[Contribution from the Department of Chemistry of the University of South Carolina]

The Mechanisms of Diazonium Salt Reactions. II. A Redetermination of the Rates of the Thermal Decomposition of Six Diazonium Salts in Aqueous Solution[1]

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The rates of the thermal decomposition in aqueous solution of the following diazonium ions have been redetermined with high precision: benzenediazonium ion, 2-, 3- and 4-methylbenzenediazonium ion, 3-bromo- and 3-chlorobenzenediazonium ion. For the first five ions the rate data have a precision of 0.5%. Within this precision the following reaction variables have no detectable effect: anion (chloride, bisulfate, fluoborate), acidity (0.005 M H_2SO_4, 0.05 M H_2SO_4, 0.01 M HCl), and the presence of 0.0005 M cupric sulfate. The data have been obtained and treated in accordance with modern statistical methods. These methods make it possible to examine a reaction over its complete course (0–100%) for compliance with a given rate expression. The data are summarized in Tables III–V.

In acidic aqueous solutions diazonium salts undergo decomposition to give a phenol as the principal product. This type of reaction involves a heterolytic cleavage[3,4] of the carbon–nitrogen bond of the diazonium ion, probably by an SN1 type of mechanism. The reaction rate varies widely with structure, from the 2- and 3-methylbenzenediazonium ions which have half-lives of about an hour at room temperature to the nitrobenzenediazonium ions with half-lives of several weeks. The rates have been investigated by many workers, the early work[5] being concerned primarily with problems of stabilization of diazonium salts for commercial purposes. This early work is useful primarily in indicating broad differences in reactivity. For a variety of reasons it is of limited accuracy (± 25% or so). More recent work[6–10] has usually been directed toward various theoretical ends, and the use of modern techniques has yielded considerably higher accuracy (about 1.5% for the best work,[6,7] 5–10% for the rest).

The present study has been motivated by a number of factors. In connection with a research program on the mechanism of the cleavage of the carbon–nitrogen bond of diazonium salts, reliable kinetic and product data pertaining to the reactions in aqueous systems are of fundamental importance. A second consideration comes from a preliminary study[11] of the complex kinetics of the reactions of benzenediazonium fluoborate in methanolic solutions in the presence of acetate buffers. It seemed important to utilize the apparatus and the techniques of calculation on typical well-behaved reactions in order to establish beyond question their validity for the study of complex systems. Moelwyn-Hughes and Johnson[7] have shown that the thermal decomposition of benzenediazonium chloride in aqueous solution is an accurate first-order reaction, and this type of reaction appeared to be especially suitable for testing purposes. Preliminary runs showed that the method[12] is capable of giving kinetic results of higher precision than have heretofore been reported. It was therefore of interest to carry out a redetermination of the rates of decomposition of several diazonium ions. The selection of those for the present study was made largely on the basis of their having a convenient rate of reaction in the 15–65° range. Of these six ions, only the unsubstituted benzenediazonium ion has previously received an adequate study.

Experimental

Experimental Design.—As a result of the previous work of others it was known that reaction variables such as concentration, acidity and the presence of trace impurities, *e.g.*, cupric ion, would have at most secondary effects on the rates. The problem was to carry out a moderate number of runs on each diazonium salt and yet to embody a reasonable range of variation of reaction conditions in order that the results might have general validity. The design adopted (Table I) included three different reaction media (0.010 M HCl, 0.005 M H_2SO_4 and 0.05 M H_2SO_4), two different crystalline diazonium salts (fluoroborate and bisulfate), a 50% variation in diazonium ion concentration, and five different temperatures. In addition the effect of 0.0005 M cupric sulfate and the effect of extra recrystallizations of the diazonium salts were tested.

Table I

Experimental Design for Studying the Rates of the Thermal Decomposition of Diazonium Salts in Aqueous Solution

Temp., °C.	Salt	Concn., mM	Medium, concn., mM	Special conditions
t	ArN_2BF_4	3	H_2SO_4, 5	Extra recryst.
$t + 5$	ArN_2BF_4	2	H_2SO_4, 5	
$t + 5$	ArN_2BF_4	3	H_2SO_4, 50	
$t + 10$	ArN_2BF_4	3	H_2SO_4, 5	
$t + 10$	ArN_2HSO_4	3	H_2SO_4, 5	
$t + 10$	ArN_2HSO_4	3	HCl, 10	
$t + 15$	ArN_2BF_4	3	H_2SO_4, 5	Extra recryst.
$t + 15$	ArN_2BF_4	2	H_2SO_4, 50	
$t + 15$	ArN_2BF_4	3	HCl, 10	0.0005 M $CuSO_4$
$t + 20$	ArN_2BF_4	3	H_2SO_4, 5	

Complete randomization was impractical, but the order of runs at a given temperature was chosen at random, and the

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[2] From the Ph.D. Thesis of A. R. Ballentine, University of South Carolina.

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[5] (a) J. Hausser and P. Müller, *Bull. soc. chim.*, [3] **7**, 721 (1892); (b) J. C. Cain and F. Nicoll, *J. Chem. Soc.*, **81**, 1412 (1902); (c) A. Hantzsch, *Ber.*, **33**, 2517 (1900); (d) H. Euler, *Ann.*, **325**, 292 (1902); (e) E. Yamamoto, *J. Soc. Chem. Ind. Japan, Suppl. Binding*, **32**, 279B (1929); *C. A.*, **24**, 1033 (1930); last paper in series is *ibid.*, **39**, 15B (1936); (f) for a further summary see K. H. Saunders, "The Aromatic Diazo-Compounds," Second Ed., Longmans, Green and Co., New York, N. Y., 1949, p. 61.

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[8] M. L. Crossley, R. A. Kienle and C. H. Benbrook, This Journal, **62**, 1400 (1940).

[9] J. E. Taylor and T. J. Feltis, *ibid.*, **74**, 1331 (1952).

[10] E. S. Lewis and E. B. Miller, *ibid.*, **75**, 429 (1953).

[11] D. F. DeTar and M. N. Turetzky, *ibid.*, **78**, 3925, 3928 (1956).

[12] D. F. DeTar, *ibid.*, **78**, 3911 (1956).

order of selecting the temperatures was also random. Either a freshly prepared or a freshly recrystallized sample of diazonium salt was used for each run. The amine samples were carefully redistilled or recrystallized, and the acids and other reagents were of reagent grade.

These considerations suggest the use of the randomized block design using temperatures as the block. Such a design is, however, impractical for the range of reactivities and hence of temperatures required in the present study. Instead the much more elementary method of between and within columns analysis was adopted. The columns consisted of each of the ten reaction conditions listed in Table I as carried out on each of the salts. The analysis is summarized in Table II. The analysis was carried out on the F_0 values (multiplied by 100); $100F_0$ is the per cent. deviation of the observed rate from that calculated from the Arrhenius parameters of Table V. Because of the larger error for the rate data for the *m*-chlorobenzenediazonium ion, the data for this ion were omitted in the variance analysis. The calculation of F_0 values for each ion required 2 D.F. (in deriving the Arrhenius equation); these calculations therefore use up 10 D.F. for the five ions. Since F_0 values are based on least squares adjustments of the Arrhenius parameters, the grand total sums to zero and does not require an additional D.F. As can be seen from Table II, the between reaction conditions mean squares is not significant. Furthermore, the largest single sum of five $100F_0$ values for any one reaction condition was 1.70. The 95% confidence limits for such a sum are 0 ± 2.2, and it is therefore clear that no one of the conditions showed any significant deviation. Within the 0.5% precision of the present data, therefore, none of the reaction conditions given in Table I had a detectable effect.

Table II

Variance Analysis of Effect of Reaction Variables

Entries refer to F_0 values coded by multiplication by 100 (Table III, column 12) $F_0 = \ln k_{\text{obsd}} - \ln k_{\text{calc}}$. The calculated values of k were obtained from the Arrhenius equation parameters (Table V). The residual mean squares 0.27 becomes 0.27×10^{-4} after uncoding, and corresponds to a standard deviation of 0.0052 in $\ln k$, or a standard deviation of 0.5% relative in k.

Source of variance	Sum of squares	D.F.	Mean squares
Between reaction conditions	2.54	9	0.28
Residual	8.51	31	0.27
Calcn. of F_0 values	...	10	...

Temperature Calibration.—Because of the sensitivity of the reactions to temperature, a search was made for systematic temperature errors by making another variance analysis based on a between temperatures and within temperatures classification. The between temperatures mean squares, coded as in Table II, was 0.30 with 11 D.F. and was therefore not significant. Altogether some twenty-two different temperature calibrations were performed (several of which involved only a single run) by four different observers using four different 0.1° division mercury in glass thermometers and a platinum resistance thermometer which was checked at the ice point at frequent intervals. The standard deviation of the temperature during a run was 0.015° based on the deviation of the individual Beckmann differential thermometer readings from the average, an estimate with about 9 D.F. for each of some 60 runs. If all of the random error in the rate constants is charged to temperature error, then the absolute accuracy of the temperature readings has a standard deviation of about 0.04°. A still further error estimate is available by comparing the rates of the reactions of the benzenediazonium ion reactions with those reported by Moelwyn-Hughes and Johnson[7] as given in Table VII. The MHJ rates are on the average 3% faster than those obtained in the present work. If all of the difference is ascribed to temperature error, then there is a difference of 0.25° between the MHJ work and the present work. This constitutes a maximum estimate of the temperature error. There is, however, no indication in the MHJ work that the temperature calibration was referred to more than one thermometer, and for this reason the temperature values reported in the present work are believed to be reliable to ±0.04°, with 95% confidence limits of ±0.10°.

Apparatus.—The apparatus and the technique for treating the data have already been described.[12] Experiments up to 50° were carried out in the shaker apparatus (water-bath), and those at higher temperatures were carried out with the magnetically stirred apparatus (oil-bath). The experimental results are summarized in Tables III, IV, and V, and a typical calculation is summarized in Table VI.

Preparation of *o*-Methylbenzenediazonium Bisulfate.—This preparation illustrates the method followed in obtaining crystalline diazonium bisulfates. A mixture of 7.6 g. (0.071 mole) of freshly distilled *o*-toluidine, 100 ml. of glacial acetic acid, 20 ml. of methanol (to prevent freezing) and 12 ml. (0.22 mole) of concd. sulfuric acid was stirred at −1 to +2° while 10 ml. of *n*-butyl nitrite was added (30 min.). After another 15 minutes 150 ml. of cold ether was added to precipitate an oil that solidified upon standing in an ice–salt-bath. The solid was redissolved in 100 ml. of glacial acetic acid and 150 ml. of acetone and reprecipitated with 250 ml. of ether. The salt was dried in a desiccator for a short time, and could be kept for several days at the temperature of solid carbon dioxide.

Discussion

A detailed summary of the rate data for benzenediazonium salts is presented in Table III.[13] A summary of rate constants for the other diazonium salts is given in Table IV. Columns 1–3 of Table III are self-explanatory. Nitrogen yields in column 4 were calculated as described[3,12] and have an accuracy of about ±1.5%. The cause of low yields is not known with certainty but relates in part to difficulty in handling the crystalline diazonium salts. There is no correlation between nitrogen yields and deviations between observed and calculated rates. These yields therefore had no detectable effect on the precision of the rate data.

For a first-order reaction $p = a + be^{ct}$ ($a = p_\infty$, $b = p_0 - p_\infty$, $c = -k$).[12] The values of the parameters appearing in columns 6, 7 and 10 reproduce the observed values of p (in mm. of *p*-xylene) with the standard deviation given in column 8 and over the extent of reaction given in column 9. As discussed elsewhere,[12] the p_∞ values are of lower accuracy than the rest of the p values. Nevertheless, the deviation between $p_{\infty\text{obsd}}$ (column 5) and $p_{\infty\text{calcd}}$ (a, column 6) is not very great for the unsubstituted and the methyl-substituted diazonium salts. It can therefore be concluded that these reactions follow the first-order expression from less than 5% to greater than 98% of their extent. The precision of the data may be seen from a comparison of the rate constants calculated by the Arrhenius equation (column 11) with those observed (column 10); the per cent. deviation is given in column 12 ($100F_0$ = per cent. deviation).

The complete tables[13] include not only the values for the ten best runs on each diazonium salt, but also data for all other runs which were carried out (except for a few runs discarded because of obvious experimental difficulties). Runs which showed a deviation of more than 1% between observed and calculated rate constants were repeated. The cause of discrepancy was traced in most cases to

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(13) Similar tables summarizing the rate data for the other diazonium salts reported in this paper and in Papers III–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 III

RATE DATA FOR DECOMPOSITION OF BENZENEDIAZONIUM SALTS IN AQUEOUS SOLUTION

ArN_2X,[a] mmoles	Reaction medium	Temp.,[b] °C.	% N_2[c]	p_∞ Obsd.	p_∞ Calcd.[a]	$-b$	s_p[d]	% Reaction[e]	$k \times 10^5$ sec.$^{-1}$ Obsd.	$k \times 10^5$ sec.$^{-1}$ Calcd.[f]	100 F_0[g]
0.4652[j]	5 S	25.28	94.6	322.5	326.83	321.47	0.31	12–95	4.767	4.762	0.10
.4040	5 S	28.611	95.3	277.5	277.51	269.66	.12	4–97	7.898	7.885	.15
.6810	50 S	28.615	91.9	481.6	482.66	470.07	.15	5–93	7.880	7.889	− .12
.5798	5 S	36.508	94.5	395.9	391.70	396.23	.08	16–97	24.89	24.94	− .29
.6130B	5 S	36.505	73.3	331.6	329.55	325.36	.07	10–96	24.76	24.94	− .67
.6522B	10 H	36.505	95.2	474.9	471.89	474.18	.12	10 96	25.05	24.94	.46
.6020[j]	5 S	39.295	92.1	432.1	422.33	426.44	.22	2–95	36.91	36.95	− .08
.4030	50 S	39.295	88.8	284.3	286.83	278.25	.14	4–95	37.29	36.95	.90
.6158	10H[h]	39.294	89.0	406.8	402.78	401.92	.06	12–96	36.79	36.95	− .46
.5997	5 S	44.267	80.8	385.9	385.92	387.31	.26	6–100	73.24	73.19	.06
.3995[j]	5 S	24.03	70.9	201.5	199.69	202.68	.27	7–96	4.02	(3.91)	(2.44)[i]

[a] Diazonium fluoborate used except for runs marked B for which the diazonium bisulfate was used. Reaction medium consisted of 200 ml. of 5 mM H_2SO_4 (5 S), of 50 mM H_2SO_4 (50 S) or of 10 mM HCl (10 H). [b] Constancy during run 0.015° (std. deviation of readings of Beckmann thermometer); accuracy is estimated to be about ±0.040. A temperature variation of 0.02° from one run to another leads to a difference in rate constants of about 0.3%. [c] Based on $b(-b = p_{\infty \text{ calcd}} - p_0)$. [d] Standard dev. of p based on 7–10 D.F. per run. [e] Calculated p values outside of this reaction range had larger deviations; compare $p_{\infty \text{ obsd}}$ with $a(a = p_{\infty \text{ calcd}})$, for example. [f] Calculated from the Arrhenius equation parameters in Table V. [g] $F_0 = \ln k_{\text{obsd}} - \ln k_{\text{calcd}}$, the calculated value being based on the Arrhenius equation parameters of Table V. 100 F_0 is the relative % error in k. [h] Contained 0.0005 M $CuSO_4$. [i] This run was omitted in the calculation of the Arrhenius parameters. [j] Diazonium salt recrystallized three times. In all other runs it was recrystallized twice.

TABLE IV

SUMMARY OF RATE CONSTANTS FOR THE THERMAL DECOMPOSITION OF DIAZONIUM SALTS IN AQUEOUS SOLUTION[a]

2-Methylbenzenediazonium salts Temp., °C.	$k \times 10^5$	3-Methylbenzenediazonium salts Temp., °C.	$k \times 10^5$	4-Methylbenzenediazonium salts[b] Temp., °C.	$k \times 10^5$	3-Chlorobenzenediazonium salts[c,d] Temp., °C.	$k \times 10^5$	3-Bromobenzenediazonium salts[c] Temp., °C.	$k \times 10^5$
14.99	5.05	14.98	4.28	39.62	3.92	47.98	5.40	45.38	7.06
17.85	7.88	17.86	6.59	44.27	7.76	49.88	7.13	49.69	13.1
17.84	7.78	19.73	8.68	44.27	7.78	48.90	6.37	49.69	13.2
24.02	19.7	25.28	19.7	49.69	16.8	54.41	13.6	54.50	26.1
24.03	19.9	24.09	16.8	49.88	17.5	54.23	13.0	54.46	26.1
24.03	19.9	24.03	16.7	49.88	17.3	54.13	13.1	54.46	25.9
28.78	39.1	28.61	32.0	55.03	35.4	57.96	22.7	57.96	41.8
28.78	39.3	28.61	32.1	55.03	35.2	57.96	22.7	57.96	42.1
28.62	37.9	28.62	32.2	54.47	32.8	57.96	21.9	57.96	42.1
36.50	113.9	34.04	68.0	57.96	52.7	62.27	39.6	63.29	85.5

[a] These were carried out under the same conditions, run for run, as in Tables I and III.[13] Units of k are sec.$^{-1}$ [b] Twelve additional runs had standard deviations from the Arrhenius equation of 2.7%; see text. [c] These runs were first order only for the first 70–85% reaction. [d] The 3-chlorobenzenediazonium salt runs had a higher deviation than the others; see Table V.

TABLE V

ARRHENIUS PARAMETERS AND HEATS AND ENTROPIES OF ACTIVATION FOR THE DECOMPOSITION OF DIAZONIUM SALTS IN WATER

	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]	$100 s_{\ln k}$[a,b]	$k_{25°} \times 10^{-6}$, (calcd.) sec.$^{-1}$
$C_6H_5N_2^+$	15.5162	0.04	27.0980	0.05	10.41	0.17	26.49	0.05	0.48	4.56
2-$CH_3C_6H_4N_2^+$	15.1775	.04	25.6832	.05	8.92	.17	25.09	.05	.56	22.8
3-$CH_3C_6H_4N_2^+$	15.0452	.05	25.6066	.06	8.35	.22	25.02	.06	.51	19.1
4-$CH_3C_6H_4N_2^+$	15.9810	.04	29.1881	.06	12.45	.19	28.55	.06	.51	0.391
3-$ClC_6H_4N_2^+$[d]	15.8016	.16	29.4872	.24	11.59	.72	28.84	.24	1.9	.166
3-$BrC_6H_4N_2^+$[d]	16.2333	.04	29.7197	.05	13.57	.16	29.07	.05	0.37	.285

[a] Arrhenius equation 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 III with the precision given by 100 $s_{\ln k}$. This term represents the relative per cent. error in k. [b] All data in this table were obtained by least squares procedures; the various error estimates were obtained by standard statistical methods and are standard deviations with 8 D.F. For purposes of calculation T was assumed error-free, an assumption which is not valid, but which does not affect the calculated parameters. [c] Parameters for the expression $\ln k = \ln (k/h) + \ln T - \Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R$; $\ln (k/h) = 23.7600$. $s_{\ln k}$ is the same for both this and for the Arrhenius equation. [d] The results for the first four compounds are believed to be unbiased since the first order expression is valid throughout the reaction. With the m-chloro- and the m-bromobenzenediazonium salts the first order expression was valid only up to 80 or 90% of reaction and further work may show that the values reported for these compounds are biased.

uncertain temperature readings or to inadequate temperature control. Special care was taken in the repeat runs to ensure temperature reliability. Evaluation of the temperature data as described in more detail in the Experimental section indicates that temperatures have a reliability of about 0.04°. Within their lesser precision the less accurate runs are consistent with the other data. This is il-

TABLE VI

ILLUSTRATION OF PROCEDURE FOR COMPUTATION OF RATE CONSTANTS[12,14] (RUN D 127)

$F = p - a - be^{ct}$ (ΣF^2 is to be a minimum)
$F_0 = p - 340.071 + 344.517e^{-0.00471438t}$ (initial estimate)
$F_0' = p - 339.621 + 344.198e^{-0.00473043t}$ (least squares adjusted values)

Time, min.	Crude p	Cor. p^a	e^{ct} ($= -F_b$)^b	$F_c \times 10^{-4}$	F_0^c	F_0'
14	17.4	17.40	0.936130	0.451518	−0.158	−0.079
24	32.4	32.41	.893021	0.738387	.000	.043
44	60.1	60.12	.812668	1.231904	.027	.020
64	85.3	85.41	.739545	1.630630	.125	.078
94	118.9	118.96	.642010	2.079125	.072	− .016
154	173.4	173.50	.483834	2.567013	.118	.002
164	181.0	181.11	.461553	2.607812	.052	− .063
214	214.4	214.51	.364628	2.688281	.060	− .037
264	240.8	240.87	.288058	2.619961	.040	− .021
344	272.0	272.07	.197554	2.341290	.060	.072
454	299.6	299.55	.177617	7.839657	.000	.118
526	310.9	310.92	.083763	1.517920	− .293	− .112

$[F_aF_a]^{bd} = 12$ $[F_aF_b] = 6.020381$ $[F_aF_c] = 22.313498$ $[F_aF_0] = -0.1018$
$[F_bF_b] = 4.016294$ $[F_bF_c] = -9.61058$ $[F_bF_0] = -.1142$
$[F_cF_c] = +47.899734$ $[F_cF_0] = +.7129$
$[F_0F_0] = .158$

[a] Observed p corrected for manometer temperatures and for the p^2 term.[12] [b] For general method of computation see Deming.[15] F_b is $(\partial F/\partial b)$, etc. [c] The F_0 values are obtained using initial estimates of a, b and c. The F_0' values are obtained using the least squares adjusted values of a, b and c. [d] These constitute the terms of the normal equations for the least squares adjustment. $[F_bF_b]$ represents the sum of the squares of the F_b values, etc.

lustrated best by a consideration of the data for 4-methylbenzenediazonium ion. For this ion a total of twenty-two runs was made, including five by Miss Sara Kwong. The best Arrhenius equation for all twenty-two runs is $\ln k = 15.9213 \ln 10 - 29{,}100.7/RT$. This equation reproduces all the ln k values with a standard deviation in k of 2.1% relative; furthermore the Arrhenius parameters of this equation do not differ significantly from the "best" values reported in Table V (*i.e.*, they lie within the 95% confidence limits of the values in Table V). The data are therefore self-consistent.

The halogen-substituted ions were less well-behaved. The reaction began to deviate appreciably from the first-order expression after about 75–85% of reaction. The nitrogen yields based on b are therefore an overestimate. A certain amount of caution is required in using rate data for these two compounds. The method of calculation adopted[12] is based on the use of b (column 7 of Table III) as proportional to the amount of diazonium salt initially present. In turn this involves using a (column 6) as an estimate of p_∞. If $p_{\infty\ \text{obsd}}$ differs from $p_{\infty\ \text{calcd}}$ by an amount which is, *e.g.*, 10% of b, then the estimate of k may be in error by 10% (*i.e.*, k may be as much as 10% too large). While the precision of the rate constants for the 3-chloro- and the 3-bromobenzenediazonium ions given in Table IV is good, the constants themselves may be subject to a systematic bias that will affect their accuracy. The point can be settled only by additional experimental work.

The Arrhenius parameters and activation heats and entropies are given in Table V. The precision of the various parameters is given in columns 3, 5, 7 and 9 and is based on standard statistical procedures.[3,14] The values are given to sufficient significant figures to reproduce ln k values without rounding-off errors. The precision with which ln k is reproduced is given in the last column; the number recorded is the relative per cent. standard deviation of $(k_{\text{obsd}} - k_{\text{calcd}})$. The accuracy for the first four compounds is believed to be comparable to the precision, but the values for the halogen derivatives may be subject to bias as discussed above.

A comparison of the results obtained in this work with the best of those previously reported is given in Table VII. Moelwyn-Hughes and Johnson[7] carried out an extensive and precise study of the reactions of the benzenediazonium ion. The selection of values presented in Table VII is typical of some twenty runs that are directly comparable with the present work. The standard deviation of the MHJ data can be estimated from two groups of five runs each at a single temperature; the first of these groups consists of the first five runs given in Table VII. The estimated standard deviation is 1.6% (8 D.F.). The data of MHJ can be averaged with those of Table III on a weighted basis (based on standard deviations). The appropriate weights are 1 for the MHJ values and 10 for the first ten values in Table III. Arrhenius parameters calculated by an averaging method utilizing these weights led to the equation: $\ln k = 15.5975 \ln 10 - 27.2108/RT$. This equation reproduced the first ten rate constants of Table III with a standard deviation of 1.1% relative and the twenty values of MHJ with a standard deviation of 3.6% relative. There were no trends with temperature, and hence no reason to suppose that the energy of activation does vary with temperature, a point strongly suggested by Moelwyn-Hughes and Johnson. Any such variation is too small to be detected with data of the precision available. There is a general discrepancy between the present work

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

(15) W. Deming, "Statistical Adjustment of Data," John Wiley and Sons, Inc., New York, N. Y., 1943.

Table VII

Comparison with Rate Data Reported by Other Workers

Temp., °C.	$10^5 k$, sec.$^{-1}$	$100F_0$[a]	Ref.
	Benzenediazonium salts		
59.97	567	+ 2.30	7
59.97	561	1.24	7
60.05	566	1.13	7
59.67	565	5.61	7
60.08	571	1.63	7
15.00	0.93	− 0.93	7
19.83	2.01	− 1.28	7
24.64	4.35	+ 0.76	7
29.91	9.92	3.61	7
34.97	20.7	3.31	7
55.04	301	0.43	7
45.76	93.9	4.83	10
55.44	291.5	− 7.84	10
5.0	0.15	−12.7	8
25.0	4.10	−11.7	8
35.2	20.0	− 2.0	8
50.0	140.0	−11.3	8
30.0	9.59	− 1.13	6
40.0	41.1	+ 0.70	6
50.0	155	− 1.16	6

Temp., °C.	$10^5 k$, sec.$^{-1}$	$100F_0$	Ref.
	2-Methylbenzenediazonium salts		
35.0	96	+ 3.30	8
35.4	95.6	− 2.56	8
	3-Methylbenzenediazonium salts		
29.96	39.2	+12.0	10
40.31	153	−29.5	10
	4-Methylbenzenediazonium salts		
40.31	4.4	1.5	10
52.98	23.9	−11.3	10
62.23	77.9	−17.3	10
30.0	0.96	+ 8.6	9
39.96	4.11	− 0.3	9
49.9	157	−10.4	9

[a] This is $100(\ln k_{\mathrm{obsd}} - \ln k_{\mathrm{calcd}})$ and represents the relative per cent. difference in the reported rate constant and that calculated from the Arrhenius parameters of Table V.

and that of Moelwyn-Hughes and Johnson amounting to about 3%, the values of these authors being consistently higher than those of the present work. The cause of the discrepancy is not known. If it were due to a temperature calibration error, this error would amount to about 0.25°. It is interesting and significant that the combined Arrhenius parameters lie within the 95% confidence limits of the values in Table V.

The data of other workers given in Table VII are complete insofar as available. It is obvious that some of these data agree quite well while other data are rather divergent. In one case[10] the discrepancies are largely due to choice of experimental procedure: a jacketed reaction flask was used; this resulted in a significant, variable, and unknown temperature drop between the constant temperature bath and the reaction flask.

A comparison of the Arrhenius parameters reported by other workers is pointless. Except for the excellent values reported by Moelwyn-Hughes and Johnson which lie within the 95% confidence limits of the values in Table V, the values presently available in the literature are based on far too few data. In fact a rough but fair estimate of the standard deviation of previous literature values of the activation energy of diazonium salt decompositions is ±1.5 kcal. or more. No valid conclusions can be drawn by considering differences between such activation energies unless the differences amount to about 4 kcal. or more.

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