The Rearrangement of Isotopically Labeled Diazonium Salts[1]

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Abstract: The extent of rearrangement of $\mathrm{Ar^{15}N^{+}\equiv N}$ to $\mathrm{ArN^{+}\equiv {}^{15}N}$ accompanying hydrolysis has been studied for Ar = p-$\mathrm{CH_3C_6H_4}$, m-$\mathrm{CH_3\ C_6H_4}$, p-$\mathrm{CH_3OC_6H_4}$, and p-$\mathrm{ClC_6H_4}$. The rate of rearrangement is 0.026 ± 0.012 times the hydrolysis rate in these cases and for the unsubstituted compound studied before, and thus parallels the hydrolysis closely, but the rate does not follow the Hammett σ or ordinary migratory aptitudes. The reaction is kinetically first order, has the same activation energy as the hydrolysis, and is not suppressed by 3 M sodium bromide. It is unaffected by the isotopic composition of dissolved nitrogen. Suppression by nucleophiles is a necessary consequence of a previously suggested mechanism through a diazirine cation; this mechanism must therefore be rejected for this thermal reaction. In only one minor feature is the original evidence wrong: there is no reason to suspect a markedly greater selectivity at low concentration of added nucleophiles. The parallel to the isoelectronic isonitrile rearrangement is very poor.

The rearrangement of diazonium ions labeled with $^{15}\mathrm{N}$ (eq 1) has been observed for benzenediazonium ion[2] and for p-toluenediazonium ion.[3] Some question

$$\mathrm{Ar^{15}N^{+}\equiv N \longrightarrow ArN^{+}\equiv {}^{15}N} \tag{1}$$

was directed at this work when another $^{15}\mathrm{N}$ analysis failed to detect the reaction.[4] The preliminary publication[1] was aimed primarily at dispelling the doubt and resolving the conflicting evidence. In this latter aim it was not successful, but the weight of evidence now favors the reality of eq 1 and in this paper we shall be concerned with a study of the characteristics of the reaction.

Results and Discussion

Several α-$^{15}\mathrm{N}$ labeled substituted benzenediazonium salts were prepared about as before,[3] and the extent of rearrangement following partial hydrolysis (in most cases carried to 80% completion) measured using the degradation with azide. The ratio of rearrangement rate to solvolysis rate ($R = k_r/k_s$) was calculated from the equation $R = -\log(1 - 2p)/2 \log(D_0/D)$, in which p is the fraction of rearrangement in the recovered diazonium salt, and D_0 and D are the initial and final diazonium salt concentrations and values of R found are for the indicated substituent on benzenediazonium ion: p-$\mathrm{CH_3}$, 0.031 (0.029);[3] m-$\mathrm{CH_3}$, 0.018; p-$\mathrm{OCH_3}$, 0.038; p-Cl, 0.023; no substituent, 0.014.[2] Using the rates measured in the course of this work, and activation energies from the literature,[5] the rates at 50° of all reactions were calculated and are presented in Figure 1, as a logarithmic plot comparing k_r with k_s and also with the Hammett σ, to show the absence of correlation. In making this plot it was assumed that the activation energy for rearrangement and that for hydrolysis are identical in every case, although in only two cases has this been shown, as described below.

Table I. Extent of Rearrangement of p-Toluenediazonium Ion

Temp, °C	D/D_0	p_{sec}, %	p_{ars}, %	R_{sec}	R_{ars}
35.9	0.20	5.06	4.67	0.034	0.030
39.8	0.20	4.44	4.64	0.029	0.030
48.8	0.20	4.44	4.92	0.029	0.032
48.8	0.20	(7.57)[a]	4.33	(0.052)[a]	0.029
48.8	0.20	(6.93)[a]	4.17	(0.047)[a]	0.028
48.8	0.20	4.87	4.33	0.032	0.029
62.2	0.20	4.45	4.98	0.029	0.034
48.8	1.00	0.16	0.00	...	...
48.8	1.00[b]	0.08[b]	0.00[b]	...	...
48.8	0.20	4.30[b]	4.57[b]	0.029[b]	0.030[b]
48.8	0.20	4.21	4.84	0.028[c]	0.032[c]
48.8	0.20	4.28	4.12	0.029[c]	0.029[c]
48.8	0.20	4.74	(7.07)[a]	0.031[d]	(0.048)[a,d]
48.8	0.20	3.87	3.97	0.024[d]	0.026[d]
48.8	0.20	4.28	4.63	0.029[d]	0.030[d]
48.8	0.20	4.45	4.53	0.029[e]	0.030[e]
48.8	0.20	4.38	5.14	0.029[f]	0.034[f]
48.8	0.80	0.99	0.97	0.045	0.044
48.8	0.80	1.26	1.04	0.052	0.047
48.8	0.60	2.14	1.78	0.043	0.035
48.8	0.60	2.14	1.77	0.043	0.035
48.8	0.60	1.52	1.40	0.030	0.028
48.8	0.40	3.13	2.90	0.035	0.033
48.8	0.40	2.95	3.48	0.033	0.039
48.8	0.10	7.32	6.97	0.034	0.033

[a] These results are rejected. [b] Dilute solution with ion-exchange work-up. [c] Sodium bromide added after hydrolysis, before sodium azide. [d] Hydrolysis in the presence of 2.93 M sodium bromide. [e] Hydrolysis in sealed system. [f] Tank nitrogen passed through during hydrolysis.

The most extensive studies on the rearrangement have been on p-toluenediazonium ion, and these results are presented in Table I, which shows all the new measurements on the extent of rearrangement of this compound accompanying the thermal hydrolysis. Of a total of over 80 measurements on this and the other diazonium salts, three seemed so far out of line that they have been rejected. They are presented parenthetically and marked *a;* but no important results would be changed if they were included. In each case the two analyses were not concordant. The subscripts sec and ars refer respectively to analyses based upon secondary nitrogen and upon nitrogen resulting from arsenite reduction of the p-tolyl azide. The extents of rearrange-

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(1) From a part of the Ph.D. thesis of R. E. Holliday, Rice University, 1966. This is Reactions of Diazonium Salts with Nucleophiles. XIV. Some of this work was published in preliminary form: E. S. Lewis and R. E. Holliday, *J. Am. Chem. Soc.*, **88**, 5043 (1966).

(2) J. M. Insole and E. S. Lewis, *ibid.*, **85**, 122 (1963).

(3) E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32 (1964).

(4) A. K. Bose and I. Kujayevsky, *ibid.*, **88**, 2325 (1966).

(5) (a) D. F. Detar and A. R. Ballentine, *ibid.*, **78**, 3916 (1956); (b) M. L. Crossley, R. H. Kienle, and C. H. Benbrook, *ibid.*, **62**, 1400 (1940).

ment, p, are derived from eq 2 and 3 of ref 3; in contrast to the earlier work several experiments were done with atom fractions of label initially in the α position (f_{Dp}) as low as 47%.

In the earlier work,[3] the value of R for the unsubstituted compound was believed to be temperature independent based upon only one experiment at a temperature 15° lower than the others. The first seven entries in Table I show in a more convincing way that for the p-toluenediazonium ion, R shows no trend with temperature and no variation outside of experimental error. We may therefore conclude that the rearrangement and hydrolysis reactions have the same rather high activation energy, and since they share the same very unusual substituent effects, they must be very similar in mechanism. It is necessary to demonstrate that the rearrangement reaction is kinetically first order in order to suggest further relationships. The last eight entries in the table show the extent of rearrangement at various extents of reaction from 20 to 90%. They are not in general as precise as the ones at 80% completion. At small extents of completion, the amount of rearrangement is very low and hence much less certain (the enrichment in the nitrogen collected is less than twice natural abundance) at 90% completion, the amount of diazonium salt left to work with is small. These data were presented graphically in the preliminary publication,[1] and the individual numbers confirm that R is essentially the same at all extents of completion. An independent and more rigorous test of first-order behavior is illustrated in results marked *b*. In this experiment, the initial concentration of diazonium salt was more dilute by a factor of 50, yet the relation between rearrangement and hydrolysis is unaltered. A control is also presented to show that the special ion-exchange work-up necessary for these dilute solutions did not cause rearrangement. Two other entries (marked *e* and *f*) show that dissolved nitrogen is not involved. In most of the runs, the gas evolved, largely $^{15}N{\equiv}^{14}N$, was allowed to escape into the atmosphere. In the run marked *e*, the concentration of $^{15}N{\equiv}^{14}N$ was perceptibly higher, since the nitrogen escaped only into the restricted gas phase over the liquid in a sealed system. In another run, *f*, tank nitrogen was passed through the solution during the reaction, without altering the extent of rearrangement. The run in very dilute solution also confirms that the concentration or isotopic composition of free dissolved nitrogen is irrelevant. The experiment previously described[3] showing that carbon monoxide is not incorporated is closely related.

It should be noted that the nonparticipation of nitrogen or carbon monoxide has no bearing on the presumed low selectivity of the reaction. Thus if carbon monoxide were as nucleophilic as water, the low solubility of carbon monoxide even at 60 atm leads to a predicted yield of less than 0.1% of benzoic acid since the concentration ratio of water to carbon monoxide is over a thousand. A benzoic acid yield of 1% would have been conspicuous, but less than 0.1% might have been overlooked. Thus a slight reaction with dissolved nitrogen is entirely conceivable, it is only shown that the rearrangement reaction observed can not be of this sort. We thus arrive at a description of the transition state for the rearrangement reaction very similar to that for the hydrolytic reaction,[6] namely with a very weak bond between the α-nitrogen and carbon, and no other bonds of great strength. It is in fact tempting to suggest that the very slight role of the nucleophile in the substitution reactions[6] is taken by the β-nitrogen. However, the transition state is not strongly bonded to either nitrogen, and a transition state related to that leading to the phenonium ion[7] can be rejected, because the substituent effects do not fall in the order of migratory aptitudes.

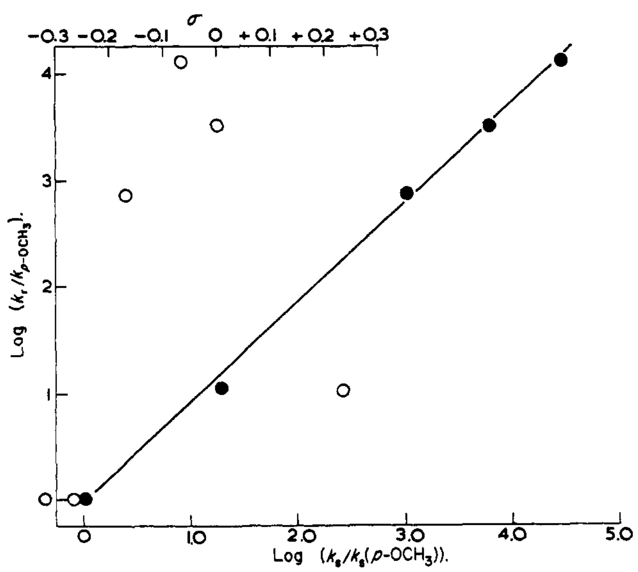

Figure 1. Relation between rearrangement rates, k_r (relative to that of the p-methoxybenzene diazonium ion), and hydrolysis rates (k_s) also relative to that of the p-methoxy compound, ●, lower scale, ○, relation between k_r and Hammett σ.

In view of this evidence on the transition state leading to rearrangement, the proposal of a stable spirodiazirine cation intermediate[8] in this reaction is open to suspicion. The basis of this proposal was a quantitative agreement between the extent of rearrangement and a component of a rate term obtained by a linear extrapolation of the rate in the presence of thiocyanate to zero concentration. The rate curve[8] is presented again in Figure 2, which also shows the rate of hydrolysis of p-toluenediazonium ion in the presence of sodium bromide,[9] and extrapolations of the linear portions to zero salt concentrations are shown for both curves. The reasonable agreement of the two intercepts was at first taken as confirmation of the mechanism, but more recent work has strongly suggested that the curvature in plots such as these is entirely attributable to a salt effect on the reaction of the diazonium salt with the anion.[6] If the mechanism through the spirocyclic intermediate is correct in detail, then one can make the unequivocal prediction that in the presence of fairly high concentrations of nucleophile, the return from the intermediate to the diazonium ion, half of which resulted in rearrangement, must be virtually totally suppressed. This must be the case with a thiocyanate concentration of about 1.5 M thiocyanate or 3 M bromide. Experiments were done with bromide ion rather than thiocyanate to avoid the introduction of extraneous ni-

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(6) E. S. Lewis, L. D. Hartung, and B. M. McKay, *J. Am. Chem. Soc.*, **91**, 419 (1969).

(7) D. J. Cram, *ibid.*, **86**, 3767 (1964).

(8) E. S. Lewis and J. M. Insole, *ibid.*, **86**, 34 (1964).

(9) J. M. Insole, unpublished measurements.

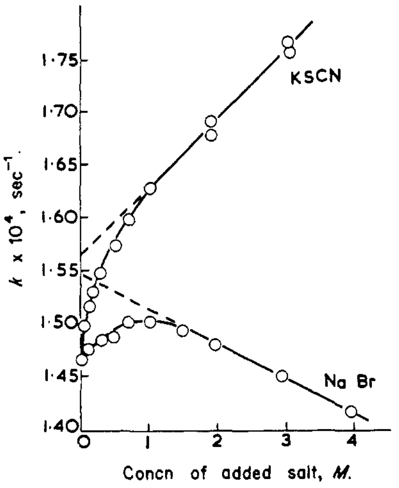

Figure 2. Effect of two salts on the rate of hydrolysis of *p*-toluenediazonium ion: upper curve, ref 8; lower curve, ref 9.

trogenous substances. The entries in Table I marked *c* show that a high bromide concentration added after partial hydrolysis does not interfere with the degradation scheme, the ones marked *d* show that there is no great reduction (if any) in the extent of the rearrangement, when the hydrolysis of the diazonium ion is conducted in 2.93 *M* sodium bromide. This failure of the prediction based on the mechanism involving the intermediate diazirine cation then forces us to the conclusion that the relation found earlier[8] between the over-all rate data in the presence of nucleophiles and the extent of rearrangement was pure coincidence. The evidence for the intermediacy of the diazirine cation having disappeared, this mechanism must be abandoned.

One further isolated piece of evidence was found for a selective intermediate in the hydrolysis. The ratio of aryl thiocyanate to aryl isothiocyanate was believed to be markedly increased at low thiocyanate concentrations, based upon a very low yield of *p*-tolyl isothiocyanate at the lowest concentration studied in one experiment. Reinvestigation shows that the yield of *p*-tolyl isothiocyanate in about 0.1 *M* potassium thiocyanate solution was about 1.6%, about ten times the yield found before. Furthermore, the ratio of peak heights of tolyl isothiocyanate and thiocyanate in a gas chromatographic analysis of an extract of the product was essentially independent of the concentration of potassium thiocyanate. The values at 0.1, 0.2, 0.4, and 0.8 *M* potassium thiocyanate were 1.44, 1.39, 1.45, and 1.45, respectively. These are not yield ratios because some of the thiocyanate is destroyed by hydrolysis,[10] but reproducibility of conditions gave reasonable assurance that this did not vary in extent.

Another demonstration of insensitivity of the selectivity to concentration was a study of the ratio of peak height ratios (uncorrected for widths and detector sensitivities) of chlorobenzene to bromobenzene when the diazonium salt was decomposed in solution containing sodium chloride and sodium bromide at equal molar concentrations. These ratios were, at sodium chloride concentration of 0.063, 0.125, 0.50, 1.00, and 2.00 *M*, respectively, 1.16, 1.14, 1.14, 0.98, and 0.89. The high concentration deviation is small, and in the direction of increased selectivity at higher concentrations. Thus the suggestion of a low concentration increase in selectivity must be abandoned.

The identification of the mechanism of the rearrangement as a simple unimolecular isomerization suggests the parallel to the reactions of the isoelectronic isonitriles, RN≡C, which rearrange to the nitriles unimolecularly in the gas phase[11] and also rearrange in solution by an apparently similar mechanism.[12] Nevertheless, although both reactions have lost a great deal of bond strength in the transition state, the diazonium salts show large substituent effects whereas the isocyanates show almost none.[12] Part of the difference certainly arises from the very large ground-state resonance stabilizations in the charged diazonium ions, part may be attributed to the significant asymmetry of the isonitrile rearrangement, but the difference still appears very large. The transition states for the isonitrile rearrangements involve imperceptible "carbonium cyanide" character, in very marked contrast to the resemblance of the transition state for the diazonium ion rearrangement to the phenyl cation.

Experimental Section

Anisamide-^{15}N. Ammonium-^{15}N chloride (1.04 g) was dissolved in a mixture of chloroform (400 ml) and water (10 ml) and cooled to 0° in an ice–salt bath. Sodium hydroxide (1.7 g) in 10 ml of water and anisoyl chloride (3.3 g) were added to the mixture, and the well-stoppered flask was shaken vigorously for 6 hr. The chloroform layer was first extracted with 1 *N* sodium hydroxide (50 ml) and then with water (50 ml). The crude product, which remained upon concentration of the chloroform layer by evaporation, was crystallized from 250 ml of water and dried under vacuum. Anisamide-^{15}N was obtained in the amount of 2.43 g (84% yield based on ammonium-^{15}N chloride). The product melted at 165–167° (lit.[13] 166.5–167.5°).

***p*-Anisidine-^{15}N.** The preparation of *p*-anisidine-^{15}N from anisamide-^{15}N closely followed the method used by Buck and Ide[14] in the preparation of 4-aminoveratrole from veratric amide.

Finely powdered anisamide-^{15}N (2.43 g) was shaken with a solution of sodium hypochlorite (100 ml) prepared by the addition of chlorine to 1 *M* sodium hydroxide at 0°. A 5% excess of hypohalite, as determined iodimetrically, was used. The mixture was slowly warmed to 70°. The amide dissolved around 35–40°. After maintaining the temperature at 70° for 45 min, more sodium hydroxide (6 g in 15 ml of water) was added, and the temperature was increased to 80° and maintained for 50 min.

After cooling in an ice-water bath, the reaction mixture was extracted with four 50-ml portions of benzene. After evaporation of the benzene on a rotary evaporator at reduced pressure, a red oil remained; this crystallized upon cooling. The crude product was purified by vacuum sublimation at 60°. After two sublimations, *p*-anisidine-^{15}N, which melted at 56.5–57° (lit.[15] 57°), was obtained. The yield was 1.36 g (68%).

***p*-Methoxybenzenediazonium-α-^{15}N Fluoroborate.** This was prepared by a method similar to that used by Ugi, Perlinger, and Behringer[16] to prepare *p*-ethoxybenzenediazonium-β-^{15}N chloride. *p*-Anisidine-^{15}N (1.36 g) was dissolved in 3 g of 37–40% fluoroboric acid and a small amount of water. The solution was evaporated to dryness on a rotary evaporator at 60°, leaving the solid amine salt, *p*-methoxyanilinium-^{15}N fluoroborate. The salt was dissolved in methanol (50 ml) and cooled to 0°. Ethyl nitrite (0.9 g in 10 ml of ether), 3 g of fluoroboric acid, and 0.5 ml of concentrated hydro-

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[10] E. S. Lewis and J. E. Cooper, *J. Am. Chem. Soc.*, **84**, 3847 (1962).

[11] F. W. Schneider and B. S. Rabinovitch, *ibid.*, **84**, 4215 (1962); **85**, 2365 (1963).

[12] J. Casanova, Jr., N. D. Warner, and R. E. Schuster, *J. Org. Chem.*, **31**, 3473 (1966).

[13] C. D. Hodgman, Ed., "Handbook of Chemistry and Physics," The Chemical Rubber Publishing Co., Cleveland, Ohio, 1960.

[14] A. H. Blatt, Ed., "Organic Syntheses," Coll. Vol. II, John Wiley & Sons, Inc., New York, N. Y., 1948, p 44.

[15] G. Harris, Ed., "Dictionary of Organic Compounds," Oxford University Press, Oxford, 1965.

[16] I. Ugi, H. Perlinger, and L. Behringer, *Ber.*, **92**, 1865 (1959).

chloric acid were added to the stirred solution. After 30 min, several hundred milliliters of ether was added to precipitate the diazonium salt.

The *p*-methoxybenzenediazonium-α-^{15}N fluoroborate was purified by dissolving it in 200 ml of methanol at room temperature. After cooling the solution in an ice–salt bath, the diazonium salt was precipitated by the addition of ether to the stirred solution. The *p*-methoxybenzenediazonium-α-^{15}N fluoroborate was filtered, dried under vacuum, and stored in the refrigerator. The yield was 2.27 g (92%); $\lambda_{\max}$[17] 313 nm (ϵ 2.53 × 10^{4}).

p-Toluamide-^{15}N. This was prepared as before,[3] it melted at 157–160° (lit.[18] 158°), and was obtained in 94% yield.

p-Toluidine-^{15}N Hydrochloride. The treatment of *p*-toluamide-^{15}N with sodium hypobromite solution was as described before.[3] The *p*-toluidine-^{15}N was steam distilled. Extraction of the distillate with ether and precipitation of the amine with anhydrous hydrogen chloride gave *p*-toluidine-^{15}N hydrochloride in 53% yield. The amine hydrochloride melted (in a sealed tube) at 239–242° (lit.[13] 243°).

p-Toluenediazonium-α-^{15}N Fluoroborate. Diazotization of the amine hydrochloride followed the procedure used by Lewis, Kinsey, and Johnson to prepare *p*-trideuteriomethylbenzenediazonium fluoroborate.[19] The diazonium salt was obtained in 95% yield; $\lambda_{\max}$ 278 nm (ϵ 1.56 × 10^{4}) (lit.[17] $\lambda_{\max}$ 277 nm (ϵ 1.63 × 10^{4})).

p-Chlorobenzenediazonium-α-^{15}N Fluoroborate. The method used to prepare *p*-methoxybenzenediazonium-α-^{15}N fluoroborate was used, except that the *p*-chlorobenzamide-^{15}N was not purified by recrystallization and *p*-chloroaniline-^{15}N was purified by vacuum sublimation at 80°. The amine, which melted at 69–70.5° (lit.[13] 70–72°), was obtained in 71% yield (1.69 g) based on ammonium-^{15}N chloride. It was converted to *p*-chlorobenzenediazonium-α-^{15}N fluoroborate in 90% yield by diazotization of *p*-chloroaniline-^{15}N with ethyl nitrite; $\lambda_{\max}$ 280 nm (ϵ 1.78 × 10^{4}) (lit.[17] $\lambda_{\max}$ 280 nm (ϵ 1.79 × 10^{4})).

m-Toluenediazonium-α-^{15}N Fluoroborate. The same procedure as *p*-methoxybenzenediazonium-α-^{15}N fluoroborate was used, except that *m*-toluamide was not purified by recrystallization, and the amine was steam distilled from the reaction mixture. Extraction of the distillate with ether and addition of anhydrous hydrogen chloride to the ether solution gave 0.67 g (50% based on ammonium-^{15}N chloride) of *m*-toluidine-^{15}N hydrochloride. The melting point was 218–220° (lit.[13] 228°). The hydrochloride was converted into the fluoroborate salt[19] and diazotized with ethyl nitrite in methanol. *m*-Toluenediazonium-α-^{15}N fluoroborate in the amount of 0.59 g (61% yield) was obtained. Although the extinction coefficient of *m*-toluenediazonium-α-^{15}N fluoroborate could not be accurately measured because of the rapid hydrolysis of the *m*-toluenediazonium ion, its uv spectrum was identical in form to the spectrum of *m*-toluenediazonium fluoroborate prepared from purified *m*-toluidine;[6] $\lambda_{\max}$ 267 nm ($\epsilon \simeq$ 1.2 × 10^{4}), with a broad shoulder at 313 nm.

Hydrolysis of the Labeled Diazonium Salts. The labeled diazonium salt was dissolved in 10 ml of preheated 0.01 *N* sulfuric acid and placed in a constant-temperature bath. The reaction vessel was covered with aluminum foil to exclude light. The extent of reaction was calculated from the first-order rate constants given in Table II. The reaction was quenched by rapid cooling in an acetone–Dry Ice bath. The reaction mixture was extracted with ether to remove the phenol. The dissolved ether was removed by bubbling air through the aqueous phase under reduced pressure. Degradation to determine the extent of nitrogen turnaround was carried out on this diazonium salt solution.

Table II. First-Order Rate Constants for the Hydrolysis of Benzenediazonium Salts

Substituent	Rate constant	Temp, °C	Ref
p-Methyl	0.244 × 10^{-4} sec^{-1}	35.9	19
	0.4065	39.8	19
	1.468	48.8	8
	8.51	62.2	19
p-Methoxy	0.55 × 10^{-4} sec^{-1}	90.5	9, this work
p-Chloro	2.31 × 10^{-4} sec^{-1}	79.8	This work
m-Methyl	15.9 × 10^{-4} sec^{-1}	40.1	6

With *p*-methoxybenzenediazonium-α-^{15}N fluoroborate it was necessary to carry out the hydrolysis in a more dilute solution and with a greater amount of added acid (250 mg of diazonium salt dissolved in 150 ml of 0.1 *N* sulfuric acid) in order to suppress coupling. After 80% reaction, the solution was concentrated to a volume of 35 ml by partial evaporation of the water. Evaporation of the water at low temperature (below 35°) was carried out effectively using a rotary evaporator and a mechanical pump.

Reaction of Diazonium Salts with Sodium Azide. The reaction of the diazonium salts with sodium azide was identical in procedure with that described by Lewis and Insole.[2,3] The azide reactions were run in aqueous ethanol (13 parts water, 10 parts ethanol by volume). The diazonium salt solution was cooled to −27° in an acetone bath and sodium azide (a threefold excess) in 2 ml of aqueous ethanol (five parts water, one part ethanol by volume) was added. After 1.5 hr the solution was placed on the vacuum line and degassed by freezing and thawing while under vacuum. The temperature of the solution containing the aryl pentazole was kept below −10° during the degassing process. When the solution was warmed to room temperature, the "secondary" nitrogen was evolved. The "secondary" nitrogen was collected for analysis. The solution containing substituted phenyl azide was saved for the next step.

Reduction of the Aryl Azides with Sodium Arsenite. A mixture of potassium hydroxide (0.6 g) and arsenic trioxide (0.34 g) in 2 ml of aqueous ethanol (5 to 1 by volume) was added to the substituted phenyl azide solution. Both solutions had previously been thoroughly degassed. The temperature of the reaction mixture was kept at room temperature for 4 hr and then increased to 50° to ensure completion of the reaction. The "arsenite" nitrogen was collected for analysis. All samples of nitrogen for analysis were transferred to an evacuated sample tube from the reaction vessel (cooled in liquid nitrogen) with a Toepler pump. The samples were then sealed until needed for analysis.

Analysis of Nitrogen Samples. All nitrogen samples were analyzed on a Bendix Time-of-Flight mass spectrometer by Mr. Peter M. Hierl of Rice University. The per cent nitrogen-15 contained in a sample was calculated from the ratio of the 29 to 28 peaks. All samples were checked for oxygen content. The size of the 32 peak (oxygen) was taken as a direct measure of air leakage in the vacuum line or in the inlet system of the mass spectrometer. Corrections were always applied but were never significant.

Hydrolysis of p-Toluenediazonium-α-^{15}N Fluoroborate in Dilute Solution. An ion-exchange technique was used in connection with the hydrolysis of *p*-toluenediazonium-α-^{15}N fluoroborate in dilute solutions. This procedure was necessary in order to utilize the normal degradative method. Since proper degassing of a large volume of solution could not be readily achieved, the diazonium salt solution was concentrated to a smaller volume by the ion-exchange technique described below.

p-Toluenediazonium-α-^{15}N fluoroborate (356 mg) was dissolved in 1000 ml of 0.01 *N* sulfuric acid. After 80% hydrolysis at 48.8°, the reaction was quenched by rapid cooling. The cold reaction mixture was then slowly passed through an ion-exchange column prepared from Amberlite IR-120H resin (1 g).

The diazonium salt was eluted from the column by slow addition of aqueous barium chloride (5 g in 100 ml of 0.01 *N* sulfuric acid). The elution of the diazonium ion was followed by coupling a small portion of the eluent with R-salt (2-naphthol-3,6-disulfonic acid disodium salt). The major part of the diazonium salt was eluted from the column by the first 35 ml of barium chloride solution. A slight excess of sodium sulfate in 10 ml of water was added to precipitate the barium ion as barium sulfate. After removal of the barium sulfate by centrifugation, the remaining 45 ml of diazonium salt solution was carried through the usual analytical degradation. All of the ion-exchange work was done in the cold room (5°).

A control run was made in which *p*-toluenediazonium-α-^{15}N fluoroborate (100 mg) was dissolved in 1000 ml of 0.01 *N* sulfuric acid at 5° and placed on an ion-exchange column. The isolation of the diazonium ion was identical with that described above.

The Rate of Hydrolysis of p-Chlorobenzenediazonium Fluoroborate. The rate was measured at 79.8° by the method of Lewis, Kinsey, and Johnson.[19] *p*-Chlorobenzenediazonium fluoroborate (50 mg) in 200 ml of 0.01 *N* sulfuric acid was allowed to warm up

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

(18) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1958, p 279.

(19) E. S. Lewis, J. L. Kinsey, and R. R. Johnson, *J. Am. Chem. Soc.*, **78**, 4294 (1956).

for 20 min in the constant-temperature bath before starting measurements.

The Rate of Hydrolysis of *p*-Methoxybenzenediazonium Fluoroborate. This rate was measured at 90.5°, and confirmed the first-order rate constant measured at this temperature by Insole.[9] The method of measurement was identical with that described above for *p*-chlorobenzenediazonium fluoroborate.

The Determination of *m*, the Fraction of Primary Nitrogen. The fraction of primary nitrogen, *m*, was determined by measuring the volumes of primary and secondary nitrogen formed in the azide reaction.

p-Chlorobenzenediazonium fluoroborate (160 mg) was dissolved in a solution of aqueous ethanol (50 ml of 0.01 *N* sulfuric acid, 39 ml of ethanol) and cooled to −27°. Carbon dioxide was bubbled through the well-stirred solution until all of the dissolved air was removed from the system. A threefold excess of sodium azide in 10 ml of 5 to 1 aqueous ethanol was added to the diazonium salt solution through a rubber septum in the top of reactor. (The azide solution had been degassed previously.) The primary nitrogen, which was evolved over a 1-hr period, was swept from the reactor with carbon dioxide and collected in a nitrometer containing 50% potassium hydroxide solution. After the primary nitrogen was collected, the pentazole solution was warmed to room temperature, and the secondary nitrogen was collected in a similar manner. Corrections were made for impurities present in the carbon dioxide by running a blank. The fraction of primary nitrogen, *m*, was calculated by simply dividing the volume of primary nitrogen collected by the total volume of nitrogen collected. The values of *m* measured were: *m*-toluenediazonium ion, $m = 0.71$; *p*-chlorobenzenediazonium ion, $m = 0.78$; *p*-methoxybenzenediazonium ion, $m = 0.64$.

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Relation between Thermal and Photochemical Hydrolyses of Diazonium Salts[1]

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Abstract: In the presence of chloride ion, aryl chlorides as well as phenols result from the photolysis of arenediazonium salts in aqueous solution, as in the thermal reaction. Benzenediazonium ion in aqueous sodium chloride yields just as much chlorobenzene in the photolysis as it does thermally at the same temperature, but others (*p*-$CH_3C_6H_4N_2^+$, *p*-$ClC_6H_4N_2^+$) give a significantly higher yield of the chloride photochemically than thermally. A similarity but not identity of product-determining steps is indicated. When *p*-$CH_3C_6H_4{}^{15}N^+{\equiv}N$ and *p*-$CH_3OC_6H_4{}^{15}N^+{\equiv}N$ are exposed to light insufficient to complete the photolysis, the residual diazonium salt is in part rearranged to $Ar^+N^{15}{\equiv}N$, and the relative extents of rearrangement to hydrolysis are significantly more than in the corresponding dark hydrolysis. There are major uncertainties in the photochemical mechanism, but it can be unequivocally concluded that there is no single intermediate common to the photochemical and thermal reactions.

The photosensitivity of diazonium salts has long been known and has been the subject of much published work[5,6] and probably a great deal of unpublished work also, since destruction of diazonium salts by light is the basis of "diazotype" processes. Very little modern photochemistry has been done on solutions of diazonium salts; a paper on *p*-nitrobenzenediazonium ion in ethanol disclosed the contribution of both radical and ionic processes,[7] but uncovered more questions than were answered. It was established that a phenol-forming reaction is important in photolysis of aqueous solutions, suggesting that the photolysis of diazonium salts constituted an alternative synthesis of the aryl cation, the proposed[8] intermediate in the thermal hydrolysis. Although the intermediate was believed to be highly reactive, it might be characterized by the result of competition for it between chloride ion and water, *i.e.*, relative the yields of chlorobenzene and phenol.[9] If the thermal and photochemical reactions passed through a common intermediate (the aryl cation or some other), then the yield of chlorobenzene in the reaction of benzenediazonium ion in a given solution of sodium chloride in water should be independent of whether the necessary energy is provided thermally or photochemically.

The intermediacy of an irreversibly formed aryl cation in the thermal reaction is now eliminated,[10] but the existence of a high-energy nitrogen containing intermediate was rejected only because no satisfactory structure could be proposed. The possibility of a common intermediate therefore remained a remote possibility and was worth investigating.

When the two nitrogens of a diazonium salt are rendered distinguishable by nitrogen labeling, a rearrangement accompanies thermal hydrolysis,[11] and the mech-

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(2) John Simon Guggenheim Fellow at the Physical Chemistry Laboratory, Oxford, 1968.

(3) National Aeronautics and Space Administration Trainee, 1964–1966.

(4) Robert A. Welch Foundation predoctoral fellow, 1963–1966.

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