or more even in 0.05 *M* sulfuric acid. As a consequence, the simple first-order rate expression is applicable only to the first 75–90% of reaction. A modified rate expression has been developed to allow for the coupling side reaction; this modified expression excellently correlates the rate data over at least 5–98% of the reaction. Arrhenius parameters have been computed for the rate constants of the carbon–nitrogen cleavage step using the modified expression. These parameters are believed to be unbiased; parameters computed from the rate constants derived by use of the simple first-order expression on the other hand are seriously in error.

In a continuation of a study of the kinetics and mechanisms of the carbon–nitrogen bond cleavage in diazonium salts[2] the rates of the thermal decomposition of α- and β-naphthalenediazonium fluoborates in aqueous solution have been investigated. Relatively little work has been done on these compounds previously,[3,4] but it has been reported that coupling occurs as a side reaction even under somewhat acidic conditions.

TABLE I

APPLICATION OF FIRST-ORDER EQUATION AND OF MODIFIED EQUATION TO RUN 107

t, min.	p, mm. p-xylene	First-order equation[a] e^{ct}	F_0[b]	e^{ct}	Modified equation[c] pe^{ct}	F_0'[d]
5	18.50	0.966407	0.162	0.963900	17.83	−0.118
15	46.71	.902570	.087	.895560	41.83	.074
30	85.33	.814630	− .257	.802028	68.44	− .088
45	120.54	.735210	− .236	.718265	86.58	− .005
65	162.50	.641330	.129	.620028	100.75	.264
90	207.14	.540608	.142	.515904	106.86	.094
115	244.67	.455705	.053	.429267	105.03	− .142
150	287.77	.358760	.200	.331855	95.50	− .025
195	329.54	.263783	− .112	.238360	78.55	− .053
225	351.09			.191171	67.12	.200
260	370.74	.169172	− .832			
295	385.73			.114252	44.07	− .181
325	396.21			.091633	36.31	− .068
330	397.81	.104850	−2.261			
420	417.57			.045567	19.03	.076
480	425.13	.037616	−4.751	.029311	12.46	.117

[a] $p = 446.527 - 443.0731e^{-0.006834t}$ (t is in minutes). The least squares adjustment was carried out from 5 to 195 min. [b] $F_0 = p_{\text{obsd}} - p_{\text{calcd}}$ $s_p = 0.20$ mm. over range covered (3–74%). [c] $p = 438.614 - 434.438e^{ct} - 0.069618pe^{ct}$; $c = -0.00735371$. [d] $s_p = 0.14$ mm.; the range of reaction covered is 4–97%.

The plan of the experiments was based on considerations similar to those discussed previously.[2] In an effort to minimize coupling, 0.05 *M* sulfuric acid was chosen as the standard reaction medium at each of the five reaction temperatures. Lower acidities, 0.005 *M* sulfuric acid and 0.02 *M* hydrochloric acid, were also employed; and the effect of 0.0005 *M* cupric sulfate was tested. Control runs were carried out with benzenediazonium fluoborate and with 4-methylbenezenediazonium fluoborate.[2]

The experimental procedure and the general methods of calculation have been described previously.[2,5]

It was discovered that the coupling side reaction occurred to some extent even in 0.05 *M* sulfuric acid. A small amount of a violet precipitate was present in all runs. The amount of precipitate increased and the nitrogen yields decreased in the more dilute acids and at the lower temperatures. Furthermore the reactions showed deviations from the first-order expression, the extent of deviation being larger for runs containing larger amounts of precipitate. This deviation is illustrated in Table I for a typical run. All of these effects are more pronounced for the α-naphthalenediazonium fluoborate than for the β-isomer. The reaction mechanism applicable to these salts is thus the one given in eq. 1–3.

$$ArN_2^+ \xrightarrow{H_2O} ArOH + N_2 + H^+ \quad (1)$$

$$ArN_2^+ + ArO^- \longrightarrow ArN_2arOH \quad (2)$$

$$ArN_2^+ + ArOH \longrightarrow ArN_2arOH + H^+ \quad (3)$$

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[1] Taken from the M.S. thesis of Sara Kwong.

[2] Part II, D. F. DeTar and A. R. Ballentine, THIS JOURNAL, **78**, 3916 (1956).

[3] E. Yamamoto, R. Goshima and T. Hashima, *J. Soc. Chem. Ind. Japan*, Suppl. Binding, **36**, 490B (1933).

[4] J. C. Cain and F. Nicoll, *J. Chem. Soc.*, **83**, 206 (1903).

[5] D. F. DeTar, THIS JOURNAL, **78**, 3911 (1956); **77**, 2013 (1955).

Summary of Terms

a, b, c, d = parameters of eq. 16
$\alpha, \beta, \gamma, \delta$ = parameters of eq. 15
$\alpha = (a + b)/(1 - d)$
$\beta = -(da + b)/(1 - d)$
$\gamma = c$
$\delta = -d$
a_0 = initial diazonium salt concn., mole/l. at the reaction temp.
$a_0 = x + y + 2z = x - y + 2u$
b_0 = initial hydrogen ion concn.
K = ionization constant for ArOH
k_1, k_2, k_3 are rate constants for eq. 1–3
$k_1 = -\gamma/m = -c/m = (da + b)c/a_0vq(1 - d)^2$ [The last relationship bases k_1 on the initial rate $= (bc + dp_0c)/(1 - d)$ and on the assumed 100% purity of the diazonium salt (so that $p_\infty - p_0 = a_0vq$)]
$m = (1 + 2a_0/\eta)^{1/2} = (1 - d)/(1 + d)$
p, p_0, p_∞ = manometer reading in mm. of xylene at any time, at zero time, and at infinite time (>12 half-lives), respectively
$p_0 = \alpha = (a + b)/(1 - d)$
$p_\infty = \alpha + \beta = a$
q = apparatus constant relating moles of reagent to manometer reading; $(p - p_0) = uvq$
t = time
$u = y + z$ (a function proportional to the moles of evolved nitrogen)
v = reaction soln. vol. at the reaction temp.
x = concn. of ArN_2^+ at time t
y = concn. of ArOH at time t
z = concn. of ArN_2arOH at time t
$\eta = b_0k_1/(k_2K + k_3b_0)$ (ratio of nitrogen evolution to coupling)
$k_2K/b_0 + k_3 = k_1/\eta = k_1(m^2 - 1)/2a_0$

Since the reaction is followed by measuring the rate of nitrogen evolution, it is necessary to obtain the rate in terms of a function u which is proportional to the amount of nitrogen evolved. The relevant differential equation is then eq. 4. Solution of eq. 4 requires an expression for y as a function of u. This is available from eq. 5 and 6. In deriving these equations y is assumed to represent accurately the naphthol concentration, since the naphthoxide ion concentration is very low. Equation 7, obtained from eq. 5 and 6, can be integrated, but the result is unmanageable. If it can be assumed that $b_0 >> y + 2z$, *i.e.*, that the hydrogen ion concentration is constant during the reaction, then eq. 7 simplifies to eq. 8 which integrates to eq. 9. Substitution of eq. 9 into eq. 4 gives eq. 10; apparently this equation cannot be integrated in closed form.

$$\mathrm{d}u/\mathrm{d}t = k_1[ArN_2^+] = k_1(a_0 - 2u + y) \qquad (4)$$

$$\mathrm{d}y/\mathrm{d}t = k_1(a_0 - y - 2z) - (k_2K/[H^+] + k_3)y(a_0 - y - 2z) \qquad (5)$$

$$\mathrm{d}z/\mathrm{d}t = (k_2K/[H^+] + k_3)y(a_0 - y - 2z) \qquad (6)$$

$$\mathrm{d}y/\mathrm{d}z = -1 + k_1(b_0 + y + 2z)/(k_2K + b_0k_3 + k_3y + 2k_3z)y \qquad (7)$$

$$\mathrm{d}y/\mathrm{d}z = -1 + k_1b_0/(k_2K + b_0k_3)y = -1 + \eta/y \qquad (8)$$

$$y = \eta(1 - e^{-u/\eta}) \qquad (9)$$

$$\mathrm{d}u/\mathrm{d}t = k_1(a_0 - 2u + \eta - \eta e^{-u/\eta}) \qquad (10)$$

If the coupling reaction is not too extensive, *i.e.*, not more than about 10% with an initial diazonium salt concn. of 0.003 M, then a series expansion of the exponential with neglect of cubic and higher terms affords a satisfactory approximation of eq. 10. The actual test of the validity of the approximation is in terms of m or d. If $(m^2 - 1) < 0.2$, the maximum error caused by this approximation is 1/600; if $(m^2 - 1) = 0.4$, the maximum error is 8/600.

Two other approximations were investigated for simplifying eq. 7. One of these was $(b_0 + y) >> z$, the other was $(b_0 + y + 2z) = b_0 + \alpha y$ in which α is an arbitrary parameter intended to make αy the best linear approximation to $y + 2z$. In the application of these approximations to eq. 10 it was still necessary to utilize the series expansion in the solution of eq. 10, with neglect of all terms higher than quadratic (otherwise integration of the resulting expression does not seem possible in usable form). When the higher terms are dropped, all three approximations give eq. 11, the differences in the approximations making their first appearance in the cubic term that was dropped.

$$\mathrm{d}u/\mathrm{d}t = k_1(a_0 - u - u^2/2\eta) \qquad (11)$$

Equation 11 is obtained from eq. 10 by carrying out the above simplifications. Integration and application of the boundary condition that $u = 0$ when $t = 0$ gives eq. 12, and this can be converted to eq. 13.

$$(1/m) \log [(1 - m)/(1 + m)][(u/\eta + 1 + m)/(u/\eta + 1 - m)] = k_1t \qquad (12)$$

$$u = \eta(m - 1)(1 - e^{-mk_1t})/[1 + (m - 1)e^{-mk_1t}/(m + 1)] \qquad (13)$$

Substitution of $u = (p - p_0)/vq$ and use of the relationship that $(m^2 - 1) = 2a_0/\eta$ leads to eq. 14.

$$p = p_0 + 2a_0vq(1 - e^{-mk_1t})/(m + 1)[1 + (m - 1)e^{-mk_1t}/(m + 1)] \qquad (14)$$

It can be seen that substitution of $m = 1$ in eq. 14 leads to an expression of the form $p = a + be^{ct}$, and this is the correct equation for a simple first-order reaction. Since $m = 1$ if the coupling reactions are negligible, eq. 14 gives the correct limiting result.

Equation 14 is of the form of eq. 15, but this form is not very convenient for making computations.

$$p = \alpha + \beta(1 - e^{\gamma t})/(1 + \delta e^{\gamma t}) \qquad (15)$$

Equation 15 readily can be transformed into eq. 16, a form which is suitable for computing. The relationships of k_1, k_2, k_3, p_0 and p_∞ to the parameters a, b, c, d of eq. 16 are given above in the Summary of Terms.

$$p = a + be^{ct} + dpe^{ct} \qquad (16)$$

In the use of eq. 16 to calculate the pressure for a given value of t, the observed value of p was substituted in the third term. This causes no difficulty since $(p_{obsd} - p_{calcd})$ is very small and since the third term also is rather small.

Table I is an abbreviated summary of the calculations carried out on one run. It can be seen that eq. 16 does an excellent job of correlating the data. Tables II and III summarize the results obtained in this work.(6)

The first two columns of Table II are self explanatory. The nitrogen yield in column 3 reflects both experimental error and shortage of nitrogen due to the coupling process. The amount of diazonium salt initially present (a_0v) is given by

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(6) Similar tables summarizing the rate data for the other diazonium salts reported in this paper and in papers II and IV 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.

TABLE II

RATE CONSTANTS AND OTHER DERIVED QUANTITIES FOR THE THERMAL DECOMPOSITION OF NAPHTHALENEDIAZONIUM SALTS IN AQUEOUS SOLUTIONS

Reaction[a] medium	Temp.,[b] °C.	% N_2 yield[c] (based on p_∞ obsd)	% ArN_2^+ accounted for[d]	$10^3k_1/\eta$[e]	$10^5 k_1$,[f] sec.$^{-1}$	$10^5 k_1$,[g] sec.$^{-1}$	Statistical wt.	$100F_0$[h]
				α-Naphthalenediazonium fluoborate				
50 S	30.54	94.0	102.3	2.8	2.55*	2.49	4	−1.47
5 S	30.53	65.8	...	...	2.64*	...[i]	2	3.92
5 S	30.53	62.2	...	...	2.64*	...[i]	2	3.92
50 S	35.50	91.7	98.9	2.8	5.33	5.38*	8	0.31
20 H	35.50	91.6	99.9	6.5	5.42	5.43*	4	1.23
50 S	40.48	91.4	99.5	5.8	10.61	10.66*	8	−3.90
5 S	40.48	81.3	95.9	15	10.87*	11.33	2	−1.97
50 S	45.25	90.6	94.0	4.9	20.5	21.8 *	8	0.23
20 H	45.30	86.5	95.1	16.2	20.9	22.0 *	2	0.42
20 H[j]	45.27	80.7	...	...	20.7 *	(15.6)	1	−5.23
20 H	45.25	89.2	95.2	10	21.3	22.4 *	2	2.92
20 H	45.25	89.9	95.7	9.5	21.5	22.4 *	4	2.92
20 H[j]	45.23	81.6	...	...	20.9 *	...[i]	1	−3.71
20 H[j]	45.23	81.2	...	...	21.1 *	...[i]	1	−2.76
20 H[j]	45.22	82.2	...	...	21.5 *	...[i]	1	−0.86
50 S	50.54	94.4	98.5	12	43.2	43.8 *	8	−2.43
5 S	50.52	87.3	93.6	23	44.2	47.3 *	2	5.51
				β-Naphthalenediazonium fluoborate				
50 S	30.55	94.1	100.4	0.77	2.37	2.35*	4	0.06
5 S	30.53	90.7	100.0	1.5	2.37	2.37*	2	0.92
50 S	35.50	97.2	100.3	1.5	4.94	4.93*	8	−0.51
20 H	35.50	94.5	101.9	2.7	4.99	4.90*	4	−1.10
50 S	40.46	95.0	97.1	0.51	9.99	10.27*	8	0.44
5 S	40.46	93.8	97.9	2.6	10.13	10.34*	2	1.10
50 S	45.26	94.3	96.5	2.4	19.4	20.1 *	8	−0.38
20 H	45.27	93.4	97.1	5.3	19.7	20.3 *	4	0.47
20 H[j]	45.31	93.6	96.0	2.3	19.9	20.7 *	4	1.86
50 S	50.51	95.4	97.3	4.7	40.0	41.1 *	8	−0.90
5 S	50.05	94.4	97.0	6.9	40.6	41.8 *	2	0.94

[a] 200 ml at 25°; 50 S = 0.050 M H_2SO_4, 5 S = 0.0050 M H_2SO_4, 20 H = 0.020 M HCl. [b] Estimated accuracy ±0.05°. [c] Standard deviation about 1.5%. [d] 100 $a_{0\text{obsd}}/a_{0\text{calcd}}$. [e] This is a measure of the rate of the coupling reaction. The given value is based on the value of k_1 in column 6 or column 7 that is marked with an asterisk. [f] Based on eq. 18; this value of k_1 was considered the more reliable estimate for reactions in which the approximations required by eq. 16 were probably not satisfied. [g] Based on c; $k_1 = -c/m$. The k_1 values believed most reliable are marked with an asterisk and were used in computing the Arrhenius and other reaction parameters in Table III. [h] $F_0 = (\ln k_{\text{obsd}} - \ln k_{\text{calcd}})$ in which k_{obsd} is the value of k_1 in column 6 or 7 which is marked with an asterisk and k_{calcd} is obtained from the Arrhenius equation given in Table III. $100F_0$ is the per cent. difference between k_{obsd} and k_{calcd}. The average values of these deviations are given in Table III. [i] Approximations used in deriving modified equation not met by this run. [j] 0.0005 M $CuSO_4$ present.

TABLE III

ARRHENIUS PARAMETERS AND HEATS AND ENTROPIES OF ACTIVATION FOR THE CARBON-NITROGEN BOND CLEAVAGE STEP IN THE THERMAL DECOMPOSITION OF NAPHTHALENEDIAZONIUM FLUOBORATES IN WATER

Diazonium fluoborate	log A[a]	$s_{\log A}$[b]	E[a] × 10^{-3}	s_E[b]	$\Delta S^{\ddagger}$[c]	$s_{\Delta S^{\ddagger}}$[b]	$\Delta H^{\ddagger}$[c] × 10^{-3}	$s_{\Delta H^{\ddagger}}$[b]	$100s_{\ln k}$[d]	$k_{25°}$ × 10^5, sec.$^{-1}$ (calcd.)
α-Naphthalene-	15.5867	0.43	28.0521	0.20	10.7	2.0	27.43	0.20	1.9	1.07
β-Naphthalene-	15.5912	0.061	28.1071	0.085	10.72	0.28	27.484	0.085	0.7	0.99

[a] Arrhenius parameters $\ln k = 2.30259 \log A - E/RT$; k has units sec.$^{-1}$; $R = 1.98773$, $T = 273.16 + t$ (centigrade). The given parameters reproduce the rate data in Table II within the precision given by the $100F_0$ column (last column of Table II). This term represents the relative per cent. error in k. The parameters were calculated by a weighted least squares method using the weights given in column 8 of Table II. The temperatures were assumed to be error-free, an assumption which is not valid, but whose lack of validity does not affect the results in this case. [b] Standard deviations, computed from the reciprocal matrix. Those for the α-naphthalenediazonium salt are based on 15 D.F., for the β-salt on 9 D.F. [c] Parameters for the expression $\ln k = \ln (K/h) + \ln T + \Delta S^+/R - \Delta H^+/RT$, $\ln (K/h) = 23.7600$. [d] This is the standard deviation for a rate constant with weight 8; for weight 4 the standard deviation is 100 $s_{\ln k} \times \sqrt{2}$; for weight 2 it is 100 $s_{\ln k} \times 2$; for weight 1 it is 100 $s_{\ln k} \times 2\sqrt{2}$.

$a_0v = -(ad + b)/q(1 - d^2)$ in terms of the reaction parameters; this quantity computed from the parameters is taken as the amount of diazonium salt accounted for. The per cent. accounted for is given in column 4; the recovery was generally quite good. The quantity k_1/η is defined in the Summary of Terms and is a measure of the rate of the coupling reaction. Two methods were used for computing the rate of the reaction involving cleavage of the C–N bond (eq. 1). In terms of the parameters of eq. 16, $k_1 = -c/m = -c(1 + d)/(1 - d)$; the values given in column 7 were so obtained. It is also possible to obtain an estimate of k_1 from the initial reaction rate, providing it is assumed that the initial concentration of diazonium salt is known. In practice this means assuming that the salt is 100% pure. The initial rate in terms of the parameters of eq. 16 is given in eq. 17.

$$(dp/dt)_0 = (bc + dp_0c)/(1 - d)\ [= k_1(p_\infty - p_0)] \qquad (17)$$

The equality in brackets is true since at the beginning of the reaction there is no naphthol present and the coupling reaction rate is therefore zero. Since $(p_\infty - p_0) = a_0vq$, the latter quantity can be substituted into eq. 17 to give eq. 18 (the value of p_0 in terms of a, b, etc., having also been substituted).

$$k_1 = c(ad + b)/(1 - d^2)a_0vq \qquad (18)$$

In using eq. 18 to estimate the rate constant, the value of a_0v is taken as the amount of diazonium salt placed in the bucket, assuming the salt to be 100% pure. Values of k_1 obtained *via* eq. 18 are given in column 6 of Table II. The first estimate of k_1 (column 7) is considered the more reliable for all runs except for the eight α-naphthalenediazonium salt runs where the extent of the coupling reaction was greater than the assumptions underlying eq. 16 could allow for. The preferred rate constants are marked with an asterisk. The least squares procedure was used to compute the eq. 16 parameters for the runs carried out in the 0.05 *M* sulfuric acid; the parameters of the remaining runs are of somewhat reduced reliability since they were obtained by an abbreviated procedure.[5] The statistical weights given in column 8 of Table II are somewhat arbitrarily assigned on the basis that (1) the rate constants from parameters derived by least squares estimates are the most reliable ones, (2) estimates based on runs in more dilute acid and at lower temperatures are less reliable, and (3) α-naphthalenediazonium fluoborate runs in the presence of 0.0005 *M* cupric sulfate are still less reliable. The values of $100F_0$ given in column 9 indicate the relative per cent. difference between the preferred "observed" rate constants and those computed from the Arrhenius equation parameters of Table III. In interpreting these error estimates, *cf.* footnote *d* of Table III.

The Arrhenius parameters and the heats and entropies of activation given in Table III were calculated by a least squares procedure using the statistical weights given in column 8 of Table II. The error estimate $\Sigma w(\ln k_{\text{obsd}} - \ln k_{\text{calcd}})^2 = \Sigma wF_0^2$ was minimized in this calculation; w is the statistical weight. The values of $100F_0$ listed in the last column of Table III represent the relative per cent. standard deviation of a k value of statistical weight 8. The 0.7% value for the β-naphthalenediazonium fluoborate is comparable with the results reported previously in the benzene series. Most of the error lies in the temperature calibration and control. With the α-naphthalenediazonium fluoborate the occurrence of the coupling process may have increased the scatter of the results. The estimates of the standard deviations of the parameters are conservative ones based on standard statistical methods utilizing the reciprocal matrix.[5]

A rough estimate can be made of the rates of the coupling reactions. The sum of the rate constants of the coupling reactions (eq. 2 and 3) taking into account the ionization constant of the naphthol and the concentration of the hydrogen ion is given by eq. 19. Values of k_1/η are tabulated in column

$$k_2K/b_0 + k_3 = k_1/\eta \qquad (19)$$

5 of Table II. The values of the hydrogen ion concentrations (b_0) are as follows: for 0.005 *M* H_2SO_4 $b_0 = 0.008$; for 0.02 *M* HCl $b_0 = 0.020$; for 0.05 *M* H_2SO_4 $b_0 = 0.059$. In these estimates the ionization constant for bisulfate ion was taken as 0.0125 at 25°; at 50° the hydrogen ion concentration would be about 5% less for the sulfuric acid solutions; this change has been disregarded.

Since the error in k_1/η is rather large, there is some question about the necessity for the k_3 term. In other words there is some question about the necessity of writing a coupling reaction with the neutral naphthol molecule in addition to coupling with the naphthoxide ion (eq. 2). If only eq. 2 is required, then the ratio of k_1/η values for two different acidities should equal the ratio of the hydrogen ion concentrations. The error in k_1/η cannot be estimated at all well: for run 74[6] the standard deviation is estimated to be less than 10% (the error in the $[m^2 - 1]$ term is 6%). A standard deviation of 50% is probably considerably too large even for such runs as 10, 16 and 17. But even with a 50% error in the rate constants k_1/η the 95% confidence limits for the ratio of these rate constants are 1.5–4.6 for runs 107 and 109 (central value is 15/5.8 = 2.6) and 1.1–3.4 for runs 103 and 101 (central value is 23/12 = 1.9). The ratio of hydrogen ion concentrations for both pairs is 0.059/0.009 = 6.5, a value which is much too far outside the limits to be chargeable to chance even with the above large error in k_1/η. Thus the coupling reaction with the neutral naphthol is required by the data.

TABLE IV

RATES OF THE COUPLING REACTIONS (EQ. 2 AND 3)

Run no.	Temp., °C.	b_0[a] av.	10^3 k_1/η	k_2K[b] × 10^3	k_3[b] × 10^3
74	30.54	0.059	2.8	0.11	0.9
80		.020	6.5		
107	40.48	.059	5.8	.10	4.2
109		.009	15		
9	45.3	.059	4.9	.21	1.3
10, 16, 17(av.)		.020	12		
103	50.54	.059	12	.12	10
101		.009	23		

[a] Approximate value of $[H^+]$ concn. [b] Moles^{-1} l. sec.$^{-1}$.

The estimates of k_2K and of k_3 are given in Table IV. The scatter is so large that the Arrhenius parameters have very wide error limits: $E_3 = 27 \pm 6$ kcal.; $\log A_3 = 16 \pm 4$; $E_2 = 8 \pm 4$ kcal., $\log A_2 = 3 \pm 3$. It is reasonable to suppose that the coupling with the neutral naphthol should have a higher activation energy than coupling with the naphthoxide ion. The roughness of the values do not justify further speculation: a value of E_2 as large as 18 kcal. would not be inconsistent with the data.

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 nonaqueous 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.