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The Reaction of Benzenediazonium Ion with Aqueous Thiocyanate and the Nature of the Intermediate[1]

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Benzenediazonium salts decompose in acidic aqueous thiocyanate solutions yielding phenol, phenyl isothiocyanate, phenyl thiocyanate (and its hydrolysis product, phenyl thiocarbamate), as well as hydrolysis products of the thiocyanate ion. Yields are not satisfactorily reproducible, but relative reactivities of a common substance toward formation of a bond to sulfur, to nitrogen and to water of about 6:2.8:1, coupled with an erratic reaction yielding more phenyl thiocyanate account roughly for the results. Rate measurements indicate an increase in rate with thiocyanate concentration amounting to less than 20% at the highest concentrations. It is concluded that there exists a reactive intermediate which can react rapidly with either thiocyanate ion or with water, but, in contrast to previous views, the intermediate can also revert to diazonium ion. Speculative structures for the intermediate are proposed.

Introduction

The decomposition of benzenediazonium salts has been studied extensively and the mechanism indicated by reactions 1 and 2 has been fairly generally accepted for most diazonium salts.

$$ArN_2^+ \longrightarrow Ar^+ + N_2 \quad \text{slow} \qquad (1)$$

$$Ar^+ + H_2O \longrightarrow ArOH + H^+ \text{fast} \qquad (2)$$

The basis for this mechanism has been summarized in an earlier paper.[2] In essence the evidence is kinetic, which shows that the transition state contains only the elements of ArN_2^+ (with minor importance of the solvent), substituent effects consistent with a transition state resembling the aryl cation, and by-products qualitatively and quantitatively explainable in terms of alternative reactions of Ar^+ with nucleophiles other than the solvent.

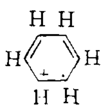
This mechanism has been questioned by Field and Franklin on the basis that toluene-diazonium ions yield unrearranged cresols on decomposition, whereas the ion produced by removal of a group from the ring of tolyl derivatives to give $C_7H_7^+$ is apparently identical with the ion derived from benzyl derivatives when studied in the mass spectrometer, and could therefore be expected to give rearranged products.[3] In addition to the diazonium salts which decompose by this kinetically well-characterized path, there are some that follow other routes. A nucleophilic attack on the aromatic system with direct substitution of the N_2 group has been identified in the reaction of tetrazotized paraphenylenediamine with chloride ion, in which the second diazonium group plays the part of the activator. In this case the reaction 3 is unaccompanied by important side reactions.[4] An earlier report of an activated nucleophilic substitution of nitrogen by bromide ion from *p*-nitrobenzenediazonium ion,[5] while apparently reasonable, will in this paper be shown to be explicable in different terms. Apparently, the diazonium ion group is not a good leaving group in bimolecular substitutions. Even 2,4-dinitrobenzenediazonium salts in weakly basic media suffer displacement of a nitro group rather than the doubly activated diazonium ion group.[6] The high reactivity of diazotized 2-aminopyridine and its facile conversion to 2-chloropyridine is suggestive of an activated nucleophilic aromatic substitution,[7] but appropriate kinetic studies have not been made and the presumed intermediate in the unimolecular reaction of this diazonium ion, the 2-pyridyl cation, might derive some special stability similar to that of benzyne, with which it is isoelectronic.

In this paper a study of the products and rates of reaction of benzenediazonium fluoroborate with aqueous thiocyanate is reported. Thiocyanate ion was selected because it is a weak base toward protons, it is a good nucleophile toward carbon,[8] and the reactivity at both ends can be studied; that is, it is an ambident ion.[9] Furthermore, thiocyanate does not form covalent diazo compounds extensively with diazonium salts, and it is

[1] Based upon the Ph.D. thesis of J. E. Cooper, Rice Institute, 1959. This paper is IX in the series "The Reactions of Diazonium Salts with Nucleophiles"; preceding paper: C. D. Ritchie, J. Saltiel and E. S. Lewis, *J. Am. Chem. Soc.*, **83**, 4601 (1961).

[2] E. S. Lewis, *ibid.*, **80**, 1371 (1958).

[3] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, p. 232. Although the analogy between gaseous ions and solution ions is imperfect, a further suggestion from this sort is interesting. On p. 144 of the same work, it is noted that the C–H bond strength in $C_6H_6^+$ is about the same as that in benzene, showing no interaction between the bonding electrons and the π-electron system. On this basis, the structure A could represent $C_6H_6^+$ and B would be $C_6H_5^+$. This unpaired electron structure for the phenyl cation is reminiscent of the CH_2 molecule where a paired structure is of great chemical importance, but the unpaired structure is more stable (D. B. Richardson, M. C. Simmons and I. Dvoretzky, *J. Am. Chem. Soc.*, **82**, 5001 (1960), among several). Indeed the unpaired structure seems to follow for both methylene and the phenyl cation from a qualitative application of the "double quartet" theory of J. W. Linnett (*ibid.*, **83**, 2643 (1961)). R. W. Taft, Jr. (*ibid.*, **83**, 3350 (1961)) has proposed that the transition state for the unimolecular decomposition has triplet character. We are indebted to Prof. Taft for a copy of this paper before publication.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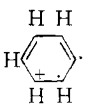
and 17 others

B

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

[5] E. S. Lewis and W. H. Hinds, *ibid.*, **74**, 304 (1952).

[6] G. T. Morgan and J. W. Porter, *J. Chem. Soc.*, **107**, 645 (1915).

[7] E. Koenigs, *Angew. Chem.*, **50**, 911 (1937); S. J. Angyal and C. L. Angyal, *J. Chem. Soc.*, 1461 (1952).

[8] C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 146 (1953).

[9] N. Kornblum, R. A. Smiley, R. K. Blackwood and D. C. Iffland, *ibid.*, **77**, 6269 (1955).

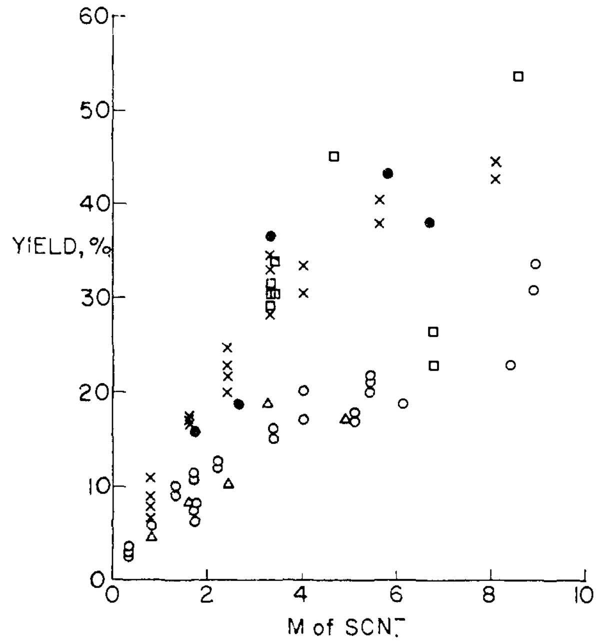

Fig. 1.—Combined yields of phenyl thiocyanate and phenyl thiocarbamate from benzenediazonium fluoroborate at various thiocyanate ion concentrations. Conditions as in Table I: A, □; B, ●; C, △; D, ○; E, ×.

isoelectronic with azide ion, which reacts with diazonium salts by a unique mechanism.[10]

Results

The decomposition of benzenediazonium fluoroborate in acidic aqueous potassium thiocyanate solution gave a variety of products. Least pertinent but contributing to the experimental difficulties are the hydrolysis products of the thiocyanate ion, of which carbon disulfide and carbon oxysulfide were identified in the gas phase. A small amount of an insoluble solid, resembling the "thiocyanogen polymer" frequently described,[11] was occasionally observed, but in negligible amount.

The identified organic products were phenol, phenyl thiocyanate and its hydrolysis product, phenyl thiocarbamate, and phenyl isothiocyanate. In a few experiments insignificant amounts of fluorobenzene were detected. These accounted within a rather large experimental error for all the starting material, but a disagreeable odor, suggestive of thiophenol, and some color in the reaction indicated the presence of some further unidentified products.

The analysis, described in the Experimental section, was based on a separation of phenol from the other organic products by extraction of a strongly basic reaction mixture with isoöctane, followed by a spectrophotometric analysis of this solution for phenyl thiocyanate, phenyl isothiocyanate and phenyl thiocarbamate. This analysis was well suited for the mixture of the first two of these, which were first believed to be the only components of the mixture. When the thiocarbamate was later found the previous results could be used only if the same analytical method was used. For this reason, the analytical precision, especially for the sulfur bonded species, is less than is desirable, but was considered adequate. Reacidification of the aqueous phase and extraction with chloroform gave the phenol in this solvent, in which the concentration could be estimated spectrophotometrically. Inorganic substances interfered with the standard bromometric phenol analysis. Since there was a little interference even in the analysis used and since the extraction may have been incomplete, we believe that these analyses are not very precise and may be low. For this reason and for consistency with experiments in which phenol was not determined, the phenol yields used in the calculations below are determined by difference. A further justification for this procedure has been presented previously.[2] The error so introduced is not greater than 15% in the phenol yields and is probably less, since we accounted for between 85 and 105% of the starting materials in the significant experiments.

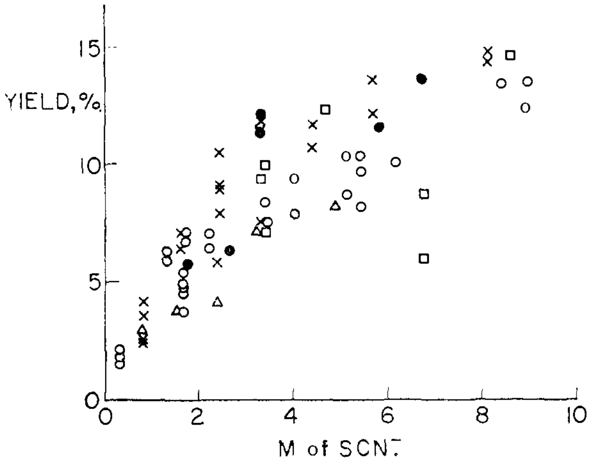

Fig. 2.—Yields of phenyl isothiocyanate from benzenediazonium fluoroborate at various thiocyanate ion concentrations; conditions and legend as in Fig. 1.

The yields of products are shown in Figs. 1 and 2, under different sets of experimental conditions. Under the assumption that all products arrive from bimolecular reactions of a common intermediate with water or thiocyanate ion, the relative reactivities or competition factors, k_S/k_O, k_N/k_O and k_S/k_N were calculated by eq. 4, 5 and 6, in which Y_S is the sum of the yields of phenyl thiocyanate and phenyl thiocarbamate (the total yield of sulfur bonded material), Y_N is the yield of phenyl isothiocyanate (the yield of nitrogen bonded material) Y_O is that of phenol or oxygen-bonded product. The k's are the rate constants for the product-determining step of the common pre cursor or intermediate, with subscripts having the same significance as before. The competition factors so calculated are given in Table I.

$$k_S/k_O = (Y_S/Y_O)(H_2O)/(SCN^-) \qquad (4)$$

$$k_N/k_O = (Y_N/Y_O)(H_2O)/(SCN^-) \qquad (5)$$

$$k_S/k_N = (Y_S/Y_N) \qquad (6)$$

If all the products arise from the reaction of one intermediate with the two nucleophiles present,

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(10) K. Clusius and H. Hürzeler, *Helv. Chim. Acta*, **37**, 798 (1954).

(11) J. Liebig, *Pogg. Ann.*, **15**, 548 (1829).

TABLE I

COMPETITION FACTORS FOR THE INTERMEDIATE IN BENZENEDIAZONIUM ION DECOMPOSITION

(SCN^-)	Conditions[a]	k_S/k_O	k_N/k_O	k_S/k_N
3.4	A	8.3	2.3	3.4[b]
4.7	A	12.2	3.5	3.5
6.8	A	2.9	0.9	3.4[b]
8.6	A	11.9	2.9	3.8
1.8	B	6.2	2.1	2.9
2.7	B	5.4	1.8	3.0
3.4	B	11.9	3.9	3.1
5.8	B	9.1	2.4	3.8
6.7	B	6.5	2.3	2.7
0.8	C	3.6	2.1	1.7
1.6	C	3.4	1.4	2.5
2.5	C	2.6	1.0	2.5
3.3	C	4.2	1.6	2.6
5.0	C	3.4	1.2	2.7
0.3	D	5.2	3.2	1.7[b]
0.9	D	4.6	3.0	1.6
1.4	D	4.6	2.9	1.6[b]
1.7	D	3.0	1.9	1.8[b]
2.3	D	3.7	2.0	1.8[b]
3.4	D	3.3	1.7	1.9[b]
4.1	D	3.2	1.6	2.1[b]
5.2	D	2.7	1.5	1.8[b]
6.2	D	2.4	1.3	1.8
8.4	D	2.4	1.4	1.7
9.0	D	3.7	1.5	2.5[b]
0.8	E	6.2	2.2	2.6[b]
1.6	E	7.6	2.8	2.6[b]
2.4	E	7.1	2.4	2.8[b]
3.4	E	9.5	2.8	3.2[b]
4.1	E	7.8	2.7	2.9[b]
5.7	E	8.2	2.6	3.1[b]
8.1	E	7.0	2.4	3.0[b]

[a] Conditions: A, 40°, light, air; B, 40°, light, no air; C, 40°, dark, no air; D, *ca.* 100°, diazonium solution added to boiling thiocyanate solution; E, *ca.* 100°, cold mixture rapidly heated to boiling. [b] These entries represent the average of at least two runs, the k_S/k_N values were determined before averaging and are hence not quite the same as the ratio of the other two entries; other discrepancies of this nature are round-off errors.

then each column in the table should be constant at any one temperature except for salt effects. It is clear that the entries in the table are not constant. One source of deviation arises from the expression for the rate of formation of phenol, which is proportional to $k_O(H_2O)$. The concentration of water is known from the molarity and the density, but it is likely that water which is in the solvation shell of a potassium ion, free water and water solvating the anion all may have different reactivities, and even a modest extent of solvation of the electrolytes involves a sizable fraction of the total water in the more concentrated solutions; we have been unable to arrive at a satisfactory solution to this problem except to note that it is not serious in the more dilute solutions. The ratio k_S/k_N is free from this difficulty, but it also shows a small upward drift with thiocyanate concentration. The rather wide scatter of the entries in the table and the scatter apparent from Figs. 1 and 2 can not be attributed to this or any other reproducible effects or side reactions. We propose that it arises from a combination of a fairly large analytical error (reflected also in our failure to get reproducibly good material balances) with the more or less serious incursion of an erratic side reaction leading to phenyl thiocyanate and accounting for the occasional very high values of k_S/k_O.

The non-constancy of the reactivity ratios is worse at 40° (conditions A, B and C) than it is at 100° (conditions D and E), and there is a suggestion that light also contributes to the scatter (condition C compared to A and B). The equations below give a rather subjective estimate of the reactivity ratios in dilute solution weighting the values from conditions C and E most heavily. Thus, k_S/k_O and k_S/k_N are roughly extrapolated to zero thiocyanate concentration, the values for k_S/k_O and k_N/k_O under condition D are ignored because the concentration of thiocyanate ion is very uncertain since the extent of hydrolysis may be very large, but the ratio k_S/k_N is independent of thiocyanate concentration and is therefore reliable. No estimate of error on k_S/k_O is given, but even the other errors may be insufficient.

k_S/k_O = 7 at 40° and 6 at 100°

k_N/k_O = 2.9 ± 0.8 at 40° and 2.8 ± 0.7 at 100°

k_S/k_N = 2.4 ± 0.5 at 40° and 2.2 ± 0.4 at 100°

We were led to the postulation of an erratic reaction from observation of the behavior of *p*-nitrobenzenediazonium ion. Thus, the rate of reaction of the highly purified *p*-nitrobenzenediazonium fluoroborate with aqueous thiocyanate solution is slow but not reproducible, but if unrecrystallized salts are used, or if the water is taken from the building deionized water system without distillation, a reaction complete in a few minutes yielding *p*-nitrophenyl thiocyanate almost quantitatively takes place.[12] We suggest that an analogous reaction subject to catalysis by trace impurities may contribute to a minor extent with the unsubstituted diazonium salt.

Reaction rates were measured by nitrogen evolution in two different devices, one measuring the volume of nitrogen produced at constant pressure, the other (more precise) measuring the pressure increase. The reactions followed a first-order course with precision, except for the complication introduced by the formation of volatile hydrolysis products of the thiocyanate, for which correction is easy. The pseudo-first-order constants are given in Table II, and there seems to be little difference between the two sets of results, nor is there any perceptible effect of air or light. The table can be summarized by eq. 7 and 8; the first represents all the data, the second only those taken in the more precise apparatus. Equation 8 fits the data to which it applies with an average deviation of 2.5% and a maximum deviation of 4%. The alternative treatment of the data, the assumption that all the rate variations are random, would give an average rate of 4.41×10^{-4}, with an average deviation of 6% and a maximum deviation of 16%. This also fails to give reasonable agreement with the literature for the rate constant in the absence of thiocyanate.

$$10^4 k_{app} = 4.08 + 0.15\,(SCN^-) \qquad (7)$$

$$10^4 k_{app} = 4.08 + 0.14\,(SCN^-) \qquad (8)$$

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[12] R. E. Kunetka, M.A. Thesis, The Rice Institute, 1954.

TABLE II

APPARENT FIRST-ORDER RATE CONSTANTS FOR THE REACTION OF BENZENEDIAZONIUM ION IN AQUEOUS THIOCYANATE AT 40.00 ± 0.05°[a]

(SCN^-)	Condition[b]	$k_{app} \times 10^4$, sec.$^{-1}$	(SCN^-)	Condition[b]	$k_{app} \times 10^4$, sec.$^{-1}$
0	F	3.93	0	H	4.10
0	F	4.12	2.75	H	4.51
0	F	4.28	4.56	H	4.56
0.90	F	4.18	5.60	H	4.70
1.76	F	4.05	0	I	3.99
2.64	F	4.24	1.38	I	4.44
3.51	F	5.12	2.75	I	4.62
1.19	G	4.50	3.43	I	4.43
2.14	G	4.44	5.15	I	4.89
4.32	G	4.78			

[a] This represents the calibration uncertainty of the thermometer; the control and constancy were somewhat better. [b] Conditions: F, volume measured, light and air present; G, volume measured, dark, air present; H, pressure measured, light present, degassed; I, pressure measured, dark, degassed.

Equations 7 and 8 are not least square lines, although the difference is small. The term 4.08×10^{-4} is the average of all runs at $(SCN^-) = 0$ and the coefficient of (SCN^-) is calculated for each point and averaged using (SCN^-) as a weighting factor. The constant term is fortuitously identical with the value calculated from the Arrhenius parameters of DeTar and Ballentine[13]; the close agreement is a justification for the use of the second term in eq. 7 and 8.

We at first believed that the deviations from eq. 7 and 8 were outside our experimental error, and represented further evidence for the unreproducible reaction previously suggested. However, at zero thiocyanate concentration, where this reaction must be absent, the deviations are only slightly smaller than for the runs in the presence of thiocyanate, so there is no convincing kinetic evidence for a non-reproducible reaction component.

Discussion

The product distribution is that anticipated from the earlier work.[2] The rough competition factors for the reactive intermediate relative to water are reasonable; that is, thiocyanate ion competes with water better than chloride ion does,[2] but the factor for thiocyanate is not nearly as large as the factor 1.3×10^4 for the trityl cation,[14] indicating that the intermediate is far less selective and hence more reactive than the trityl cation.

Kornblum and his co-workers[9] proposed that a carbonium ion would attack the electronegative atom of an ambient nucleophile to a larger extent than would the corresponding alkyl halide in a one-step SN2 reaction. There are no data for a direct comparison, but the relatively large yields of the isothiocyanate compared to those in familiar SN2 reactions are consistent with this proposal and can be compared with the results of Cannell and Taft on the *t*-butyl cation.[15] They found that the ratio which we call k_S/k_N had the value 1.9 for the intermediate in the nitrous acid–isobutylamine reaction, and the higher value 2.5 for the intermediate in the solvolysis of *t*-butyl chloride. The precision of our result of 2.4 ± 0.5 is insufficient to do more than point out the similarity.

Our data do not establish a temperature coefficient for the competition factors, although a trend toward lower selectivity with increase in temperature appears. The main value of the higher temperature runs is their greater reproducibility. In terms of an erratic side reaction we interpret this as an indication that the side reaction has a lower activation energy than the desired reaction. In this connection, it may be noted that the Sandmeyer reaction, a possible analogy to a side reaction subject to trace impurity catalysis, has a rather low temperature coefficient.[16] In sum, the product distribution results are about what might have been predicted from previous work assuming the intermediacy of the phenyl cation.

The kinetic results present a different picture. The small but definite increase in rate with thiocyanate concentration is not consistent with only a first-order irreversible formation of an intermediate which subsequently reacts with nucleophiles. The rate increase is not a simple salt effect, since the salt effect appears to be in the opposite direction.[17] The rate increase is not unprecedented; similar rate increases have been observed with high concentrations of benzenediazonium chloride,[18] with high concentrations of hydrochloric acid,[18,19] and even with thiocyanate ion,[20] although the concentration in this case was barely enough to make an effect outside of experimental error. It should be noted that Pray[20] and Blumberger[19] do not agree on the magnitude of the effect of sulfate ion. The *p*-nitrobenzenediazonium ion also shows a small but significant increase in rate in the presence of bromide ion,[5] and in dimethylformamide solution chloride gives a small rate increase.[21] These small rate increases were ascribed to the contribution of a second-order reaction,[5,18] but now that the number of these is greater, it is hard to overlook the similarity of this rate to that of the first-order reaction. The conclusion of reference 5 has been questioned on an independent basis. The change in volume of activation ($\Delta V^{\ddagger}$) appears to be the same for the formation of *p*-nitrobromobenzene as it is for *p*-nitrophenol, in contrast to expectation

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

(14) C. G. Swain, C. B. Scott and K. H. Lohmann, *ibid.*, **75**, 136 (1953).

(15) L. G. Cannell and R. W. Taft, Jr., Abstracts of Papers at the American Chemical Society Meeting, Dallas, Tex., 1956, p. 46-N.

(16) W. A. Cowdrey and D. S. Davies, *J. Chem. Soc.*, S48 (1949).

(17) The establishment of the direction of the salt effect is complicated by occasional rate increases on adding salts, such as the present one; a rate decrease appears more general and frequently has been observed with clearly unreactive anions.[5,18,19] The reported "stabilization" of diazonium salts by salt formation with the aromatic polysulfonic acids (K. H. Saunders, "The Aromatic Diazo Compounds," 2d Ed., Edward Arnold and Co., London, 1949, pp. 83–89), the stabilization of benzenediazonium ion by the highly charged molybdate ion (which disappears on adding acid and neutralizing the charge) reported by Pray,[20] and Pray's[27] other observation that the rate of decomposition increased on addition of ether to alcohol as the solvent, all suggest that the charge becomes slightly more dispersed on activation and are difficult to explain in any other terms.

(18) M. L. Crossley, R. H. Kienle and C. H. Benbrook, *J. Am. Chem. Soc.*, **62**, 1400 (1940).

(19) J. S. P. Blumberger, *Rec. trav. chim.*, **49**, 259 (1930).

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

(21) We are indebted to Dr. M. D. Johnson for communicating this result of Dr. A. J. Parker.

for a bimolecular reaction of the diazonium ion.[22] Parker[21] also believed that the effect of the solvent dimethylformamide on chloride nucleophilicity was less than he would have expected for an S_N2 reaction.

On the basis of the similarities of the first- and second-order terms and the questions raised concerning the bimolecular attack, which seems quite out of the question for the unsubstituted diazonium salt, we propose the following mechanism, the only feature of which that is necessarily different from the earlier mechanism is the reversibility of the first step, reaction 9.

$$ArN_2^+ \underset{k_{-9}}{\overset{k_9}{\rightleftarrows}} ArN_2^{+*} \quad (9)$$

$$ArN_2^{+*} + H_2O \xrightarrow{k_{10}} N_2 + H^+ + ArOH \quad (10)$$

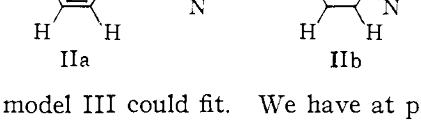
$$ArN_2^{+*} + B^- \xrightarrow{k_{11}} N_2 + ArB \quad (11)$$

Let us postpone a discussion of the intermediate ArN_2^{+*} and consider the kinetic consequences of this mechanism. If we assume that the intermediate does not accumulate, we can apply the steady state method to this system, which gives eq. 12. It can be seen readily that the right-hand side of this equation reduces to $k_9(ArN_2^+)$ if $k_{-9} << k_{10}(H_2O) + k_{11}(B^-)$. At the other extreme with $k_{-9} >> k_{10}(H_2O) + k_{11}(B^-)$, it reduces to $[k_{10}(H_2O) + k_{11}(B^-)]k_9(ArN_2^+)/k_{-9}$, an expression of the form actually observed. Since the total range of k_{app} is small, we cannot be sure of the exactness of the linear expression (such as eq. 8), so we may only conclude that the proposed mechanism fits the observed kinetics as long as k_{-9} is comparable with or greater than $k_{10}(H_2O) + k_{11}(B^-)$. This is equivalent to stating that a significant fraction of the intermediate ArN_2^{+*} returns to diazonium ion. The product distribution is insensitive to mechanism in that it only shows that the products are formed by reactions of the same order in a single substance, which might be the phenyl cation, the new intermediate ArN_2^{+*} or even the diazonium ion itself, as pointed out by Pfeil.[23]

$$-\frac{d(ArN_2^+)}{dt} = \frac{[k_{10}(H_2O) + k_{11}(B^-)]}{[k_{-9} + k_{10}(H_2O) + k_{11}(B^-)]} k_9(ArN_2^+) \quad (12)$$

It now remains to consider the nature of the intermediate. In order to explain the new data as well as all the previous work, the intermediate must have the characteristics: 1. It must explain substituent effects as well as the mechanism with the phenyl cation as an intermediate. 2. The reverse reaction to give the diazonium ion must be reasonable. 3. It must be a highly unselective and reactive substance. An attractive structure for the intermediate is the charged caged pair $\overline{Ar^+N_2}$. Clearly this would be sensitive to substituents in exactly the same way as would Ar^+ itself. The reverse reaction would be favored by the cage and is not unreasonable since the phenyl cation is presumed to be so highly reactive. The reaction is quite analogous to the familiar reactions of carbonium ions with carbon monoxide. The low selectivity obviously also follows. The kinetic effect of acceleration by nucleophiles is reminiscent of the special salt effect,[24] in which an ion-pair is intercepted and prevented from returning by various salts. There are marked contrasts with regard to the sensitivity to small salt concentrations and the stability of the carbonium ion.

Alternative structures with fewer analogies might be the π-complex or the diazacyclopropene[25] intermediate II; the high reactivity would appear to require that the structure IIa should predominate. With even less analogy, a planar bent model III could fit. We have at present no basis for distinction between these structures.



IIa IIb

III

The mechanism represented by reactions 9, 10 and 11 is of course only the simplest of a number with a whole series of intermediates, any one of which could fit the observations. We have preferred to avoid those in which external nitrogen is an agent which returns an intermediate to the diazonium salt, but the experiments now published on the possible effects of nitrogen are not completely opposed to such a course. It seemed highly improbable that this would have escaped notice, especially in the high pressure work of Brower.[22]

It is clear that the adoption of the new mechanism requires a reinterpretation of the results from the *p*-nitrobenzenediazonium bromide system of Lewis and Hinds.[5] The most important piece of evidence there presented was the kinetic law, which was of the form: $k_{app} = k_O + k'(Br^-)$. We now explain this rate law on a completely different basis without calling upon a new mode of reaction of the diazonium salt itself. The remaining evidence, that the product distribution was not exactly that predicted for a simple competition for an intermediate, suffers from the difficulty that some of the water is tied up solvating the inorganic ions and may be rendered unreactive, as mentioned previously. If we assume that four water molecules are rendered unreactive by the sodium ion, it turns out that the discrepancies attributed to the incursion of the bimolecular reaction now are in the opposite direction. We can then explain these results with a reactivity ratio k_{Br}/k_O = *ca* 9 with as good precision as any other competition factors. The competition factor 9 also fits the data of Pfeil[29] for the reaction of chloride and *p*-nitrobenzenediazonium ion.

The unselectivity of the intermediate allows the conclusion that the transition states for the reaction of the intermediate are very similar to the intermediate itself, and an extension of Hammond's postulate[26] would be that the molar volumes of

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[22] K. R. Brower, *J. Am. Chem. Soc.*, **82**, 4535 (1960).

[23] E. Pfeil, *Ann.*, **561**, 220 (1948).

[24] A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2767, 2780 (1956); A. H. Fainberg, G. C. Robinson and S. Winstein, *ibid.*, **78**, 2777 (1956); S. Winstein and E. Clippinger, *ibid.*, **78**, 2784 (1956).

[25] S. E. Paulsen, *Angew. Chem.*, **72**, 781 (1960).

[26] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

these transition states would be very close to that of the intermediate and to each other. In this way, Brower's result on the identical volume changes of activation for both products from *p*-nitrobenzenediazonium and bromide is explained. On this same basis it can be shown that the measured volume change on activation should be very close to that for reaction 9 alone.

The effect of solvents on reaction rate of benzenediazonium salts was studied by Pray,[27] and is striking mainly for the small range of rates. Within this range the rates are not exactly in the inverse order of dielectric constant. Although the alcohols as solvents give rates somewhat faster than water, the carboxylic acids, in spite of their low dielectric constants, react as slowly as water. In terms of the proposed mechanism, extended in an obvious way to non-aqueous solvents, the nucleophilic character of the solvent enters into the rate to the extent that the reversibility of reaction 9 can be prevented. In these terms the low reactivity in the very weakly nucleophilic solvents can be understood.

Further experiments of a different nature to study the nature of the intermediate are in progress.

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Experimental

Materials.—Benzenediazonium fluoroborate was prepared fresh frequently by conventional methods from the purest available starting materials. All samples used were white and crystalline. Reagent grade potassium thiocyanate of several different batches and two different manufacturers was used. No variations attributable to this source could be seen. Water was distilled in an all-glass still to avoid trace metal catalysis previously observed.[5]

Product Identification.—The gaseous reaction product was transferred to a gas cell and the infrared and ultraviolet spectrum observed. The ultraviolet spectrum showed a strong absorption rich in fine structure spaced at from 1.7 to 2.0 mμ between 199.2 and 213.7 mμ and a further maximum at 196.6 mμ. The same spectrum in all details was obtained from carbon disulfide vapor. In the infrared, carbon disulfide absorption at 6.57 μ was observed, but weaker bands at 11.64 and 4.88 μ were also found and were identical with the stronger bands of carbon oxysulfide. The absence of characteristic ultraviolet absorption showed that isothiocyanic acid, cyanogen, thiocyanogen, hydrogen cyanide and hydrogen sulfide were not important reaction products.

The non-volatile products were identified by ultraviolet spectrum and chromatographic behavior.

A pure sample of phenyl thiocyanate for comparison was not readily obtained. The method of Thurnauer[28] yielded a 27% yield of a distilled material from aniline *via* the Sandmeyer reaction, but it contained about 16% phenyl isothiocyanate by the analysis described below. Chromatography on alumina of a petroleum ether solution of this material gave a pure sample but the yield was low because of extensive hydrolysis on the column. Phenyl thiocyanate was further characterized by nitration,[29] giving a product identical to that prepared by the Sandmeyer reaction with *p*-nitrobenzenediazonium ion.

Phenyl isothiocyanate was a commercial material. Phenyl thiocarbamate, m.p. 96.8–98.6°, was prepared following Riemschneider.[30] It was also obtained in the chromatography of the phenyl thiocyanate.

Analysis.—The aqueous reaction mixtures, consisting of about 50 ml. of solution, were made basic with about 0.6 g. of sodium hydroxide. The mixture was then extracted with five successive 20-ml. portions of isoöctane (2,2,4-trimethylpentane). The isoöctane solution containing also the isoöctane rinsings of the reaction vessel was diluted appropriately and the ultraviolet spectrum was taken. The aqueous solution was acidified with concentrated hydrochloric acid and then extracted with 50 ml. of chloroform. The ultraviolet spectrum of the chloroform extract gave the amount of phenol. The Table III gives the extinction coefficients at the wave lengths used for the analysis of the isoöctane solution, and the absorbance of at least one other wave length was checked. The table shows that only phenyl isothiocyanate can be determined with high precision; the method was developed before the presence of phenyl thiocarbamate was discovered. The analysis did give satisfactory results on some known mixtures.

TABLE III

ANALYTICAL WAVE LENGTHS AND EXTINCTION COEFFICIENTS

Substance	Wave length, mμ 235	245	280
C_6H_5SCN	8.57×10^3	2.36×10^3	40
C_6H_5NCS	3.17×10^3	4.00×10^3	1.13×10^3
$C_6H_5SCONH_2$	3.92×10^3	4.30×10^3	50

Procedure for Product Determination.—A solution contained about 0.02 *M* diazonium salt, 0.035 *M* sulfuric acid and the desired amount of potassium thiocyanate in about 50 ml. These were placed in a 250-ml. flask in the thermostat at 40° for the runs identified as conditions A, B and C in Table I. Pyrex flasks were used for conditions A and B, and Corning "Low Actinic" flasks for condition C. The mixtures were degassed by repeated freezing, evacuation and thawing for conditions B and C. For condition D, most of the potassium thiocyanate solution was boiled under reflux in an oil-bath, and the diazonium salt, dissolved in the rest of the solution, was rapidly added through the reflux condenser. Under these conditions there was substantial hydrolysis of the thiocyanate, and a small amount of fluorobenzene was detected in the isoöctane extract. For condition E, the reagents were mixed cold and the flask, with a condenser attached, was rapidly plunged into an oil-bath heated to 160°. Boiling started in a few seconds. In all cases the reaction was allowed to proceed for at least ten half-lives as calculated from the data of DeTar and Ballentine.[13]

Kinetics.—The more precise apparatus was modeled after that of DeTar and Ballentine[13] except that it was much smaller and therefore did not need such vigorous stirring for our fairly slow reactions. A solution of potassium thiocyanate and acid identical with that in the sample side was placed in the reference side of the apparatus, this accomplished almost complete compensation for the formation of volatile products by the side reaction of thiocyanate hydrolysis. The rate constants were calculated from the slope of the least square line of a plot of log ($P_\infty - P_t$) *vs.* t, where P_∞ is the experimentally determined pressure after at least 10 half-lives and P_t is the pressure at time t.

The other consisted of a small flat-bottomed vessel fitted with a Teflon stirrer driven through a Tru-bore seal. The gas was passed into a jacketed gas buret. The flat-bottomed design with a very small depth of solution allows facile nitrogen evolution without requiring unusually rapid stirring. When the volume was plotted against time in this apparatus, the volume did not become constant but instead rose linearly because of the thiocyanate hydrolysis. This linear portion was extrapolated back to the start of the reaction and the volume of nitrogen was estimated by subtracting the volume at the time t from the volume given by the linear plot at the same time. Since the rate of nitrogen evolution was considerably faster than the evolution of gas by the other reaction, the error was not large. Rate constants were in this case obtained graphically from the slope of the plot of log ($V_\infty - V_t$) *vs.* t, where the volumes are the corrected ones as calculated above. In the absence of thiocyanate no correction need be made so the results are more precise and were used in calculating the average rate constant. It was not practical to operate this apparatus in the absence of air.

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[27] H. A. H. Pray, *J. Phys. Chem.*, **30**, 1477 (1926).

[28] G. Thurnauer, *Ber.*, **23**, 769 (1890).

[29] F. Challenger, C. Higgenbottom and A. Huntington, *J. Chem. Soc.*, 26 (1930).

[30] R. Riemschneider, F. Wojahn and G. Orlick, *J. Am. Chem. Soc.*, **73**, 5905 (1951).