room temperature, the precipitate dissolved with gassing. Vpc indicated the presence of only solvent and perfluorocyclopropene. Cooling back to −50° did not cause reprecipitation. Boron trifluoride was bubbled through the solution for 2 hr, resulting in re-formation of the white precipitate. Methanol (2.0 g, 62 mmol) was slowly added to the stirring suspension. On warming to room temperature, vpc showed solvent and perfluorocyclopropene. Examination of the product indicated the presence of a mixture of methanol–BF_3 products.

Free-Radical Polymerization of Perfluorocyclopropene. Benzoyl Peroxide. Perfluorocyclopropene (4 mmol) and benzoyl peroxide (5 mg) were sealed in an nmr tube and heated at 100° for 6 hr ($t_{1/2}$ = 30 min at 100°). ^{19}F nmr showed only unreacted perfluorocyclopropene.

Azobisisobutyronitrile. Perfluorocyclopropene (3 mmol) and AIBN (5 mg) were sealed in an nmr tube and heated at 80° for 2 hr (AIBN $t_{1/2}$ = 1 hr at 84°). The sample yellowed slightly, but did not increase in viscosity. ^{19}F nmr showed only unreacted perfluorocyclopropene.

Dinitrogen Difluoride. Perfluorocyclopropene (6 mmol) and dinitrogen difluoride[19] (9×10^{-4} mol) were sealed in a $^3/_8$-in. platinum tube and heated at 70° under 3000 atm pressure for 4 hr. Perfluorocyclopropene was recovered unchanged (90% recovery).

Copolymers of Perfluorocyclopropene. Equimolar quantities of perfluorocyclopropene and comonomer were added to a glass tube (18 × 4 mm i.d.) containing benzoyl peroxide (5 mg, 2×10^{-5} mol). The tube was degassed, sealed, and heated at 80–85°. The copolymers were characterized by their infrared spectrum, differential thermal analysis, and in most cases by fluorine elemental analysis. All copolymers had infrared bands absent in the homopolymer. Absorption evidently characteristic of the perfluorocyclopropene copolymer appears at 1700–1770 and 1100–1200 cm^{-1}. The 1700-cm^{-1} (unsaturated fluorocarbon) band is substantially decreased upon purification and is probably due to low molecular weight copolymer. Differential thermal analysis charts of the copolymers were different from those of the homopolymers. Several copolymers showed a large exotherm at 250–300°.

Examination of the volatile material after each polymerization showed mostly unchanged starting olefin and PFCP with only traces of other fluorine-containing materials.

1,6,7,7-Tetrafluorobicyclo[4.1.0]hept-3-ene. Butadiene (0.15 g, 2.4 mmol) and perfluorocyclopropene (2.9 mmol) were sealed in an nmr tube and heated at 100°. The reaction was followed by ^1H nmr. After 24 hr the amount of butadiene had decreased by about 60%. The tube was cooled and opened, and 1,6,7,7-tetrafluorobicyclo[4.1.0]hept-3-ene was isolated free from perfluorocyclopropene, butadiene, and polymeric by-products by trap-to-trap distillation. The ^1H nmr spectrum had multiplets at 2.4 and 5.0 ppm (area = 2 and 1, respectively); the ^{19}F nmr spectrum had an AB pattern at 152.5, 156.0, 157.5, and 161.3 ppm ($J_{AB} \sim 200$ Hz) and a multiplet (211.8 ppm) in a 1:1 ratio. The infrared spectrum had bands at 3080 (olefinic C—H), 2910, 2850 (aliphatic C—H), 1560 (weak, C=C), 4180, 1430 (CH_2), and 1200 (C—F) cm^{-1}. The time-of-flight mass spectrum had a parent ion (*m/e* 166) and fragmentation pattern consistent with the assigned structure.

Perfluorocyclopentene. Perfluorocyclopropene (3.5 mmol) and tetrafluoroethylene (3.5 mmol) were sealed in a platinum tube and heated at 135° and 3000 atm for 8 hr. The tube was opened, and perfluorocyclopentene was identified by ^{19}F nmr and vpc comparison with an authentic sample. Only traces of other products were noted. Similar results were obtained at 180° for 2 hr.

Acknowledgment. The authors wish to acknowledge the helpful suggestions of Dr. A. E. Barkdoll in devising the synthesis of perfluorocyclopropene and Mrs. N. P. Hillyard and Mr. C. B. Matthews for assistance in obtaining and interpreting the mass spectra.

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(19) Kindly supplied by Dr. C. S. Cleaver, E. I. du Pont de Nemours and Company.

The Reaction of Diazonium Salts with Nucleophiles. XIII. Identity of the Rate- and Product-Determining Steps[1]

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Abstract: The effects of several salts on the rates of disappearance of benzenediazonium ion in aqueous solution are studied. The effects are small, but at any concentration the rates increase in the order bisulfate < chloride < bromide < thiocyanate. Rates with various bisulfates are slower than in the absence of added salts. The rate reduction is attributed to the low reactivity of water solvating the cation, and hence the very small rate effect of solutions of sodium bromide or chloride is actually a combination of a retardation due to the sodium ion and an acceleration due to the chloride or bromide ion. These rate accelerations are at least enough to account for all the chlorobenzene or bromobenzene formed. Thus no products are determined by competitions after the rate-determining step—a conclusion supported by a simple reinterpretation of a great deal of earlier data. It is possible to account for the detailed shape of the plot of rate *vs.* salt concentration by a normal salt effect, so an earlier interpretation of this shape in terms of a spirocyclic diazirine cation intermediate is not supported. The relative reactivities of the different nucleophiles toward the diazonium ion differ very little, and it is shown that this unselectivity leads to an inherent and general difficulty in distinguishing between one-step reactions and two-step processes through a highly reactive intermediate.

The hydrolysis of diazonium salts follows a first-order course and is insensitive to many added salts at low concentrations[2,3] and even sometimes at high concentrations.[4] This is not always true. Tetrazotized paraphenylenediamine shows essentially pure bimolecular kinetics with chloride, bromide, or thiocyanate ions;[5] *p*-nitrobenzene diazonium ion dis-

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(1) Based upon portions of the Ph.D. theses of L. D. Hartung (1966) and B. M. McKay (1968), Rice University. Certain parts were presented at Southwest Regional Meetings of the American Chemical Society, Memphis, Tenn., 1965 and Little Rock, Ark., 1967.

(2) D. F. DeTar and A. R. Ballentine, *J. Am. Chem. Soc.*, **78**, 3916 (1956).

(3) H. A. H. Pray, *J. Phys. Chem.*, **30**, 1417 (1926).

(4) J. S. P. Blumberger, *Rec. Trav. Chim.*, **49**, 259 (1930).

(5) E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **82**, 5408 (1960).

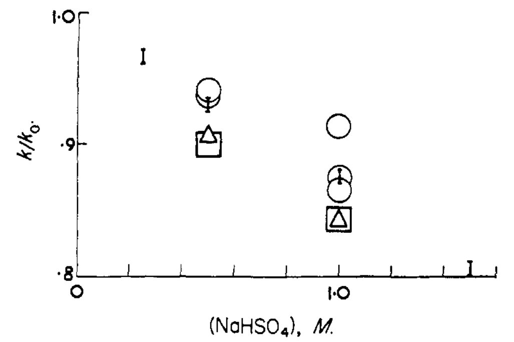

Figure 1. Effect of added sodium bisulfate on rates of hydrolysis of several diazonium salts. Symbol heights represent reproducibility of k_0, widths are meaningless. Symbols: I, $C_6H_5N_2^+$; ○, O-$CH_3C_6H_4N_2^+$; □, m-$CH_3C_6H_4N_2^+$; △, p-$CH_3C_6H_4N_2^+$.

appears more rapidly when bromide ion is present,[6] as do both benzenediazonium ion[7] and p-toluenediazonium ion in the presence of thiocyanate.[8] The long-accepted mechanism through the aryl cation, first proposed by Waters,[9] needs modification in spite of its success in accounting for substituent and solvent effects.

The least drastic modification to account for the influence of nucleophiles on the rate was the suggestion that the formation of the aryl cation from the diazonium salt was reversible.[7] This suggestion predicted that a diazonium ion labeled in the α position with ^{15}N should rearrange to the β-labeled diazonium ion, a prediction actually born out in practice,[10] but this simple mechanism predicted too much rearrangement. An alternative two-intermediate mechanism was presented[8] which we shall here reject.

Results

The observed rates of disappearance of benzenediazonium ion relative to the rates in the absence of added salts are presented in Table I. Rates were measured by the successive approximation technique previously described.[11] Some further data on several diazonium salts in the presence of added sodium bisulfate are shown in Figure 1.

Yields of chlorobenzene and bromobenzene were measured by a gas chromatographic method similar to that previously described.[12] Duplicate runs agreed within a few per cent but are consistently higher than the earlier ones.[12] The difference, which is not significant within the framework of the present arguments, is apparently due to loss of chlorobenzene by volatilization in the earlier experiments, avoided by an improved experimental design. The yields (Y_N) are presented in Table II, in which the last column, headed k_N/k_W, is calculated as described below in eq 12, and differs only a little from nearly analogous earlier[7,8,12] numbers for the relative reactivities in the product-determining step; the difference is significant only at high salt concentrations. Some further results at different temperatures are presented in Figure 2.

Solubilities of benzenediazonium hexafluorophosphate were measured in aqueous sodium chloride solution at 0°, containing also 0.01 M sulfuric acid. The results are presented in Table III.

Table I. Disappearance of Benzenediazonium Ion in Water with Various Added Salts, 40.14°

Added salt[a]	Concn, M	k/k_0[b]
$NaHSO_4$	0.25	0.967
$NaHSO_4$	0.50	0.931
$NaHSO_4$	1.00	0.876
$NaHSO_4$	1.50	0.806
$LiHSO_4$	0.25	0.944
$LiHSO_4$	0.50	0.903
$LiHSO_4$	0.75	0.874
$LiHSO_4$	1.00	0.851
H_2SO_4	0.25	0.953
H_2SO_4	0.50	0.933
H_2SO_4	0.75	0.908
H_2SO_4	1.00	0.884
Bu_4NHSO_4	0.10	0.971
Bu_4NHSO_4	0.20	0.955
Bu_4NHSO_4	0.31	0.927
Bu_4NHSO_4	0.39	0.911
NaCl	0.10	0.997
NaCl	0.25	0.999
NaCl	0.50	0.992
NaCl	1.00	0.976[c]
NaCl	1.01	0.988[c]
NaCl	2.02	0.957[d]
LiCl	0.34	0.992
LiCl	0.69	0.984
LiCl	1.00	0.981
LiCl	2.00	0.955
LiCl	3.00	0.925
Bu_4NCl	0.20	1.003
Bu_4NCl	0.31	1.017
Bu_4NCl	0.40	1.071
Bu_4NCl	0.50	1.023
Bu_4NCl	0.80	1.023
Bu_4NCl	1.01	1.013
Bu_4NCl	1.38	1.029
Bu_4NCl	1.70	1.059
NaBr	0.10	0.996
NaBr	0.20	1.002
NaBr	0.30	1.009
NaBr	0.40	1.004
NaBr	0.60	0.996
NaBr	1.00	0.984

[a] All solutions were 0.01 M in sulfuric acid. Bu_4N indicates the tetra-n-butylammonium ion. [b] The rate constant without added salt, k_0, is $(4.151 \pm 0.021) \times 10^{-6}$ sec^{-1} at the nominal but constant temperature of 40.14°, an average of about ten runs. Errors of about ±0.5% may be expected on k/k_0. [c] This pair of runs, which are almost duplicates, are shown because the discrepancy is well outside the estimated error. Several other duplicates are not shown. [d] This result is taken from Blumberger;[4] it shows that his very high concentration results are reasonably concordant with the new ones; it will not be used further.

Discussion

Inspection of the rate data of Table I, together with the results for potassium thiocyanate solutions,[7] shows that the rate in salt solutions of any concentration increase in the order $NaHSO_4 < NaCl < NaBr < KSCN$. Since this is the order of nucleophilic participation of the anions,[13] there is a strong suggestion of nucleophilic participation in the rate-determining step, and a somewhat more quantitative argument for this is the main thesis of this paper.

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[6] E. S. Lewis and W. H. Hinds, *J. Am. Chem. Soc.*, **74**, 304 (1952).
[7] E. S. Lewis and J. E. Cooper, *ibid.*, **84**, 3847 (1962).
[8] E. S. Lewis and J. M. Insole, *ibid.*, **86**, 34 (1964).
[9] W. A. Waters, *J. Chem. Soc.*, 266 (1942).
[10] J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, **85**, 122 (1963); **86**, 32 (1964).
[11] E. S. Lewis, J. L. Kinsey, and R. R. Johnson, *ibid.*, **78**, 4294 (1956).
[12] E. S. Lewis, *ibid.*, **80**, 1371 (1958).
[13] C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

Table II. Yields and Relative Reactivities in the Decomposition of Benzene Diazonium Ion in Aqueous Salt Solutions

Added salt,[a] *M*	Y_{ArN}, %	k_N/k_W
0.038 NaCl	0.53	8.1
0.066 NaCl	0.81	6.8
0.162 NaCl	1.72	5.88
0.290 NaCl	2.53	4.79
0.582 NaCl	4.22	3.91
0.864 NaCl	5.91	3.61
1.22 NaCl	7.68	3.24
2.08 NaCl	11.0	2.49
0.18 LiCl	1.90	5.83
0.29 LiCl	2.40	4.51
0.64 LiCl	4.72	3.92
0.81 LiCl	5.84	3.78
1.01 LiCl	7.05	3.59
0.056 Bu_4NCl	0.62	5.49
0.057 Bu_4NCl	0.78	7.53
0.090 Bu_4NCl	1.01	6.14
0.19 Bu_4NCl	2.04	5.76
0.47 Bu_4NCl	3.68	3.90
0.69 Bu_4NCl	4.97	3.36
1.06 Bu_4NCl	8.05	3.16
0.10 NaBr	3.12	17.5
0.20 NaBr	5.19	14.9
0.40 NaBr	5.11	7.12
0.60 NaBr	6.00	5.49
1.00 NaBr	8.61	4.60

[a] All solutions were 0.01 *M* in H_2SO_4 in addition to the salt shown. All studies were at 40° except those on NaCl, which were at 50°; the results are nevertheless directly comparable.

Table III. Solubility of Benzenediazonium Hexafluorophosphate in Aqueous Sodium Chloride

NaCl, *M*	Solubility, $M \times 10^2$
0	2.81
0.103	2.98
0.311	3.00
0.516	3.29
0.820	3.34
1.27	3.34
1.56	3.29
2.65	2.84
3.33	2.78
4.14	2.47

It must be noted however, that all of the rate data fall within the range of salt effects of modest size. It is thus defensible to attribute all the rate variations to an ill-defined medium effect, and that they are therefore not susceptible to a mechanistic explanation. The yield data then give only some new information on the reactivity of an intermediate.

The rate variations can more satisfyingly be attributed to chemically significant processes; then specific salt effects are not very large. The first problem then lies in the retardation by all of the bisulfates. The effect of these presumably inert salts has precedent. Thus solution of diazonium salts is stabilized by arenesulfonates, as summarized by Saunders,[14] and by Zollinger,[15] and both authors have presented evidence on the great stability of crystalline diazonium salts with inert anions, such as bisulfates, aranesulfonates, fluoroborates, chlorozincates, etc., which are also relevant.

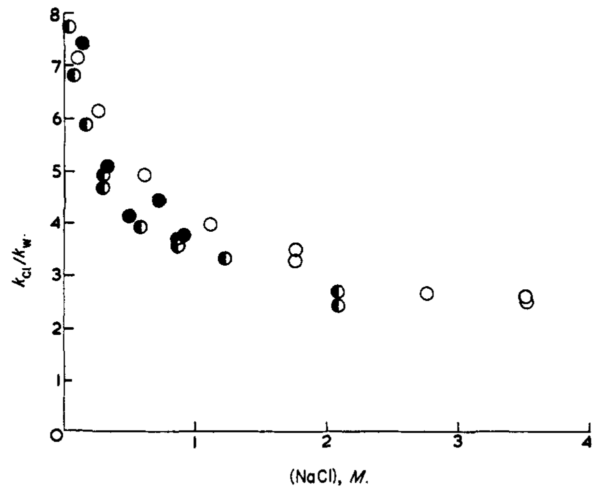

Figure 2. Dependence of k_{Cl}/k_W for benzenediazonium ion on sodium chloride concentration at various temperatures: ○, 3°; ●, 40°; ◐, 50°.

We propose that the stability in solution is due to the reduction in concentration of nucleophilic water, and the solids are also stable when a nucleophilic ion is absent. Blumberger[4] presented a closely related idea, but was unable to give it strong support because there was no good understanding of the variations of nucleophilic character among different anions. The assumption that bisulfate ion is inert leads to the idea that the rate reduction is due to the reduction in actual water concentration, $(H_2O)_{act}$. The rate expression should then be given by eq 1, and Figure 3 shows that the rate

$$-d(ArN_2^+)/dt = k(ArN_2^+)(H_2O)_{act} \qquad (1)$$

does in fact closely follow the actual water concentration for solutions of tetrabutylammonium bisulfate, which has a rather large effect on both the rate and the actual water concentration. However, eq 1 does not apply to the other bisulfates.

The rates in solutions of sodium, and lithium bisulfate and sulfuric acid are fairly well represented by eq 2, 3, and 4, but the actual water concentrations for the

$$k = k_W[55.5 - 7.22(NaHSO_4)] \qquad (2)$$

$$k = k_W[55.5 - 7.5(LiHSO_4)] \qquad (3)$$

$$k = k_W[55.5 - 6.6(H_2SO_4)] \qquad (4)$$

first and last are given by eq 5 and 6 (the densities required to calculate a corresponding equation for lithium bisulfate solutions have not been measured).

$$(H_2O)_{act} = 55.5 - 2.35(NaHSO_4) \qquad (5)$$

$$(H_2O)_{act} = 55.5 - 2.1(H_2SO_4) \qquad (6)$$

The term $(H_2O)_{act}$ is used for distinction from the term $(H_2O)_{eff}$ defined experimentally by eq 7 for solutions of bisulfates or other nonnucleophilic salts. The

$$k = k_W(H_2O)_{eff} \qquad (7)$$

term k_W is derived from measurements without added salts by eq 2.

Combining this equation with the conclusion from Figure 3 leads to the conclusion that for solutions of tetrabutylammonium bisulfate, eq 8 is obeyed, but for the other two cases eq 9 and 10 are required. It can be

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[14] K. H. Saunders, "The Aromatic Diazo Compounds," 2nd ed, E. Arnold and Co., London, 1942.

[15] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

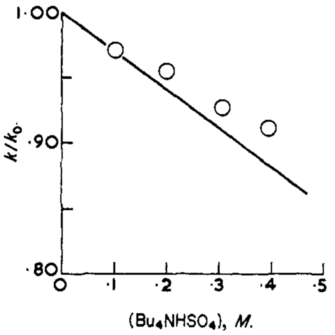

Figure 3. Depression of rate of hydrolysis of benzenediazonium ion by tetrabutylammonium ion. The line shows the depression in water concentration, $(H_2O)_{act}/55.5$.

$$(H_2O)_{eff} \simeq (H_2O)_{act} \text{ (for } Bu_4NHSO_4) \qquad (8)$$

$$(H_2O)_{eff} = (H_2O)_{act} - 4.87(Na^+) \text{ (for } NaHSO_4) \qquad (9)$$

$$(H_2O)_{eff} = (H_2O)_{act} - 4.5(H^+) \text{ (for } H_2SO_4) \qquad (10)$$

seen that $(H_2O)_{eff}$ is significantly less than $(H_2O)_{act}$.[16] In eq 9 and 10, Na^+ and H^+ are written because it seems reasonable to attribute the existence of these terms to some of the water becoming unreactive by solvating the cation. The absence of this term in eq 8 then reflects the small extent of solvation of this large cation.[17] The coefficients of (Na^+) and (H^+) in eq 9 and 10 should not be taken as exact solvation numbers of the two ions, both because it is unlikely that water molecules fall into sharp classes of totally unreactive or totally unaltered molecules, and because the term solvation number has an uncertain meaning.[18]

There is then a plausible, if not rigorous, demonstration that the rate depends on the water concentration. In the presence of nucleophilic anions one would then expect the two-term expression of eq 11. Equation 11

$$k = k_W(H_2O)_{eff} + k_N(N^-) \qquad (11)$$

is more useful if $(H_2O)_{eff}$ can be established for solutions of the salt M^+N^- where N^- is not inert. This can be done in two ways. For sodium salts where the densities necessary to establish $(H_2O)_{act}$ have been measured, eq 9 can be reasonably extended to any sodium salt. When some of the data are not available, we assume that $(H_2O)_{eff}$ for a salt M^+N^- is the same as that of $M^+HSO_4^-$ of the same molar concentration. This is equivalent to saying that $(H_2O)_{act}$ is independent of the nature of the anion, which is not far wrong for many salts.

It is assumed above that the effect of the bisulfates is only on the water and is independent of the nature or rate of reaction of the diazonium ion. In Figure 1 it is shown that the rates of the reactions are all retarded by about the same relative amounts by sodium bisulfate solutions, thus adding support to this view.

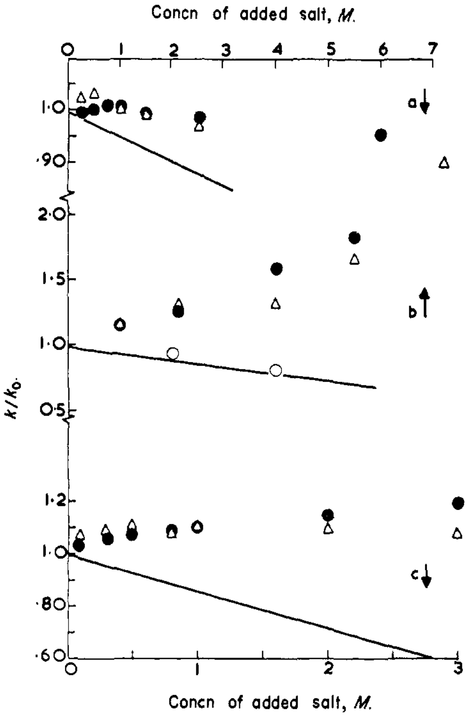

Figure 4. Calculated (△) and observed (●) relative rates for reaction of diazonium salts with several added salts. The straight line shows the rate calculated in the absence of nucleophilic participation, with data shown as open circles where appropriate: a, $C_6H_5N_2^+$, NaBr, lower concentration scale; b, p-$NO_2C_6H_4N_2^+$, NaBr, upper scale; c, p-$CH_3C_6H_4N_2^+$, KSCN, lower scale.

A more searching test of the generality of eq 11 is to relate the product yields to the rate effects. If the first term corresponds to the formation of ArOH and the second to the formation of ArN, then one can write for the ratio of yields of ArN(Y_{ArN}) to that of phenol (Y_{ArOH}) eq 12, which was used to calculate the ratio k_N/k_W in Table II, assuming only that $Y_{ArN} + Y_{ArOH} = 1$.

$$Y_{ArN}/Y_{ArOH} = k_N(N^-)/k_W(H_2O)_{eff} \qquad (12)$$

The combination of eq 11 and 12 yields eq 13. In

$$k = k_W(H_2O)_{eff}(1 + Y_{ArN}/Y_{ArOH}) \qquad (13)$$

Figure 4 this calculated k is plotted for three cases: Ar = C_6H_5, M^+N^- = NaBr from this work; Ar = p-$NO_2C_6H_4$, M^+N^- = NaBr;[6] Ar = p-$CH_3C_6H_4$, M^+N^- = KSCN.[8] In Figure 5, the same plots for Ar = C_6H_5 and M^+N^- = NaCl, LiCl, and Bu_4NCl, all from this work, are shown. The observed rates are also shown, and also $(H_2O)_{eff}/55.5$ is calculated with the following approximations. In Figure 4, the assumption is made that $(H_2O)_{eff}$ in sodium bromide is the same as it is in the nitrate, and that nitrate ion is inert; the calculation for potassium thiocyanate solutions assumes that eq 9 also applies to potassium ion. In Figure 5, $(H_2O)_{eff}$ in lithium and tetrabutylammonium chloride solutions is assumed the same as in the corresponding bisulfates.

The agreement between the calculated and observed rates in Figure 4 is quite satisfactory; in Figure 5 the calculated rates for chloride solutions are mostly too low.[19] The discrepancy is most serious for solutions

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[16] Linear expressions are used throughout for eq 2–10 and hereafter, but some results suggest that the plot of k $vs.$ $MHSO_4$ may be concave upward. No important error is introduced by the assumption of linearity for interpolation purposes, but extrapolation to high concentrations may be unreliable.

[17] In fact, the equations for tetrabutylammonium bisulfate are more precisely $k = k_W[55.5 - 16.2(BuNHSO_4)]$ and $(H_2O)_{eff} = (H_2O)_{act} + 3.5(Bu_4NHSO_4)$, but the second positive term is small compared to the first negative term, hence the apparent success of eq 1 and 8. No refinements such as different reactivities for different water structures are considered, nor are these ions believed to be so large that their effect on $(H_2O)_{act}$ is the same and as chemically insignificant as particles of inert sand.

[18] J. O'M. Bockris, *Quart. Rev.* (London), 3, 173 (1949).

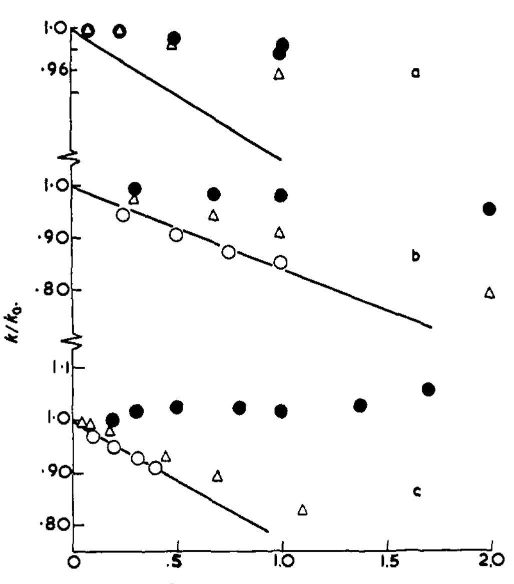

Figure 5. Same as Figure 4 for $C_6H_5N_2^+$ with some chlorides: a, NaCl; b, LiCl; c, Bu_4NCl.

of lithium and tetrabutylammonium salts, for which the $(H_2O)_{eff}$ term is both large and uncertain. There is a possible explanation of the discrepancy in other terms. If water becomes unreactive when it solvates small cations, then it should become more reactive when it solvates small anions, especially chloride ion. Thus some of the second term in eq 11 may be a chloride ion catalyzed phenol formation, an effect less conspicuous with the larger anions. The data do not allow the calculation of the magnitude of this term; it might be as large as the term yielding chlorobenzene.

The conclusion may now be drawn that the rate- and product-determining steps are the same, and that we can use either rates or yields to evaluate the rate constants. This conclusion lacks rigor because of the poor agreement in Figure 5 discussed above, but it is nevertheless fairly clear that the description as product diversion without rate effect is much worse. In Table II the last column is calculated from eq 12 and is the same as the similarly headed quantity in earlier work[7,12] except that $(H_2O)_{eff}$ is used instead of 55.5. These values of k_N/k_W are not constant for any one nucleophile, N^-, but decrease with (N^-). A reasonable interpretation is that k_W is independent of salt concentration, but k_N decreases, according to eq 14, in which k^0_N is the rate constant at infinite dilution and the f's are activity coefficients. The solubility (c) of another diazonium salt,

$$k_N = k^0_N f_{ArN_2^+} f_{Cl^-} / f^{\ddagger}_{ArN_2Cl} \qquad (14)$$

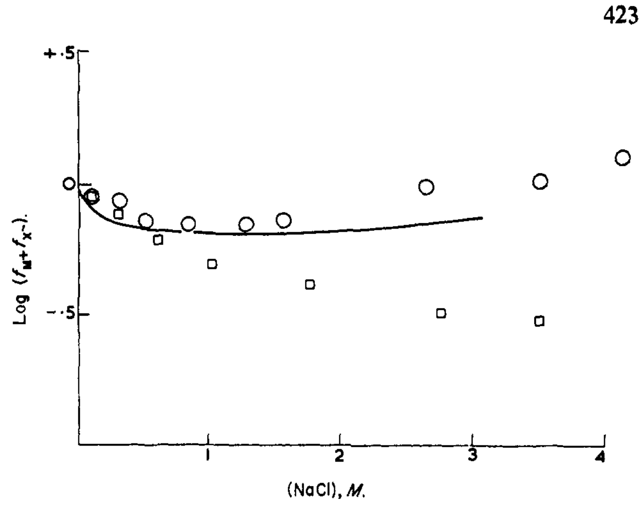

Figure 6. "Activity coefficients" in sodium chloride solutions: ○, log ($c^{-2}/7.90 \times 10^{-4}$) from solubility of benzenediazonium hexafluorophosphate; □, log ($k_{Cl}/8.04k_W$) from product yields for benzenediazonium ion at 3°; —, log($f_{Na^+}f_{Cl^-}$).

benzenediazonium hexafluorophosphate, in aqueous sodium chloride varies as shown in eq 15. Figure 6

$$c^2 f_{ArN_2^+} f_{PF_6^-} = K_{sp} \qquad (15)$$

shows log $k_N/8.04k_W$, log $7.90 \times 10^{-4}/c^2$, and literature values of log $f_{Na^+}f_{Cl^-}$ for various concentrations of sodium chloride. The numbers do not represent accurate values of k^0_N or K_{sp}, since we have no data at low enough ionic strength to warrant an extrapolation, they simply are approximations to put the three curves on a comparable scale. The similarity in form of the three curves, two of which are authentic activity coefficient measures and the third from the product yields, serves to confirm the interpretation of the variation of k_N/k_W as a salt effect.

In further confirmation of the correspondence of rate and yield effects, it should be noted that the most successful feature of the correlation in Figures 4 and 5 is the prediction of the initial curvature of these plots. We may then conclude that the source of this curvature is that the rate expression contains a term due to a reaction between oppositely charged ions.

This reasonable explanation of the curvature in the rate plots bears upon the proposal of a spirocyclic diazirine cation as a second intermediate in the solvolysis.[8] A quantitative description of the curvature, neglecting salt effects, was an essential part of the argument. This neglect now appears unjustified, and the curvature seems explicable without resort to an extra intermediate. The evidence for this second intermediate therefore becomes unconvincing. An independent demonstration of the absence of this intermediate from a consideration of isotopic rearrangements is presented separately.[20]

The rather normal activity coefficients of the diazonium hexafluorophosphate in sodium chloride solution is worthy of comment. They show that the equilibrium in eq 16 can not lie very far to the right, for this

$$ArN_2^+ + Cl^- \rightleftarrows ArN{=}NCl \qquad (16)$$

would lead to high solubilities in the presence of sodium chloride. Earlier studies on p-nitrobenzene–diazonium fluoroborate also showed no large effects of sodium

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(19) All satisfactory published data on both rates and yields are (to our knowledge) included, but some other data lend support. Thus the reaction of benzenediazonium ion with thiocyanate[7] are consistent with $k_{calcd} = k_{obsd}$, but neither rate nor yield data are of high enough precision. The rates of solvolysis of p-toluenediazonium and p-methoxybenzenediazonium ions in the presence of bromide have been determined with precision (J. M. Insole, unpublished), but the yields were determined by difference as in ref 8, and are small enough to have very low precision. Within this precision, $k_{calcd} = k_{obsd}$.

Another unexpected partial correlation of rates and yields arises in the use of sodium perchlorate as an inert salt (B. M. McKay, ref 1). In such solutions there is a significant but nonreproducible rate acceleration, and a significant yield of nonphenolic unidentified product is found. Both rate and product criteria show that this ion is not inert, in agreement with the notorious instability of the very hazardous crystalline diazonium perchlorate.

(20) E. S. Lewis and R. E. Holliday, *J. Am. Chem. Soc.*, **91**, 426 (1969).

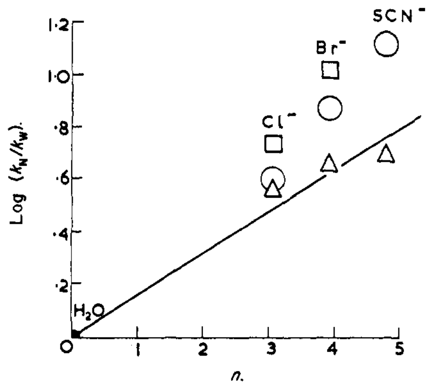

Figure 7. Dependence of log (k_N/k_W) on Swain-Scott n: △, $C_6H_5N_2^+$; ○, p-$CH_3C_6H_4N_2^+$; □, p-$NO_2C_6H_4N_2^+$. The origin is a point for each compound.

chloride on solubility or uv spectra,[21] and the equilibrium constant should be at least 500 times greater than with no substituent.[22] The covalent compound cannot be excluded on this basis as a reactive intermediate.

The temperature dependence of k_N/k_W can yield the difference in activation energies of the two reactions. Figure 2 shows the data of Table II on sodium chloride solutions at 50° together with a few results at 40° and an extensive series at 3°. There seems to be a higher yield of chlorobenzene at low temperatures which at high sodium chloride concentrations is outside of experimental error. The variation might be a temperature effect on $(H_2O)_{eff}$ or a real activation energy difference, but it can be accounted for by $E_{aW} - E_{aN} = 0.6$ kcal, which is small compared to E_{aW} of 27.1 kcal.[2]

The relative reactivities of N^- and water given in Table II and Figure 2 can be expanded by the inclusion of yield data from several other sources (Table IV). Estimates of $(H_2O)_{eff}$ are made as in Table II. All temperature effects are ignored.

The values of k_N/k_W are plotted against n following Swain and Scott[13] in Figure 7, using data at 1 M N^-.[23] A line is sketched for the unsubstituted diazonium salt with a slope $s = 0.16$. Higher, but still very small, values of s fit the other two diazonium salts.

The fact that the lines through any of these sets of prints go reasonably close to the origin shows that the reactivity of water is about what would be expected on the basis of its nucleophilic character, and hence the mechanisms for the reaction with water and with the nucleophiles N^- must be about the same, and special mechanisms, such as those through covalent ArN_2Cl, etc., are not attractive.

The very small s values are even smaller than that reported for the acid-catalyzed hydrolysis of diazoacetic ester[24] ($s = 0.43$) and that estimated ($s \sim 0.7$) for the similar reactions of diazo sulfones.[25] In each of these cases correlation between kinetic and yield data made nucleophilic participation in the rate-determining step more convincing.

Table IV. Relative Reactivities of Anions and Water with Several Diazonium Salts

Ar in ArN_2^+	Added salt	Concn, M	k_N/k_W	Ref
p-$CH_3C_6H_4$	KSCN	0.5	19.6[a]	8
p-$CH_3C_6H_4$	KSCN	1.0	13.4[a]	8
p-$CH_3C_6H_4$	KSCN	2.0	10.6[a]	8
p-$CH_3C_6H_4$	NaBr	1	7.7	*b*
p-$CH_3C_6H_4$	NaCl	1	3.95	*c*
p-$NO_2C_6H_4$	NaBr	1.0	10.5	6
p-$NO_2C_6H_4$	NaBr	2.1	9.4	6
p-$NO_2C_6H_4$	NaBr	4.0	6.9	6
p-$NO_2C_6H_4$	NaBr	6.0	8.8	6
p-$NO_2C_6H_4$	NaCl	0.5	7.5–8.5	*d*
C_6H_5	KSCN	1.0	5[e]	7
C_6H_5	NaCl	1.0	3.7	This work
C_6H_5	NaBr	1.0	4.6	This work

[a] The yields are based on a smooth curve through the yield data, with greater weight given to the high concentration results. [b] J. M. Insole, unpublished, using rate data rather than yields as explained in ref 19. [c] R. E. Holliday, thesis, Rice University, 1966; this is one of an extensive series. [d] E. Pfeil, *Ann.*, **561**, 220 (1949). The range given covers nearly all of his results, mostly in very concentrated solutions. [e] This number is very rough.

The demonstration of nucleophilic participation becomes increasingly difficult as the reaction becomes less selective, or s becomes smaller, for high concentrations of N^- will become necessary to produce even a small rate effect and medium effects will become more serious. This is a general characteristic of unselective reactions, not limited to this specific case. Competition between solvent and an added substance for a reagent or a highly reactive intermediate is easily measured if different stable products result. The usual method of distinguishing between one-step formation of these products and rate-determining formation of a highly reactive intermediate is to see whether the rate is sensitive to the concentration of the added substance. When the reaction is unselective (for example when s is small), the rate effects get down in the range of ordinary medium or salt effects. Thus the demonstration in the present case that the rate- and product-determining steps are identical does not lack rigor principally because of any failings of experimental design. The low value of s makes the demonstration inherently difficult and necessarily confused by medium effects.

In a similar vein, demonstrations of the intermediacy of highly reactive and unselective intermediates, such as unstable carbonium ions or carbenes are not likely to be able to exclude rigorously the alternative one-step mechanism. Indeed, most of the examples of such intermediates in the literature now seem to rely heavily on analogy with cases of more stable, selective intermediates.

The demonstration of identity of product- and rate-determining steps does not necessarily show that the reaction is a one-step process. As pointed out before,[7] mechanism A (reactions A1, A2, A3, and A4) is kinetically equivalent to mechanism B (reactions B1, B2, and B3). In each $ArN_2^+(r)$ refers to the diazonium salt which has undergone rearrangement of the position of a nitrogen isotopic label. However, we shall attempt to show that no reasonable structure for the intermediate X exists so that mechanism B is to be preferred.

Mechanism A is acceptable only if $k_{-1} > k_2(H_2O)$, $k_3(N^-)$, and k_4 to account for the fact that rate accel-

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[21] R. E. Kunetka, M.A. Thesis, Rice Institute, 1952.

[22] C. D. Ritchie, J. Saltiel, and E. S. Lewis, *J. Am. Chem. Soc.*, 83, 4601 (1961).

[23] It would have been desirable to use relative rates at zero ionic strength, but both yield and product data lose precision before any extrapolation becomes reliable.

[24] W. J. Albery, J. E. C. Hutchins, R. M. Hyde, and R. H. Johnson, *J. Chem. Soc., B*, 219 (1968).

[25] J. B. F. N. Engberts and B. Zwanenburg, *Tetrahedron*, 24, 1737 (1968).

$$ArN_2^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X \qquad (A1)$$

$$X + H_2O \xrightarrow{k_2} ArOH \qquad (A2)$$

$$X + N^- \xrightarrow{k_3} ArN \qquad (A3)$$

$$X \xrightarrow{k_4} ArN_2^+(r) \qquad (A4)$$

$$ArN_2^+ + H_2O \xrightarrow{k_W} ArOH \qquad (B1)$$

$$ArN_2^+ + N^- \xrightarrow{k_N} ArN \qquad (B2)$$

$$ArN_2^+ \xrightarrow{k_r} ArN_2^+(r) \qquad (B3)$$

erations do not become saturated, and that the extent of isotopic rearrangement is quite small.[10] Since all reactions of X are of about the same small activation energy, the transition states surrounding X must closely resemble X, and therefore X resembles the phenyl cation (from substituent effects), and the bond to nitrogen is very weak (from the substituent effect and the large nitrogen isotope effect).[8,26] The unselectivity (low *s*) shows that the transition states leading from X to products have very weak and little developed bonds to the attacking nucleophile. Since it is necessary to postulate k_4 as rather small, X has two distinguishable nitrogens. Of the structures suggested before, we can reject summarily the distorted diazonium ion because it can not represent an energy minimum. Likewise the "caged pair," $\overline{Ar^+N_2}$, seems to have no obvious barrier to recombination, and is therefore rather far-fetched. An electronically excited state of the diazonium ion for X must be rejected because there is no reason to suspect a state at such a low level.

We thus are forced to accept mechanism B, and it is extremely interesting that the transition states for this one-step mechanism resemble so closely those for the reactions of the unbelievable intermediate X and those for the often postulated aryl cation. Mechanism B is much closer to this aryl cation intermediate mechanism which we reject than it is to other cases of nucleophilic aromatic substitution, such as those passing through Meisenheimer complexes. It is quite possible that this sort of one-step mechanism, simulating a path through a reactive intermediate, may be quite general. The demonstrated presence of an alternative in this case emphasizes the real significance of the mechanistic ambiguity previously mentioned arising from low selectivity.

Experimental Section

Materials. Diazonium salts were prepared by conventional aqueous diazotization and precipitated as the fluoroborates with fluoroboric acid. Benzene diazonium and *p*-toluenediazonium fluoroborate were recrystallized and the purity was assayed by uv absorption. Extinction coefficients were in agreement with the literature.[27] The *o*- and *m*-toluenediazonium fluoroborates had λ_{max} 264 nm (ϵ 1.1 × 10^4) and λ_{max} 267 nm (ϵ 1.2 × 10^4), respectively. Since both these salts hydrolyze rapidly, and no other anions were studied, the values of ϵ are not very precise.

All water was carefully distilled and found to be free of copper salts, which have been shown to be reactive under some circumstances.[6] Highest purity inorganic salts commercially available were used.

Tetrabutylammonium Chloride. The published procedure[28] was used to make an iodide-free aqueous solution of this salt. Solutions of the desired concentration were made by evaporation of the solvent, and the concentration determined by Mohr titration of the chloride. A sample evaporated to dryness, further dried over phosphorus pentoxide in a vacuum desiccator melted at 52–55° (lit.[28] 52–54°).

Tetrabutylammonium Bisulfate. The procedure for the chloride was followed using silver oxide instead of chloride. After the iodide had disappeared, the solution was filtered, treated with the calculated amount of sulfuric acid, and assayed by titration with standard sodium hydroxide. Densities were determined by standard pyconometric methods.

Rates. Rates were measured by analysis of diazonium salt by coupling following the successive approximation method of Lewis, Kinsey, and Johnson.[11] No final corrections were greater than 5%, and precision of about 0.5% is readily achieved when the reactions are not too fast. If the diazonium salt concentrations are much greater than 10^{-2} *M*, a first-order course is not followed, presumably because of coupling with the phenolic product. Observed rates in the absence of added salts are given in Table V. All solutions are 0.01 *M* in sulfuric acid and are reported at a nominal temperature of 40.14°, constant to 0.01° but determined with a thermometer calibrated to 0.1°. They are compared to the values calculated from the Arrhenius constants of DeTar and Ballentine.[2] The agreement between all results is entirely satisfactory and temperature uncertainties account for the discrepancies.

Table V. Rates of Hydrolysis of Diazonium Salts

Diazonium salt	Rate constant found,[a] sec^{-1}	Lit.,[2] sec^{-1}
$C_6H_5N_2^+$	(4.151 ± 0.021) × 10^{-4}	4.157 × 10^{-4}
o-$CH_3C_6H_4N_2^+$	(1.852 ± 0.017) × 10^{-3}	1.848 × 10^{-3}
m-$CH_3C_6H_4N_2^+$	(1.592 ± 0.020) × 10^{-3}	1.541 × 10^{-3}
p-$CH_3C_6H_4N_2$	(4.223 ± 0.013) × 10^{-5} [b]	4.227 × 10^{-5}

[a] Errors given are maximum deviations of three to seven measurements from the mean. [b] The value interpolated in the data of ref 11 is 4.273 × 10^{-5}.

Yield Measurements. Yields of chlorobenzene and bromobenzene were determined by the extraction and gas chromatographic process described before,[12] with ethylbenzene as the internal standard for chlorobenzene, and chlorobenzene as internal standard for bromobenzene. The use of a hydrogen flame detector allowed measurement of much lower yields; the lower limit was determined by solvent purity rather than sensitivity. All runs reported were in sealed vessels to avoid loss of chlorobenzene by evaporation, comparable experiments give about 20–25% larger relative yields than those reported before in open systems[12] and are more reproducible.

Solubility of Benzenediazonium Hexafluorophosphate. Solubilities in 0.01 *M* sulfuric acid and various concentrations were measured at 0° by stirring a suspension of the pure solid in the appropriate solution which was immersed in an ice bath. From time to time samples were quickly filtered and an aliquot was analyzed for diazonium ion by coupling with disodium 2-naphthol-3,6-disulfonate (R-salt) dissolved in saturated sodium bicarbonate. After coupling and acidification the optical density was measured and the concentration calculated from the known λ_{max} 490 nm (ϵ 2.1 × 10^4) for this compound. When the concentration became constant, usually in only a few minutes, the solution was considered saturated. The method is essentially that of Kunetka.[21] The major error is an absolute one in the value of ϵ and does not influence the relative values.

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(26) L. L. Brown and J. S. Drury, *J. Chem. Phys.*, **43**, 1688 (1965).

(27) E. S. Lewis and M. P. Hanson, *J. Am. Chem. Soc.*, **89**, 6268 (1967).

(28) K. D. McMichael and R. A. Clement, *J. Org. Chem.*, 26, 620 (1961).