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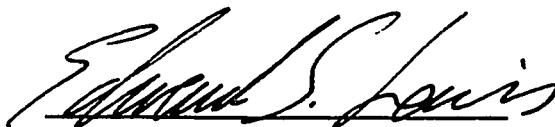
The Rearrangement of Isotopically
Labeled Diazonium Salts

by

Robert E. Holliday

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
Doctor of Philosophy

Thesis Director's signature:

A handwritten signature in black ink, reading "Edmund S. Lewis", written over a horizontal line.

Houston, Texas

June 1966

To
L.A.B.H.

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Dr. E.S. Lewis, who conceived and directed this work, and to Mr. Peter M. Hierl, who carried out all mass spectrometric analyses.

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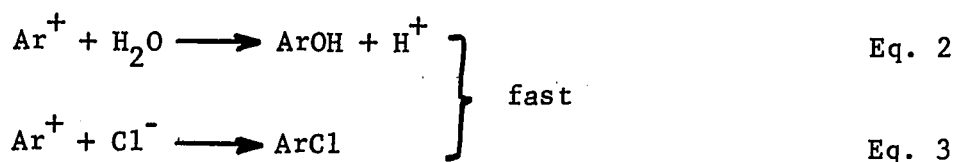
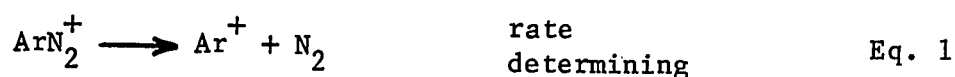
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INTRODUCTION

Numerous studies of the hydrolysis of benzenediazonium salts have appeared in the chemical literature in recent years. The structure of the intermediate(s) in the reaction has received considerable attention.

The phenyl cation has often been proposed as an intermediate in the reaction (1,2). In this mechanism the rate-determining step is the unimolecular loss of nitrogen to produce the very reactive phenyl cation, Eq. 1. Once formed, the phenyl cation rapidly reacts with a nucleophile such as water or chloride ion to yield phenol or chlorobenzene, Eq. 2-3. According to this mechanism, the rate of reaction



should be solely a function of the diazonium ion concentration, Eq. 4.

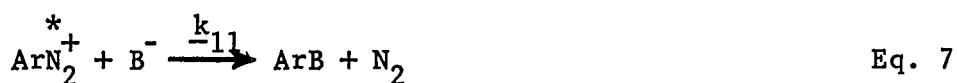
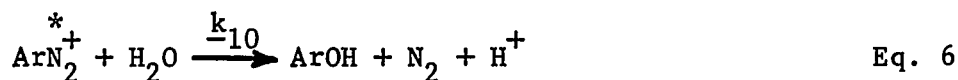
$$-\frac{d(\text{ArN}_2^+)}{dt} = k(\text{ArN}_2^+) \quad \text{Eq. 4}$$

Decomposition of the diazonium ion by a mechanism involving a highly reactive intermediate such as the phenyl cation is supported by the following observations: the rate of reaction is changed very little by the addition of nucleophiles (3,4); the rate is almost independent of acid concentration over a wide range (4-6); the rate has a

low solvent sensitivity (7); and the intermediate has a low selectivity toward various nucleophiles in competitive experiments (2,8,9).

Lewis and Cooper found that the rate of disappearance of diazonium ion is increased by the addition of the thiocyanate ion (8). This observation is inconsistent with the mechanism involving the irreversibly formed phenyl cation, Eq. 1-3. Although this rate increase is small (less than 20% at 5 M thiocyanate ion), it is too large to be explained by salt effects. In fact, it appears that the effect of most salts operates in the opposite direction. When salts containing poorly nucleophilic anions are added to the reaction mixture, the rate of decomposition of the diazonium ion is slightly suppressed (4,9,10). Thus sodium bisulfate (9), sodium sulfate (4), and potassium nitrate (4) suppress the rate.

The mechanism proposed by Lewis and Cooper to explain the acceleration in rate by the thiocyanate ion (8) includes a reversibly formed intermediate which can return to diazonium ion or react with a nucleophile, B^- , Eq. 5-7. In these equations and in the following discussion, the nomenclature of Lewis and Cooper is used.

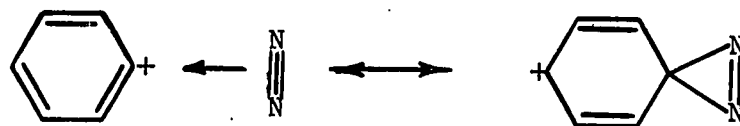


If the assumption is made that the intermediate, ArN_2^{*+} , does not accumulate, the steady-state approximation (11) can be applied to the system, and Eq. 8 is obtained.

$$-\frac{d(\text{ArN}_2^+)}{dt} = \frac{[k_{-10}(\text{H}_2\text{O}) + k_{11}(\text{B}^-)]}{[k_{-9} + k_{10}(\text{H}_2\text{O}) + k_{11}(\text{B}^-)]} k_9(\text{ArN}_2^+) \quad \text{Eq. 8}$$

If $k_{-9} \ll k_{10}(\text{H}_2\text{O}) + k_{11}(\text{B}^-)$, the right-hand side of Eq. 8 reduces to $k_9(\text{ArN}_2^+)$. The expression is then identical to Eq. 4 and cannot account for the acceleration in rate by the thiocyanate ion. However, if $k_{-9} > k_{10}(\text{H}_2\text{O}) + k_{11}(\text{B}^-)$ (or is at least comparable in magnitude), the right-hand side of Eq. 8 reduces to $[k_{10}(\text{H}_2\text{O}) + k_{11}(\text{B}^-)]k_9(\text{ArN}_2^+)/k_{-9}$. This new expression accounts for the acceleration in rate by the thiocyanate ion and fits the observed kinetics. The conclusion of the work is that a significant fraction of the intermediate, ArN_2^{*+} , returns to the diazonium ion in a reversible step.

Several structures have been proposed for the reversibly formed intermediate (8). Among these are a charged caged pair, I, $\text{Ar}^+ \text{N}_2^-$, and a π -complex or diazacyclopentadiene intermediate, II. Both of these



II

intermediates should be similar to the phenyl cation in reactivity, and the experimental data which has been presented in support of the phenyl cation as an intermediate in the reaction should also be applicable to structures I and II.

The possibility of the existence of II as an intermediate is of considerable interest, since in this structure the nitrogens are equivalent, whereas in the diazonium ion they are distinctly different (12). A label in the diazonium ion would show scrambling upon partial hydrolysis if II is the structure of the reversibly formed intermediate.

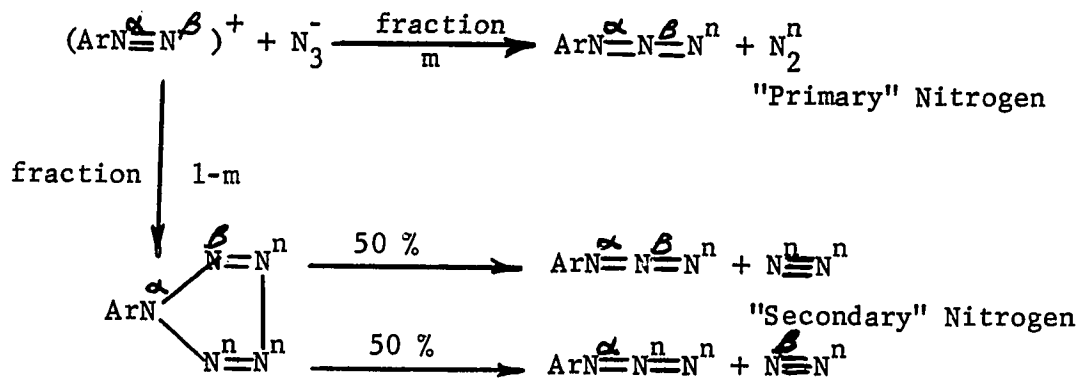
Investigations using nitrogen-15 as a label were carried out by Lewis and Insole, who prepared the benzenediazonium- α - ^{15}N and *p*-toluenediazonium- α - ^{15}N fluoborates and found that upon partial hydrolysis and subsequent workup of the remaining diazonium salt, a small amount of scrambling of the nitrogen label (which they termed the "turnaround" reaction) had occurred (13,14). At 80% hydrolysis the values for the turnaround reaction were roughly 2.2% for benzenediazonium ion and 4.5% for *p*-toluenediazonium ion.

Degradation of the diazonium ion to determine the extent of turnaround is based upon the reaction of the azide ion with the diazonium ion. The mechanism of this reaction has been elucidated by the work of Clusius (15), Huisgen, and Ugi (16). A review of this reaction is presented in Advances in Heterocyclic Chemistry (17). Chart I shows the degradation scheme.

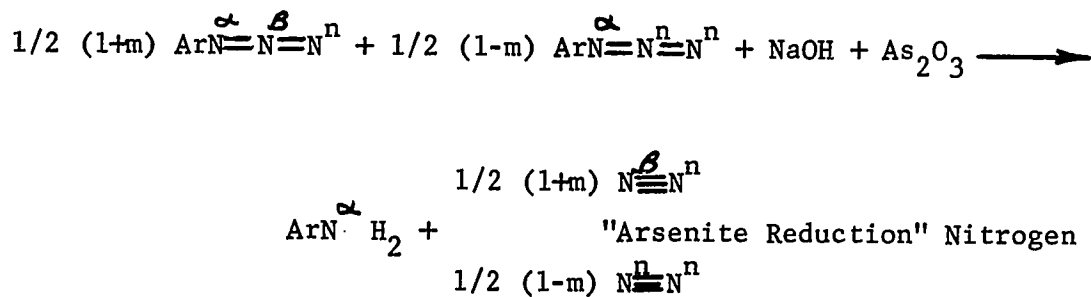
The reaction with azide ion is carried out in aqueous ethanol at -27°C. The products of this reaction are phenyl azide, phenyl pentazole, and nitrogen. Upon warming the solution to room temperature, the phenyl pentazole decomposes to phenyl azide and "secondary" nitrogen. The phenyl azide from both reaction routes is reduced with sodium arsenite to aniline and nitrogen (18,19). Upon analysis of the

Chart I
Degradation Scheme

Azide Reaction



Sodium Arsenite Reduction



various fractions of nitrogen with a mass spectrometer, the fraction of molecules that have undergone the turnaround reaction, p , can be calculated using Eq. 9-10 (14).

$$p = 4(f_S - f_N)(1 - f_N) / (f_D - f_N) \quad \text{Eq. 9}$$

$$p = \frac{4(f_A - f_N)(1 - f_N)}{(m+1)(f_D - f_N)} \quad \text{Eq. 10}$$

where m = the fraction of "primary" nitrogen

f_S = the atom fraction of ^{15}N in the "secondary" nitrogen

f_A = the atom fraction of ^{15}N from reduction of the aryl azide

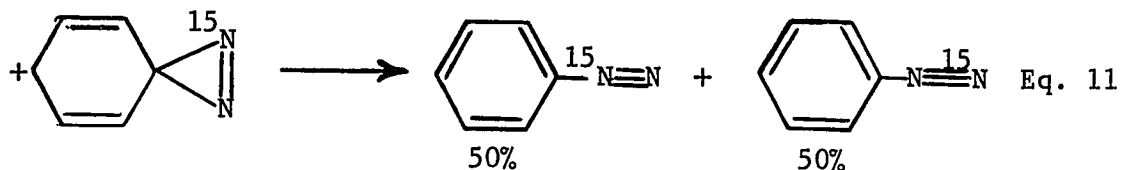
f_D = the atom fraction of ^{15}N in the α -position of the diazonium salt

f_N = natural abundance of ^{15}N

p = the fraction of molecules of diazonium salt which have undergone the turnaround reaction.

Benzenediazonium - α - ^{15}N fluoborate and *p*-toluenediazonium- α - ^{15}N fluoborate were degraded both before and after hydrolysis to show that the turnaround reaction occurred only under the conditions of hydrolysis.

Although these labeling experiments clearly demonstrate the presence of a reversible step in the hydrolysis of the benzenediazonium ion as was proposed by Lewis and Cooper (8), the intermediate responsible for the turnaround reaction cannot account for all of the observed acceleration of the rate by the thiocyanate ion. If the turnaround reaction goes through a symmetrical intermediate such as II, rearranged material will be formed half the time, Eq. 11. Therefore, the rate of



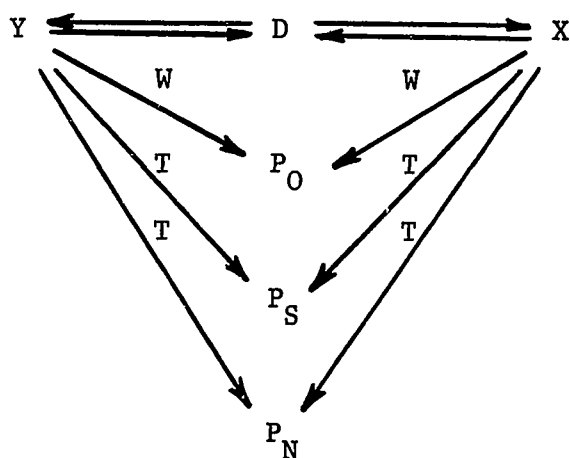
return to the diazonium ion will be twice the rate of rearrangement. Twice the rate of rearrangement (1.4% of the hydrolysis rate for the benzenediazonium ion) is too small to account for the 20% acceleration of rate in the presence of the thiocyanate ion.

If one intermediate is responsible for both the relatively large acceleration by thiocyanate ion and for the small amount of isotopic turnaround, the nitrogen atoms in this intermediate cannot be equivalent. The turnaround reaction could occur by a subsequent reaction of the intermediate responsible for thiocyanate acceleration, or there could be an independent route for the turnaround reaction.

A further study by Lewis and Insole on the decomposition of *p*-toluenediazonium ion with thiocyanate ion led to the proposal of two intermediates in the reaction (20). The sharp initial increase in rate of disappearance of *p*-toluenediazonium ion in the presence of thiocyanate and the decrease in *p*-cresol yields could be explained by the reaction schemes, I and II. These two schemes become indistinguishable when the principal reaction of X is to return to D. The intermediate, Y, is very selective, but it becomes saturated with thiocyanate ion around 0.6 M; therefore it is important only at low thiocyanate ion concentration. The intermediate, X, is very

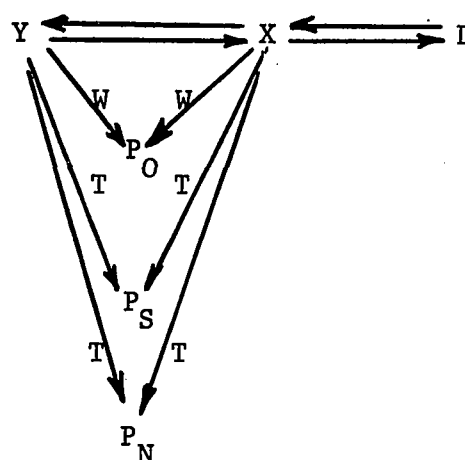
SCHEME

I



SCHEME

II



where D = diazonium ion

X = unselective intermediate

Y = selective intermediate

W = water as nucleophile

T = thiocyanate ion as nucleophile

P_O , P_S , and P_N represent products in which the p-tolyl group is bonded to oxygen, sulfur, and nitrogen, respectively.

unselective, but the reaction between X and thiocyanate ion becomes the principal product forming route at higher salt concentrations.

When the apparent first-order rate constant, k_{app} , is plotted as a function of added salt concentration as in Figure 1, and the flat portion of the curve is extrapolated to zero added salt, the difference between k_{app} and k_o appears to be roughly twice the rate of

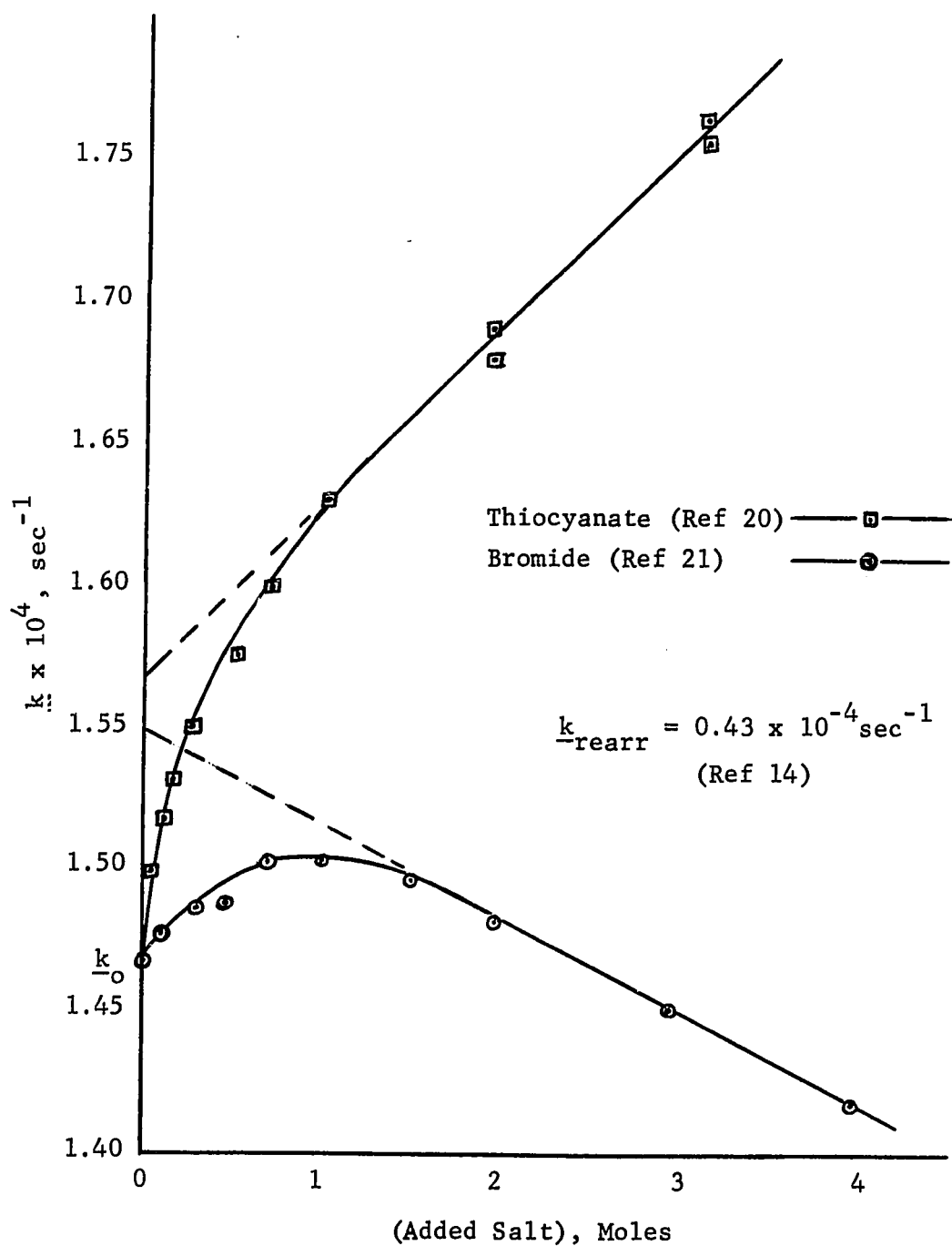


Figure 1. Apparent First-order Rate Constants as a Function of Concentration of Potassium Thiocyanate and Potassium Bromide in the Decomposition of *p*-Toluenediazonium Ion in Water at 48.8°C.

isotopic rearrangement for *p*-toluenediazonium- α -¹⁵N ion. From this it appears that there is an intermediate, identical with Y in Schemes I and II, which has equivalent nitrogens and reverts to diazonium ion, Eq. 11. This intermediate accounts for all of the rearranged material. From Figure 1 it can be seen that both potassium thiocyanate data (20) and potassium bromide data (21) lead to the same conclusion. Reexamination of the data for the hydrolysis of benzenediazonium ion in the presence of thiocyanate ion (8) also leads to this conclusion, except that the fit is not as good as it was for *p*-toluenediazonium ion.

If the steady-state approximation (11), Eq. 12, is applied to the concentration of the intermediate, Y, in Scheme I, an expression for the concentration of Y can be obtained, Eq. 13. The rate of the

$$\underline{k}_{YW} + \underline{k}_{YT} + \underline{k}_{YD}' = \underline{k}_{DY} D \quad \text{Eq. 12}$$

where \underline{k}_{YW} = rate constant for the reaction of Y with W

\underline{k}_{YT} = rate constant for the reaction of Y with thiocyanate ion

\underline{k}_{YD} = rate constant for return of Y to D

\underline{k}_{DY} = rate constant for formation of Y from D

$$Y = \frac{\underline{k}_{DY} D}{\underline{k}_{YW} + \underline{k}_{YT} + \underline{k}_{YD}} \quad \text{Eq. 13}$$

turnaround reaction is given by Eq. 14. Substitution of Eq. 13 into Eq. 14 leads to Eq. 15, an expression relating the rate of turnaround to the amount of added thiocyanate ion.

$$\frac{k_{\text{rearrangement}}}{k_{\text{YD}}} = \frac{k_{\text{YD}}^{\text{Y}}}{2} \quad \text{Eq. 14}$$

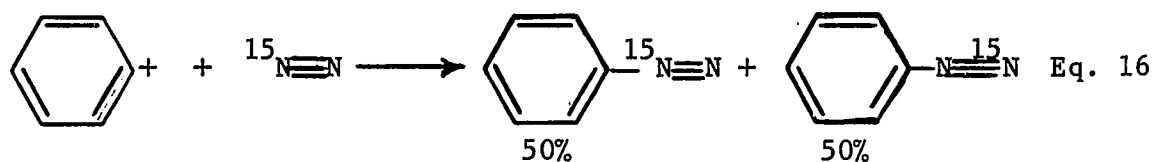
$$\frac{k_{\text{rearrangement}}}{k_{\text{YD}}} = \frac{k_{\text{YD}}}{2k_{\text{YW}}} \frac{k_{\text{DY}}^{\text{D}}}{W + \frac{k_{\text{YT}}}{k_{\text{YW}}}T + \frac{k_{\text{YD}}}{k_{\text{YW}}}} \quad \text{Eq. 15}$$

The values for $k_{\text{YD}}/k_{\text{YW}} = 21$, $k_{\text{YT}}/k_{\text{YW}} = 470$, $k_{\text{DY}} = 0.349 \times 10^{-4} \text{sec}^{-1}$, and $W = 55$ are obtained from Ref. 20. If these values are substituted in Eq. 15 and the rate of turnaround calculated for various thiocyanate concentrations, it is obvious that the amount of rearranged product should decrease with added thiocyanate. For example, when the thiocyanate concentrations are none, 1 M, and 3 M, the relative ratios of rearranged product are 1, 1/7, and 1/20. Therefore, if the intermediate, Y, accounts for both the observed nitrogen turnaround and the sharp increase in rate of disappearance of diazonium ion, the mechanism proposed by Lewis and Insole predicts according to Eq. 15 that the amount of isotopic rearrangement should decrease with added nucleophiles, and that at high concentrations the amount of turnaround should be suppressed almost entirely.

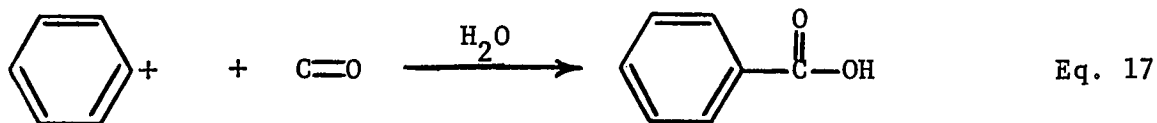
A simple experiment, the measure of turnaround in the presence of nucleophiles, can test the validity of the two-intermediates mechanism. If the amount of turnaround is suppressed by the addition of nucleophiles as Eq. 15 predicts, this mechanism will be more firmly established; however, if the rate of turnaround is unchanged by the addition of nucleophiles, or an increase in the rate is observed, the proposed mechanism must be modified or altogether discarded.

The other evidence that supports a two-intermediates mechanism is based on product yields. It was found that the ratio of *p*-tolyl thiocyanate to *p*-tolyl isothiocyanate was not constant but increased favoring the better nucleophile at low thiocyanate ion concentrations (20). Since only a few product measurements were made, it would seem advantageous to perform additional experiments of this nature.

To demonstrate that the isotopic rearrangement did not occur by the reaction of some highly energetic intermediate (such as the phenyl cation) with nitrogen gas dissolved in the reaction medium, Eq. 16, Lewis and Insole (13,14) decomposed benzenediazonium ion in the presence of carbon monoxide at 700 p.s.i. Carbon monoxide, a molecule



which is isoelectronic in structure with nitrogen, is known to react with carbonium ions to form carboxylic acids (22,23). Upon workup of the reaction mixture, no benzoic acid, which should have been the major product of the reaction of the intermediate with carbon monoxide, Eq. 17, was detected.

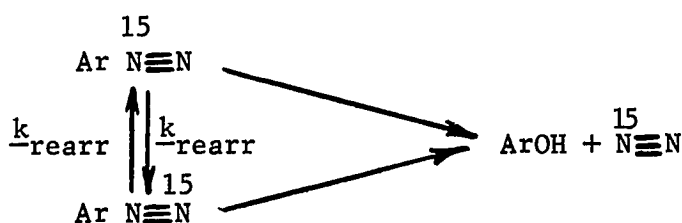


By analogy this result was interpreted to mean that dissolved nitrogen did not react with the diazonium ion or an intermediate to account for the observed isotopic scrambling. Lewis and Insole made no further attempts to determine the molecularity of the turnaround reaction.

The order of the turnaround reaction should be more closely investigated to establish definitely that the reaction is actually unimolecular as written in the two-intermediates mechanism. If unimolecular, the reaction will be independent of the concentration of the diazonium ion; it will also be independent of the concentration of nitrogen-29 dissolved in the reaction medium.

Further, if the turnaround reaction is kinetically a first-order process accompanying the first-order solvolysis as in Scheme III, the concentration of α - ^{15}N and β - ^{15}N diazonium ion as a function of time is given by Eq. 18-19 (14).

SCHEME III



$$\text{ArN} \equiv \text{N}^* = \frac{A_0}{2} \left[e^{-k_{\text{solv}} t} - e^{-(k_{\text{solv}} + 2k_{\text{-rearr}}) t} \right] \quad \text{Eq. 18}$$

$$\text{ArN} \equiv \text{N}^* = \frac{A_0}{2} \left[e^{-k_{\text{solv}} t} + e^{-(k_{\text{solv}} + 2k_{\text{-rearr}}) t} \right] \quad \text{Eq. 19}$$

p , the amount of turnaround, is given by Eq. 20.

$$p = \frac{\text{ArN}\equiv\overset{*}{\text{N}}}{\text{ArN}\equiv\overset{*}{\text{N}} + \text{Ar}\overset{*}{\text{N}}\equiv\text{N}} \quad \text{Eq. 20}$$

By substituting Eq. 17 and 18 into Eq. 20, Eq. 21 can be obtained.

$$p = \frac{e^{-\frac{k}{k_{\text{solv}}}t} - e^{-(k_{\text{solv}} + 2k_{\text{rearr}})t}}{2e^{-\frac{k}{k_{\text{solv}}}t}} \quad \text{Eq. 21}$$

Define $R = k_{\text{rearr}}/k_{\text{solv}}$ and let $D/D_0 = e^{-\frac{k}{k_{\text{solv}}}t}$.

Upon substitution of these values into Eq. 21 and simplification, Eq. 22 is obtained.

$$2R = - \frac{\log(1 - 2p)}{\log(D_0/D)} \quad \text{Eq. 22}$$

If the reaction is kinetically first-order as assumed in the calculations, a plot of $\log(1 - 2p)$ vs $\log(D_0/D)$ will be a straight line of slope $-2R$. In this derivation the nitrogen isotope effect, which is small for a diazonium salt (24), is neglected.

Investigation of the turnaround reaction for benzenediazonium- α - ^{15}N at two temperatures shows that the temperature dependence of the reaction is negligible (14). This result indicates that the energy of activation for the turnaround reaction is very similar to that for the solvolysis reaction. Examination of the temperature dependence for *p*-toluenediazonium- α - ^{15}N fluoborate, for which the isotopic rearrangement is larger, might lead to a more reliable comparison between the activation energies for the two processes.

p-Toluenediazonium- α -¹⁵N ion rearranges roughly twice as fast as benzenediazonium- α -¹⁵N ion (14), a result which suggests that the turnaround reaction might be dependent on either of two effects, 1) the migratory aptitude of the phenyl group or 2) the energy of activation for the solvolysis reaction. The *p*-tolyl group migrates in the acid catalyzed pinacol rearrangement 16 times faster than the phenyl group (25). This suggests an order *p*-tolyl > phenyl in the turnaround reaction; however, this same order is suggested by the activation energies for the hydrolysis reaction. The energy of activation for *p*-toluenediazonium ion is larger than that of benzenediazonium ion (5).

A study of other substituents should lead to a better understanding as to which effect actually is responsible for the increase in the rate of the turnaround reaction.

The intermediate in the hydrolysis of benzenediazonium salts is believed to be some highly energetic species which resembles the phenyl cation. It is conceivable that this intermediate might be formed by a different process -- that of solution photolysis.

The photolysis of aqueous *p*-nitrobenzenediazonium chloride in the presence of chloride ion (26) showed that the photochemical intermediate was fairly unselective toward different nucleophiles. Hartung found that the yields of chlorobenzene obtained from the thermal decomposition of benzenediazonium ion in sodium chloride solutions were almost identical to the yields of chlorobenzene obtained in the photolysis of similar solutions (9). The similarity in yields suggests the intermediates in the two processes are also similar.

An investigation using labeled diazonium salts should demonstrate just how similar the two processes are. If the photochemical intermediate were identical to the thermal intermediate, partial decomposition of a labeled diazonium salt should produce rearranged diazonium ion, and the amount of turnaround observed should be identical to that found in the thermal decomposition.

EXPERIMENTAL

Synthesis of p-Methoxybenzenediazonium- α - ^{15}N Fluoborate.

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°C 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 six hours. 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°C (lit.(27) 166.5-167.5°C).

p-Anisidine- ^{15}N . The preparation of p-anisidine- ^{15}N from anisamide- ^{15}N closely followed the method used by Buck and Ide (28) 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 chloride to 1 M sodium hydroxide at 0°C. A five percent excess of hypochlorite, as determined iodimetrically, was used. The mixture was slowly warmed to 70°C. The amide dissolved around 35-40°C. After maintaining the temperature at 70°C for 45 minutes, more sodium hydroxide (6 g in 15 ml of water) was added, and the temperature was increased to 80°C and maintained for 50 minutes.

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°C. After two sublimations, *p*-anisidine-¹⁵N, which melted at 56.5-57°C (lit.(29) 57°C), was obtained. The yield was 1.36 g (68%).

p-Methoxybenzenediazonium- α -¹⁵N Fluoborate was prepared by a method similar to that used by Ugi, Perlinger, and Behringer to prepare *p*-ethoxybenzenediazonium- β -¹⁵N chloride (30). *p*-Anisidine-¹⁵N (1.36 g) was dissolved in 3 g of 37-40% fluoboric acid and a small amount of water. The solution was evaporated to dryness on a rotary evaporator at 60°C, leaving the solid amine salt, *p*-methoxyanilinium-¹⁵N fluoborate. The salt was dissolved in methanol (50 ml) and cooled to 0°C. Ethyl nitrite (0.9 g in 10 ml of ether), 3 g of fluoboric acid, and 0.5 ml of concentrated hydrochloric acid were added to the stirred solution. After 30 minutes, several hundred ml of ether was added to precipitate the diazonium salt.

The *p*-methoxybenzenediazonium- α -¹⁵N fluoborate 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 -¹⁵N fluoborate was filtered, dried under vacuum, and stored in the refrigerator. The yield was 2.27 g (92%).

$\lambda_{\max} = 313\text{m}\mu$; $\epsilon = 2.53 \times 10^4$ (lit.(31) $\lambda_{\max} = 305\text{m}\mu$; $\epsilon = 2.45 \times 10^4$).

The discrepancy in the values of λ_{\max} can be readily explained. Examination of Hanson's original spectrum showed that he had misread the chart. λ_{\max} was actually 315m μ , not 305m μ as he reported. As a check, the spectrum was taken for recrystallized *p*-methoxybenzenediazonium fluoborate prepared from purified commercial *p*-anisidine. $\lambda_{\max} = 313\text{m}\mu$; $\epsilon = 2.51 \times 10^4$. These values are almost identical to those obtained for the ^{15}N -labeled compound.

p-Toluenediazonium- α - ^{15}N Fluoborate was prepared by the method of Lewis and Insole (14) with only slight modification.

p-Toluamide- ^{15}N , which melted at 157-160°C (lit.(32) 158°C), was obtained in 94% yield.

p-Toluidine- ^{15}N Hydrochloride was obtained by treatment of *p*-toluamide- ^{15}N with sodium hypobromite solution. 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°C (lit.(27) 243°C).

p-Toluenediazonium- α - ^{15}N Fluoborate was prepared from the amine hydrochloride according to the procedure used by Lewis, Kinsey, and Johnson to prepare *p*-trideuteromethylbenzenediazonium fluoborate (33). The diazonium salt was obtained in 95% yield. $\lambda_{\max} = 278\text{m}\mu$; $\epsilon = 1.56 \times 10^4$ (lit. (31) $\lambda_{\max} = 277\text{m}\mu$).

p-Chlorobenzenediazonium- α - ^{15}N Fluoborate was prepared in a manner identical to that used to prepare p-methoxybenzenediazonium- α - ^{15}N fluoborate.

p-Chlorobenzamide- ^{15}N was not purified by recrystallization.

p-Chloroaniline- ^{15}N was purified by vacuum sublimation at 80°C. The amine, which melted at 69-70.5°C (lit.(27) 70-72°C), was obtained in 71% yield (1.69 g) based on ammonium- ^{15}N chloride.

p-Chlorobenzenediazonium- α - ^{15}N Fluoborate was prepared in 90% yield by diazotization of p-chloroaniline- ^{15}N with ethyl nitrite. $\lambda_{\text{max}} = 280\text{m}\mu$; $\epsilon = 1.78 \times 10^4$ (lit.(31) $\lambda_{\text{max}} = 280\text{m}\mu$; $\epsilon = 1.79 \times 10^4$).

m-Toluenediazonium- α - ^{15}N Fluoborate was synthesized by the same procedure as p-methoxybenzenediazonium- α - ^{15}N fluoborate, except that m-toluidine- ^{15}N was isolated as the amine hydrochloride.

m-Toluamide was not purified by recrystallization.

m-Toluidine- ^{15}N Hydrochloride. m-Toluidine 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°C (lit.(27) 228°C).

m-Toluenediazonium- α - ^{15}N Fluoborate. m-Toluidine- ^{15}N hydrochloride was converted into the fluoborate salt (33) and diazotized with ethyl nitrite in methanol. m-Toluenediazonium- α - ^{15}N fluoborate in the

amount of 0.59 g (61% yield) was obtained. Although the extinction coefficient of m-toluenediazonium- α -¹⁵N fluoborate could not be accurately measured because of the rapid hydrolysis of the m-toluene-diazonium ion, its U.V. spectrum was identical to the spectrum of m-toluenediazonium fluoborate prepared from purified m-toluidine (9) $\lambda_{\text{max}} = 267\text{m}\mu$ with a broad shoulder at $313\text{m}\mu$.

Hydrolysis of the Labeled Diazonium Salts

The labeled diazonium salt was dissolved in 10 ml of pre-heated 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 I.

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

<u>Substituent</u>	<u>Rate Constant</u>	<u>Temperature</u>	<u>Reference</u>
<u>p</u> -Methyl	$0.24_4 \times 10^{-4} \text{sec}^{-1}$	35.9°C	(33)
	0.4065	39.8	(33)
	1.468	48.8	(21)
	8.51	62.2	(33)
<u>p</u> -Methoxy	$0.55 \times 10^{-4} \text{sec}^{-1}$	90.5	(21)
<u>p</u> -Chloro	$2.31 \times 10^{-4} \text{sec}^{-1}$	79.8	This Work
<u>m</u> -Methyl	$15.9 \times 10^{-4} \text{sec}^{-1}$	40.1	(9)

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.

With *p*-methoxybenzenediazonium- α -¹⁵N fluoborate 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°C) was carried out effectively using a rotary evaporator and a mechanical pump.

Reaction of Benzenediazonium Ion with Sodium Azide

The reaction of the diazonium salts with sodium azide was identical in procedure to that described by Lewis and Insole (13,14). The azide reactions were run in aqueous ethanol (13 parts water, 10 parts ethanol by volume). The diazonium salt solution was cooled to -27°C in an acetone bath and sodium azide (a three-fold excess) in 2 ml of aqueous ethanol (five parts water, one part ethanol by volume) was added. After 1.5 hours the solution was placed on the vacuum line and degassed by freezing and thawing while under vacuum. The temperature of the solution was kept below -10°C during the degassing process. When the solution was warmed to room temperature, the "secondary"

nitrogen was evolved. The "secondary" nitrogen was collected for analysis. (See the section on vacuum line technique for details.)

Reduction of the Phenyl 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 phenyl azide solution. Both solutions had previously been thoroughly degassed. The temperature of the reaction mixture was kept at room temperature for four hours and then increased to 50°C to insure completion of the reaction. The "arsenite" nitrogen was collected for analysis.

Vacuum Line Technique

The apparatus used for collection of the nitrogen samples is shown in Figure 2. The general operation of this vacuum line is described in the following two sections.

"Secondary" Nitrogen. The solution containing the pentazole was degassed by repeated freezing and thawing under vacuum. This process was repeated three times, using the mechanical pump. The solution was then frozen in liquid nitrogen and opened to the high vacuum line. After 15 to 20 minutes, a pressure of 10^{-6} mm Hg was achieved. The vessel was closed off from the line, and the temperature of the pentazole solution was slowly increased to room temperature. The evolution of the "secondary" nitrogen was completed in approximately

1.5 hours. The solution was frozen in liquid nitrogen, and the "secondary" nitrogen was conducted into the sample tube by means of the Toepler pump. The sample tube was then sealed.

Arsenite Reduction. The azide solution was degassed to remove the remaining "secondary" nitrogen. The sodium arsenite solution in the side-arm vessel was also degassed. The solutions were frozen in liquid nitrogen, and the pressure was reduced to 10^{-6} mm Hg by opening the vessel to the high vacuum line. The vessel was closed off from the line. After the solutions were thawed, they were mixed by turning the side arm until its contents poured into the larger flask. After completion of the reaction, the "arsenite" nitrogen was collected in the same manner as the "secondary" nitrogen.

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.

Legend to Figure 2.

A	Oil Diffusion Pump	F	Liquid Nitrogen Trap
B	Liquid Nitrogen Trap	G	Reaction Vessel
C	Sample Collection Tube	H	To Mechanical Pump
D	Automatic Toepler Pump	I	By-pass
E	McLeod Gauge.		

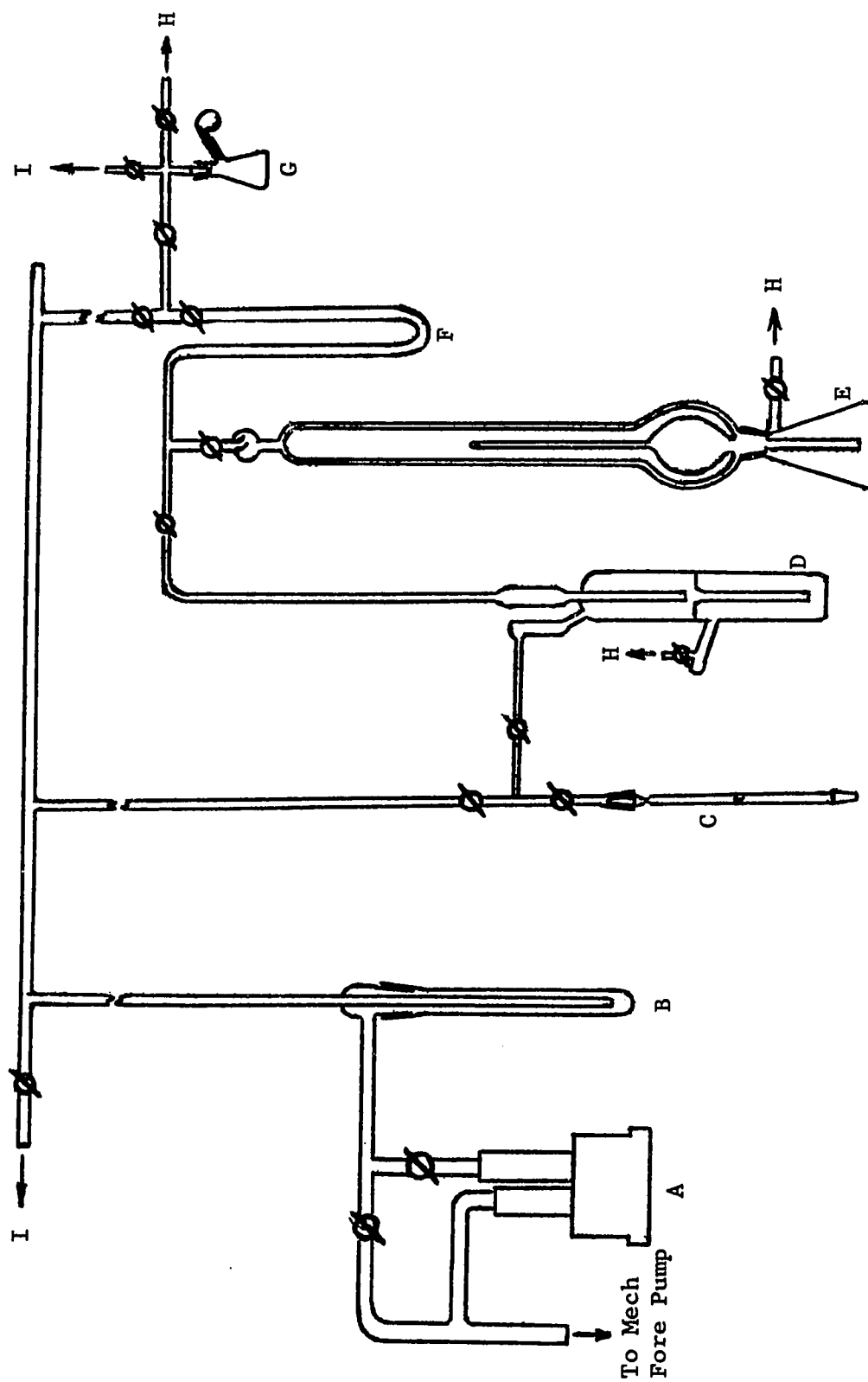


Figure 2. Vacuum Line Apparatus Used in the Collection of Nitrogen Samples.

Hydrolysis of p-Toluenediazonium- α - ^{15}N Fluoborate
in the Presence of Potassium Bromide

The procedure for the hydrolysis of p-toluenediazonium- α - ^{15}N fluoborate in 2.93 M potassium bromide was identical to that described previously with no added salt. The first-order rate constant is $1.451 \times 10^{-4} \text{ sec}^{-1}$ at 48.8°C (21). In a control run, potassium bromide was added after 80 per cent hydrolysis of the labeled diazonium salt.

Hydrolysis of p-Toluenediazonium- α - ^{15}N Fluoborate in Dilute Solution

An ion exchange technique was used in connection with the hydrolysis of p-toluenediazonium- α - ^{15}N fluoborate 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 fluoborate (356 mg) was dissolved in 1000 ml of 0.01 N sulfuric acid. After 80 per cent hydrolysis at 48.8°C , 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°C).

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

Removal of Nitrogen-29 During Hydrolysis. p-Toluenediazonium- α - ^{15}N fluoborate (200 mg) in 10 ml of 0.01 N sulfuric acid was placed in a reaction vessel constructed from a 20 mm sintered-glass funnel. Tank nitrogen saturated with water vapor at 48.8°C was passed through the stem of the funnel producing a cloud of fine bubbles. A well-fitting rubber stopper equipped with a long glass tube (8 mm O.D.) served as the exit for the gas. The vessel was placed in the temperature bath (48.8°C) with only a portion of the exit tube above the level of the bath water. After 80 per cent hydrolysis, the reaction was quenched by cooling. The remaining diazonium ion was degraded by the normal procedure.

Hydrolysis in a Sealed Ampule. p-Toluenediazonium- α - ^{15}N fluoborate (160 mg) was dissolved in 10 ml of 0.01 N sulfuric acid and sealed in

a 10 ml ampule. After 80 per cent hydrolysis at 48.8°C, the reaction was quenched, and the ampule was opened. The normal degradative procedure followed.

Photochemical Decomposition of Benzenediazonium Salts

The photolyses of the diazonium salts were carried out at 0-5°C in an annular reaction cell constructed so that the path length of the light passing through the solution was short (0.35 cm). A high pressure lamp (Hanovia No. 654A, 200 watts, 4.5 inch arc) in a water-cooled immersion well was used as the light source. A diagram of the apparatus is shown in Figure 3.

Kinetics of the Photolytic Decomposition of the Diazonium Salts were followed by coupling the unreacted diazonium salt with R-salt. At 10^{-3} M p-toluenediazonium fluoborate, the photolysis was approaching a first-order reaction in diazonium ion.

Photolysis of p-Toluenediazonium- α - ^{15}N Fluoborate. The U.V. lamp was turned on and allowed to warm up. An amount of 100 ml of p-toluenediazonium- α - ^{15}N fluoborate solution (200 mg of diazonium salt in 0.01 N sulfuric acid, temperature 5°C) was pipetted into the reaction vessel using a fast flow 100 ml pipette (4 seconds to empty). After 2.5 minutes (roughly 50 per cent reaction), the lamp was turned off. Samples of diazonium salt before and after photolysis were coupled with R-salt to determine the actual extent of reaction.

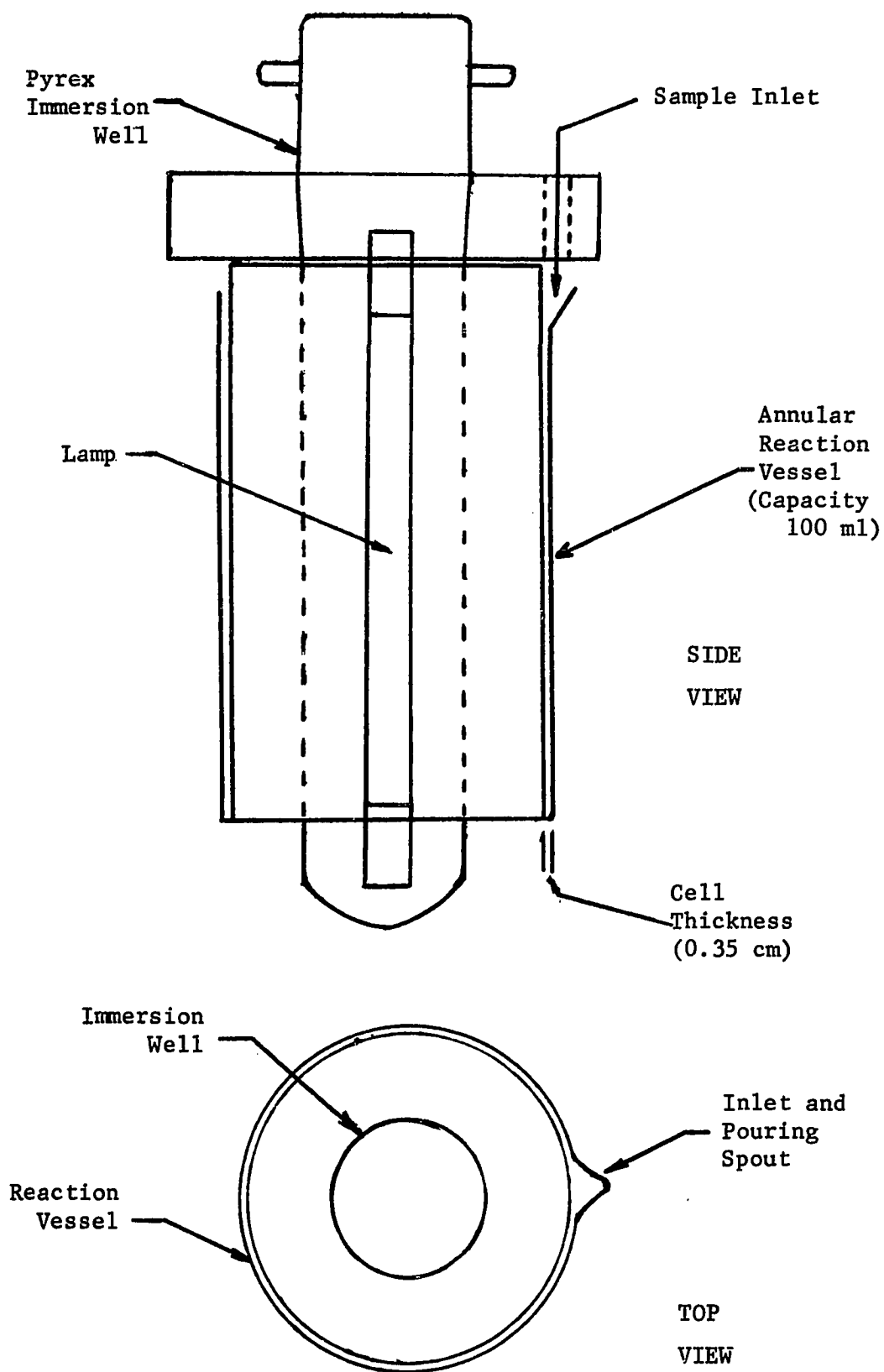


Figure 3. Apparatus Used in the Photolysis of the ^{15}N -Labeled Diazonium Salts.

After all ten portions of the diazonium salt solution had been photolyzed in this manner, the reaction solution was concentrated by use of the ion exchange technique previously described. After concentration of the solution, the normal degradative workup followed.

Photolysis of p-Methoxybenzenediazonium- α -¹⁵N Fluoborate was identical to that of p-toluenediazonium ion except in the method used to concentrate the solution after reaction. This diazonium salt solution was concentrated by evaporation of the water on a rotary evaporator using a mechanical pump to obtain a low pressure. The temperature was kept below 35°C during this process.

The Rate of Hydrolysis of p-Chlorobenzenediazonium Fluoborate

The rate was measured at 79.8°C by the method of Lewis, Kinsey, and Johnson (33). p-Chlorobenzenediazonium fluoborate (50 mg) in 200 ml of 0.01 N sulfuric acid was allowed to warm up for 20 minutes in the constant temperature bath. Aliquots were taken at appropriate times calculated from the guessed rate constant. The amount of diazonium ion remaining in the reaction mixture could be determined spectrophotometrically by coupling a measured amount of the diazonium salt solution with R-salt.

The Rate of Hydrolysis of p-Methoxybenzenediazonium Fluoborate

This rate was measured at 90.5°C as a check on the first-order rate constant measured at this temperature by Insole and Lewis (21). The method of measurement was identical to that described above for p-chlorobenzediazonium fluoborate.

Thermal Product Yields

p-Chlorobenzediazonium fluoborate (330 mg, 98.6 per cent pure by U.V. analysis based on the reported extinction coefficient (31)) was dissolved in 150 ml of 0.01 N sulfuric acid containing a known amount of sodium chloride. The solution was sealed in a 200 ml glass bulb to prevent any loss of product by evaporation. The sealed vessel was placed in a constant temperature bath (79.8°C) for 11 hours, a long enough time to insure at least 99 per cent reaction (over 7 half-lives). After cooling the solution in an ice-water bath and opening the bulb, the reaction mixture was poured into a separatory funnel and the bulb was thoroughly washed with petroleum ether (30-60°C. b.p.). A known weight of p-chloroanisole in petroleum ether was added. The mixture was shaken vigorously with 100 ml of petroleum ether to extract the p-dichlorobenzene. Sodium hydroxide in water was added to remove the p-chlorophenol. The layers were separated, and the ether phase was concentrated on a Nester-Faust spinning-band column to a volume of 5-10 ml. This solution was analyzed on an Aero-graph Model A-600-B gas chromatograph using a 1/8 inch column of 20% carbowax 20 M on 60/80 mesh firebrick. The length of the column was

4 feet. The yield of *p*-dichlorobenzene was calculated from the peak height ratio of *p*-chloroanisole to *p*-dichlorobenzene by the use of a calibration curve.

Photochemical Product Yields

The yields for the photochemical decomposition were done in the same manner with the following exceptions: 1) the solutions were more dilute (400 mg in 470 ml of 0.01 N acid); 2) the temperature of the reaction was between 0-8°C. The time of photolysis was 1.5 hours.

Figure 4 is a diagram of the apparatus used in measuring the photochemical yields. The reaction vessel had a capacity of 500 ml. During the photolysis, the reaction solution was continuously stirred with a magnetic stirring bar.

The Determination of \bar{m} , the Fraction of Primary Nitrogen

The fraction of primary nitrogen, \bar{m} , was determined by measuring the volumes of primary and secondary nitrogen formed in the azide reaction. (See Chart I.)

p-Chlorobenzenediazonium fluoborate (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°C. Carbon dioxide was bubbled through the well-stirred solution until all of the dissolved air was removed from the system. A three-fold 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 the reactor. (The azide solution had been

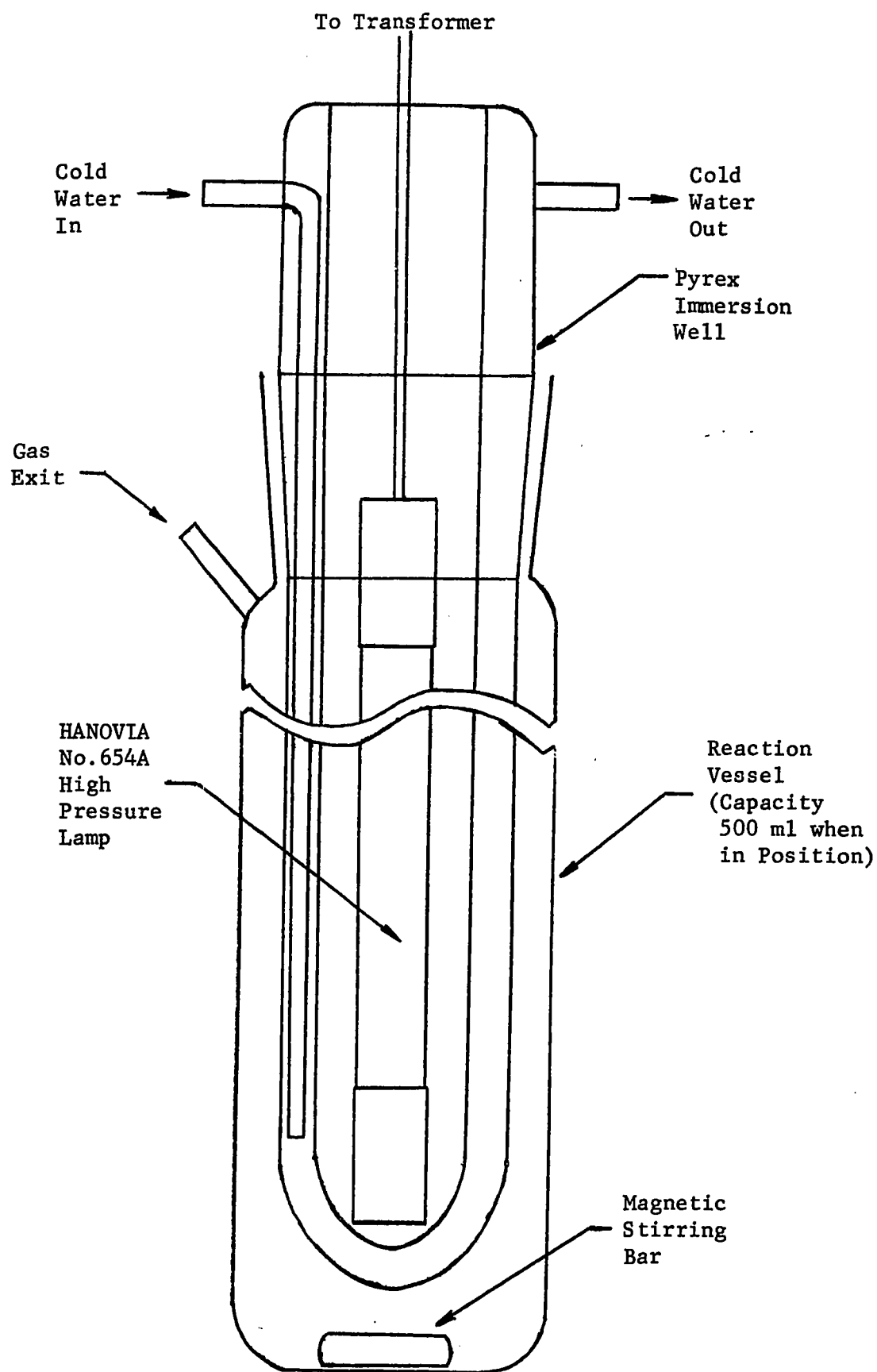


Figure 4. Apparatus Used in Photolytic Yield Experiments.

degassed previously.) The primary nitrogen, which was evolved over a one hour period, was swept from the reactor with carbon dioxide and collected in a nitrometer. The nitrogen was separated from the carbon dioxide by passing the gas through a 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, \underline{m} , was calculated by simply dividing the volume of primary nitrogen collected by the total volume of nitrogen collected.

RESULTS

Table II shows the percent turnaround observed under the conditions described in the first column. The percent turnaround, p , was calculated from the secondary nitrogen using Eq. 9 and from the arsenite-reduction nitrogen using Eq. 10. For m the following values were used: 0.62 for p -toluenediazonium ion, 0.71 for m -toluenediazonium ion, 0.78 for p -chlorobenzenediazonium ion, and 0.64 for p -methoxybenzenediazonium ion. The last three values were determined by measuring the volumes of primary and secondary nitrogen evolved in the reaction of sodium azide with the diazonium ion, Chart I. The first value is the same as that used by Lewis and Insole (14). In most instances the manufacturer's analysis on ammonium- ^{15}N chloride was taken as the atom fraction of ^{15}N in the α -position of the diazonium ion. The 97% enriched ammonium- ^{15}N chloride was obtained from Merck, Sharp, and Dohme of Canada; the 99% material from Bio-Rad Laboratories. p -Toluenediazonium- α - ^{15}N ion was prepared twice from p -toluidine- ^{15}N hydrochloride diluted with an equal amount of unlabeled p -toluidine hydrochloride. In these two cases the atom fraction of ^{15}N in the α -position was determined by the mass spectrometric analysis of the nitrogen formed in the total decomposition of the diazonium salt.

In the thermal decomposition of p -toluenediazonium- α - ^{15}N fluoborate, the maximum deviation of p for two or more runs is of the order of 10% for all reactions carried to 60% or greater decomposition. At lower extents of reaction, the maximum deviation is roughly 20%. This larger deviation probably results from measuring the relatively small

isotopic enrichment. Although only a few measurements were made for the other diazonium salts, the reliability of these runs should be comparable to that obtained in the study of *p*-toluenediazonium- α - ^{15}N fluoborate.

Table III shows the yield of chlorobenzene, *p*-chlorotoluene, and *p*-dichlorobenzene obtained from the decomposition of benzenediazonium fluoborate, *p*-toluenediazonium fluoborate, and *p*-chlorobenzenediazonium fluoborate in aqueous sodium chloride solutions. The maximum deviation from the mean of several runs is 3% or less for the photolytic runs; for the thermal runs it is less than 2%.

Most of the thermal decompositions of *p*-toluenediazonium fluoborate were carried out in a flask equipped with a cold-water condenser. Runs which were done in a sealed vessel gave slightly higher yields. This is probably due to the partial loss of *p*-chlorotoluene through evaporation. Examination of the yields of *p*-chlorotoluene in 1 M sodium chloride shows that the results for the open vessel are some 9% low.

The competition factor, $k_{\text{Cl}}/k_{\text{W}}$, was calculated from the yield of aryl chloride, Y_{ArCl} , using Eq. 23 (2). In these calculations it

$$\frac{Y_{\text{ArCl}}}{Y_{\text{ArOH}}} = \frac{k_{\text{Cl}}}{k_{\text{W}}} \frac{(\text{Cl}^-)}{(\text{H}_2\text{O})} \quad \text{Eq. 23}$$

was assumed that $Y_{\text{ArOH}} = 1 - Y_{\text{ArCl}}$ and that both (Cl^-) and (H_2O) remained constant during the entire reaction. The water concentration, (H_2O) , was estimated from the specific gravity of sodium chloride solutions (27).

p-Toluenediazonium fluoborate was decomposed thermally in aqueous potassium thiocyanate, and the ratio of p-tolyl thiocyanate to p-tolyl isothiocyanate was measured. Table IV shows the results of these experiments.

Table IV also shows the results obtained when p-toluenediazonium ion was decomposed thermally in equimolar mixtures of sodium bromide and sodium chloride.

The reliability of these measurements should be comparable to that obtained for the product yields in Table III.

Figure 5 shows the first-order plot of the photolytic decompositions of p-toluenediazonium ion and p-methoxybenzenediazonium ion. These are the conditions which were used to determine if the turn-around reaction occurred during photolysis of a diazonium salt. The decomposition of p-toluenediazonium ion approximates a first-order reaction with only slight curvature observed in the plot. The photolytic decomposition of p-methoxybenzenediazonium ion is not as good and deviates a considerable amount from a first-order reaction.

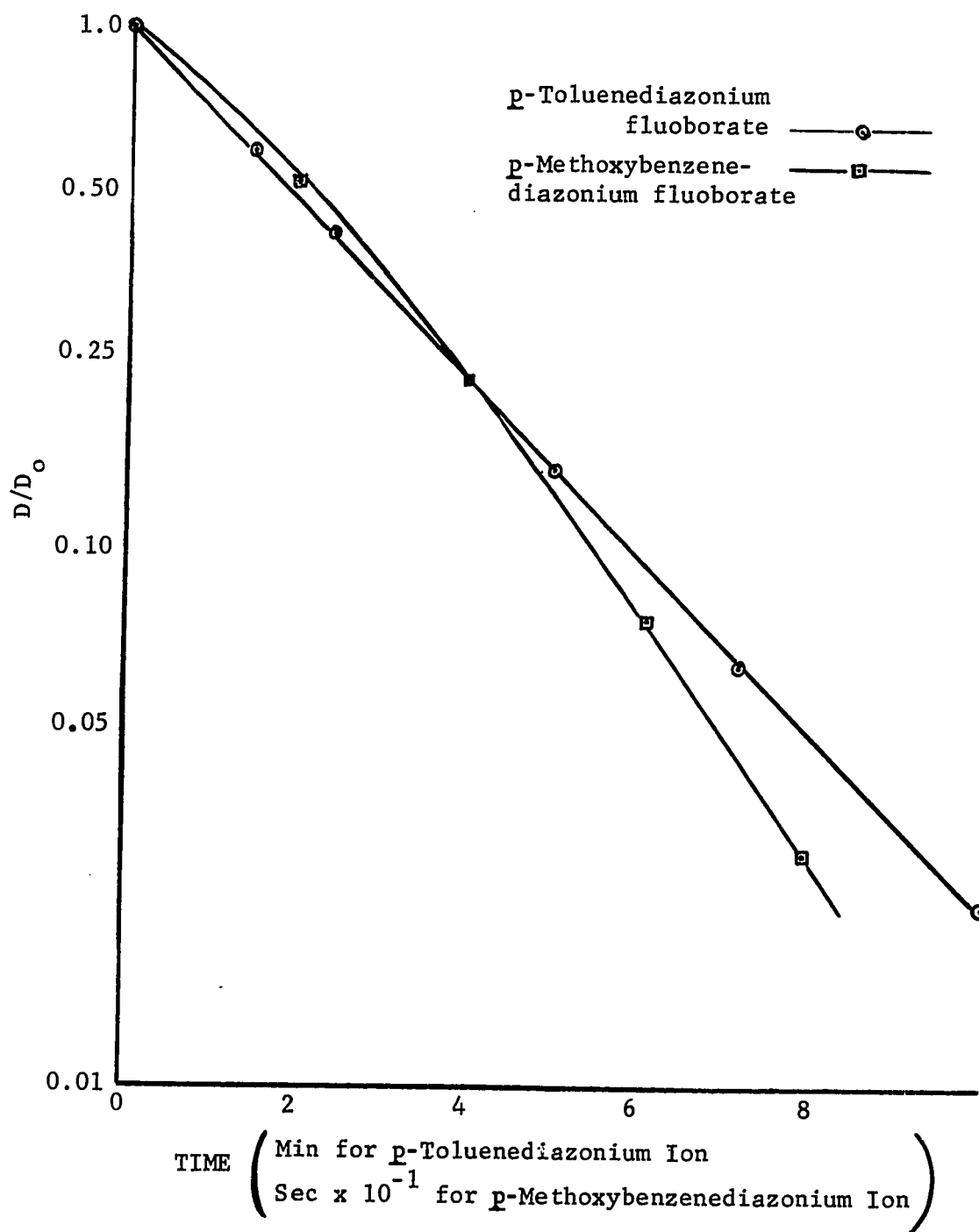


Figure 5. The Photolytic Decomposition of p-Toluenediazonium Fluoborate and p-Methoxybenzenediazonium Fluoborate in 0.01 N Sulfuric Acid at 0-5°C.

Table II. The Extent of Rearrangement of Benzenediazonium- α - ^{15}N Fluoroborates

Substituent	Conditions	^{15}N (sec.Nitrogen)	p(sec)% (ars Nitrogen)	^{15}N (ars Nitrogen)	p(ars)% α -position	^{15}N % α -position
p-Methyl	0% decomposition	0.41	0.16	0.36	0	97 %
	0% decomposition	near nat. abund.	----	0.38	0.05	48.7
	0% decomposition; ion exchange control run	0.38	0.08	0.36	0	47.7
	80% hydrolysis at 48.8°C	1.45	4.44	2.30	4.92	97
	Same as above	1.29	(7.57)*	1.22	4.33	48.7
	Same as above	1.21	(6.93)*	1.19	4.17	48.7
	Same as above (Ref. 14)	1.58	4.87	2.11	4.33	99.3
	80% hydrolysis at 48.8°C, 3.5 g of KBr added prior to the reaction with azide	0.88	4.21	1.32	4.84	48.7
	Same as above	0.89	4.28	1.18	4.12	48.7
	80% hydrolysis at 48.8°C in the presence of 2.93 M KBr	1.52	4.74	3.15	(7.07)*	97
	Same as above	0.84	3.87	1.14	3.97	48.7
	Same as above	0.89	4.28	1.28	4.63	48.7
	80% hydrolysis at 35.9°C	0.97	5.06	1.27	4.67	47.7
	80% hydrolysis at 39.8°C	1.45	4.44	2.19	4.64	97
	80% hydrolysis at 62.2°C	0.91	4.45	1.33	4.98	47.7

Table II (con't.)

P-Methyl (con't.)	80% hydrolysis at 48.8°C in a sealed ampule	0.91	4.45	1.26	4.53	48.7
	80% hydrolysis at 48.8°C with nitrogen sweep	0.89	4.38	1.36	5.14	47.7
	80% hydrolysis at 48.8°C in dilute solution (50-fold dilution)	0.88	4.30	1.25	4.57	47.7
	20% hydrolysis at 48.8°C	0.49	0.99	0.55	0.97	47.7
	Same as above	0.52	1.26	0.57	1.04	47.7
	40% hydrolysis at 48.8°C	0.63	2.14	0.72	1.78	47.7
	Same as above	0.63	2.14	0.71	1.77	47.7
	Same as above	0.55	1.52	0.64	1.40	47.7
	60% hydrolysis at 48.8°C	0.75	3.13	0.94	2.90	47.7
	Same as above	0.72	2.95	1.04	3.48	47.7
	90% hydrolysis at 48.8°C	1.25	7.32	1.71	6.97	47.7
	40.5% photolysis at 0-8°C	1.19	6.91	1.44	5.56	47.7
	44.2% photolysis at 0-8°C	1.04	5.65	1.44	5.56	47.7
	47.5% photolysis at 0-8°C	1.23	7.25	1.75	7.17	47.7
P-Methoxy	0% decomposition	0.36	0	0.38	0.03	97
	80% hydrolysis at 90.48°C	1.72	5.56	2.79	6.08	97
	Same as above	1.77	5.76	2.84	6.22	97

Table II (con't.)

p-Methoxy (con't.)	0%, isolation only	0.44	0.29	not collected	----	97
	56% photolysis at 0-8°C	1.45	4.45	"	----	97
	55% photolysis at 0-8°C	1.48	4.57	"	----	97
p-Chloro	0% decomposition	0.38	0.08	0.36	0	99
	80% hydrolysis at 79.8°C	1.26	3.58	1.75	3.13	99
	Same as above	1.25	3.63	1.90	3.47	99
m-Methyl	0% decomposition	0.38	0.08	0.40	0.07	99
	80% hydrolysis at 40.1°C	1.08	2.86	1.56	2.82	99
	Same as above	1.05	2.74	1.52	2.72	99
Hydrogen	80% hydrolysis at 35°C (Ref. 14)	0.91	2.17	1.22	2.02	99.3
	80% hydrolysis at 50°C (Ref. 14)	0.93	2.25	1.33	2.27	99.3

* The values in parentheses are believed to be in error and were not used in the calculations.

Table III. Chlorobenzene Yields Obtained from the Decomposition of Benzenediazonium Fluoborates in Aqueous Sodium Chloride Solutions

Substituent	Conditions	Conc. NaCl	ArCl Yield (%)	k_{-Cl}/k_{-W}
p-Methyl	Hydrolysis at 48.8°C in an open flask	3 M	16.4	3.43
			16.7	3.53
			16.6	3.49
		2 M	12.0	3.68
			11.8	3.61
			12.0	3.68
	Hydrolysis at 48.8°C in a sealed tube	1 M	6.9	4.07
			6.9	4.08
			6.7	3.97
		0.5 M	4.4	5.11
			4.4	5.08
			2.1	6.05
	Hydrolysis at 35.9°C in a sealed tube	1 M	2.1	6.07
			7.6	4.48
			7.6	4.48
		0.2 M	7.3	4.29
			7.3	4.36
			7.5	4.45
			7.7	4.59

Table III (con't.)

P-Methyl (con't.)	Hydrolysis at 62.2°C in a sealed tube	1 M	7.4	4.40
			7.2	4.28
			7.4	4.38
	Photolysis at 0-8°C with pyrex filter	3 M	24.3	5.35
			24.1	5.56
			24.7	5.75
			23.3	5.34
			17.5	5.71
			18.2	5.97
			17.9	5.86
		1 M	11.1	6.85
			10.6	6.42
			11.0	6.78
			11.2	6.93
			6.7	8.03
			6.9	8.21
			3.1	8.34
	Photolysis as above; buffered at pH7 with 0.025 M KH_2PO_4 and 0.025 M Na_2HPO_4	1 M	3.2	8.44
			9.9	6.02
	Photolysis in strong acid solution	(1 M) HCl	11.5	7.34

Table III (con't.)

p-Chloro	Hydrolysis at 79.8°C in a sealed tube	3 M	18.7	4.05
		2 M	13.7	4.26
		1 M	7.7	4.57
		0.5 M	4.5	5.23
		0.2 M	2.5	7.08
	Photolysis at 0-8°C in pyrex vessel	3 M	24.2	5.59
		2 M	17.5	5.71
		1 M	11.9	7.41
		0.5 M	7.7	9.28
		0.2 M	3.8	11.0
Hydrogen	Photolysis at 0-8°C in pyrex reactor	3 M	19.3	4.20
		2 M	14.2	4.44
		1 M	8.5	5.12
		0.5 M	5.0	5.82
		0.2 M	2.5	7.20

Table IV

The Relative Product Yields from the Decomposition of
p-Toluenediazonium Fluoborate in Aqueous Thiocyanate
and Aqueous Chloride-Bromide Solutions

Conc. KSCN	Peak Height [*] Ratio	Peak Area [*] Ratio
0.1 M ^{**}	1.44	1.88
0.2	1.39	1.98
0.4	1.45	2.03
0.8	1.45	2.04

These reactions were run at 48.8°C in a lightly stoppered flask. Oxygen was removed from the system prior to the run by bubbling nitrogen through the solution.

Conc. NaBr	Conc. NaCl	Peak Height [*] Ratio
2 M	2 M	0.89
1 M	1 M	0.98
0.5	0.5	1.14
0.125	0.125	1.11
0.063	0.063	1.16

These reactions were run at 48.8°C in a sealed tube.

- * The column was 20% Carbowax 20M on 60/80 firebrick.
The oven temperature was 205°C.
Ratio = p-tolyl thiocyanate/p-tolyl isothiocyanate.
- ** The yield of p-tolyl isothiocyanate at 0.1 M was measured using naphthalene as an internal standard.
The yield was 1.6%.
- *** The column was identical to that above. The oven temperature was 185°C.
Ratio = p-chlorotoluene/p-bromotoluene.

DISCUSSION

Disproof of the Two-Intermediates Mechanism

On the basis of rate studies and yield measurements in aqueous potassium thiocyanate solutions, Lewis and Insole proposed that the hydrolysis of *p*-toluenediazonium ion proceeded via a mechanism which involves two intermediates (20). They showed that both the yields and the rates could be explained by Schemes I and II (page 8).

One prediction that follows from this mechanism is that the rate of rearrangement of *p*-toluenediazonium- α -¹⁵N ion will be suppressed by the addition of thiocyanate or bromide ion to the reaction mixture, Eq. 15 (page 11).

In order to test the validity of this mechanism, the effect of bromide ion on the rate of rearrangement of *p*-toluenediazonium- α -¹⁵N fluoborate was studied. Bromide ion was the nucleophile chosen, since in its reaction with *p*-toluenediazonium ion no nitrogenous products are formed which might interfere with the degradation scheme, Chart I (page 5). Control runs demonstrated that bromide ion had no effect on the degradation scheme.

In 2.93 M potassium bromide the rate of *p*-toluenediazonium salt decomposition is almost identical to the rate observed in water alone (21). This facilitates comparison of the turnaround reaction observed under these conditions to that observed with no bromide present.

Contrary to the prediction of Eq. 15 and the two-intermediates mechanism, the rate of rearrangement of *p*-toluenediazonium- α -¹⁵N

fluoborate in 2.93 M potassium bromide at 48.8°C was found to be identical, within experimental error, to the rate of rearrangement observed with no added bromide.

Lewis and Insole calculated the competition factors, $\frac{k_s}{k_n}$, of 4.5, 4.4, and 34 from their yield data at 3 M, 0.66 M, and 0.105 M thiocyanate. The value of $\frac{k_s}{k_n} = 34$ was supposed to indicate an increased selectivity of the intermediate Y for the more nucleophilic end of the ambident ion. They state, "While the minimum is clearly unreasonable, the markedly higher value at low (T) [thiocyanate ion] is clear and confirms the higher selectivity of Y" (20). This increased selectivity was presented as an independent indication of the validity of the two-intermediates mechanism.

In a re-examination of the product yields of this reaction, the relative yields of *p*-tolyl isothiocyanate and *p*-tolyl thiocyanate obtained from the reaction of *p*-toluenediazonium fluoborate in thiocyanate ion concentrations from 0.1 M to 0.8 M were measured by gas chromatographic analysis. The relative ratio of the two products was fairly constant for the various thiocyanate ion concentrations. There was no indication of an increase in $\frac{k_s}{k_n}$ in the more dilute solutions.

Although the above measurements did not include the yield of *p*-tolyl thiocarbamate, it was assumed that the same percentage of *p*-tolyl thiocyanate would be hydrolyzed to thiocarbamate at each concentration. This is a reasonable assumption, since the reactions were run for identical lengths of time under the same conditions.

In a similar experiment, *p*-toluenediazonium fluoborate was decomposed in an equimolar sodium bromide-sodium chloride solution. The

ratio of bromide to chloride was always 1 to 1, but the concentration varied from 0.063 M to 2 M in each ion. The relative yields of *p*-chlorotoluene to *p*-bromotoluene were again measured by gas chromatographic analysis. If the intermediate Y were actually more selective at low ion concentrations, the competition factor, $\frac{k_{\text{Br}}}{k_{\text{Cl}}}$, should increase, since bromide ion is a better nucleophile than chloride ion (34). However, the results show that this does not occur. There is a slight decrease in $\frac{k_{\text{Br}}}{k_{\text{Cl}}}$ in going from 2 M to 0.5 M solution. From 0.5 M to 0.063 M the relative product ratio remains constant. Again there is no indication of increased selectivity for nucleophiles in more dilute solutions.

From these experiments it may be concluded that the competition factor, $\frac{k_{\text{s}}}{k_{\text{n}}} = 34$, at 0.105 M thiocyanate is erroneous. The value at 0.105 M should be similar to the values of 4.4 and 4.5 which were obtained at higher thiocyanate concentrations.

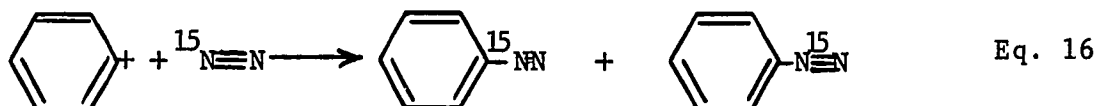
In their experiments Lewis and Insole measured the yield of *p*-tolyl isothiocyanate by gas chromatography and the yield of *p*-cresol by the titration of the acid formed in the reaction with standard base. The yield of *p*-tolyl thiocyanate was then determined by difference, assuming that these were the only three products formed in the reaction. As they pointed out, "The principal limitation of the accuracy in the yield data is the purity of the diazonium bisulfate" (20). It is obvious that an error of 2 to 3 percent in the *p*-cresol yield, coupled with a small error in the yield of *p*-tolyl isothiocyanate, could easily result in a large experimental error in the determination of $\frac{k_{\text{s}}}{k_{\text{n}}}$ at low thiocyanate concentrations. Furthermore, the yield of *p*-tolyl

isothiocyanate in 0.1 M thiocyanate was re-measured and found to be over 1%, rather than 0.17% as previously reported.

Since the rate of rearrangement of *p*-toluenediazonium- α - ^{15}N ion is unaffected by the addition of bromide ion, contrary to the prediction of the two-intermediates mechanism, and since the intermediate does not become more selective in low thiocyanate or bromide-chloride solutions, it is concluded that the two-intermediates mechanism as proposed by Lewis and Insole is inconsistent and should be abandoned. The fact that the flat portions of the rate curves for thiocyanate ion and bromide ion can be extrapolated to a value which is approximately twice the rate of rearrangement (Fig. 1) is believed to be only a coincidence. The initial sharp curvature in both the rate and the yield of *p*-cresol as a function of added salt can be explained in terms of a salt effect (9).

Investigations of the Turnaround Reaction

The Effect of Nitrogen-29 on the Rate of Rearrangement. Lewis and Insole were able to detect no benzoic acid when benzenediazonium ion was decomposed in the presence of carbon monoxide at 700 psi (14). Since carbon monoxide is isoelectronic in structure with nitrogen (but more reactive), they concluded that the rearranged benzenediazonium ion was not formed by the reaction of some intermediate such as the phenyl cation with nitrogen dissolved in the solution, Eq. 16.



More direct evidence that the reaction shown in Eq. 16 does not occur was obtained in other experiments. If Eq. 16 were the proper explanation of the rearrangement process, the extent of turnaround should be dependent upon the concentration of nitrogen-29 dissolved in the diazonium salt solution. For this reason the effect of changing the nitrogen-29 concentration was investigated.

In one experiment the nitrogen-29 produced during the hydrolysis of p-toluenediazonium- α - ^{15}N fluoborate was removed from the reaction vessel by passing a fine stream of normal nitrogen through the solution. In another experiment, the decomposition of p-toluenediazonium- α - ^{15}N fluoborate was carried out in a sealed ampule. Degradation of the remaining diazonium salt in both experiments showed that the extent of rearrangement was identical to that observed under normal conditions. These results demonstrate that the turnaround reaction is independent of nitrogen-29 concentration and prove that the rearrangement of p-toluenediazonium- α - ^{15}N ion does not occur by the reaction of an intermediate with dissolved nitrogen.

The Effect of Dilution on the Rate of Rearrangement. The hydrolysis of p-toluenediazonium- α - ^{15}N fluoborate was carried out in dilute solution. Approximately a fifty-fold dilution was used. It was found that the extent of rearrangement was independent of the concentration of p-toluenediazonium- α - ^{15}N ion. This demonstrates that the turnaround reaction is an intramolecular process.

The Kinetic Order of the Turnaround Reaction. The extent of rearrangement of p-toluenediazonium- α - ^{15}N as a function of the solvolysis reaction is given by Eq. 22.

$$2R = - \frac{\log(1-2p)}{\log(D_0/D)} \quad \text{Eq. 22}$$

This expression was derived by assuming that the turnaround reaction was a first-order reaction. Fig. 6 shows a plot of the experimental data. A reasonable fit to Eq. 22 is obtained, demonstrating that the turnaround reaction is kinetically a first-order process.

The Effect of Temperature on the Turnaround Reaction. Examination of the turnaround reaction for p-toluenediazonium- α - ^{15}N ion at four temperatures shows that the rate of rearrangement as compared to the rate of the solvolysis reaction is independent of temperature, the is $k_{\text{rearr}}/k_{\text{solv}}$ is constant over a fairly large range of temperatures. This is the same result as was obtained by Lewis and Insole for benzenediazonium- α - ^{15}N ion (14). This independence of temperature indicates that the energy of activation for the rearrangement process is very similar to that of the solvolysis process.

If the maximum deviations of p and the extreme temperatures are used to calculate the difference in the activation energies for the two processes, this difference is found to be only 1.7 kcals. Experimentally, however, no trend in the values for p is observed, and the values obtained for p are almost identical at all the temperatures studied. The difference in the activation energies for the two

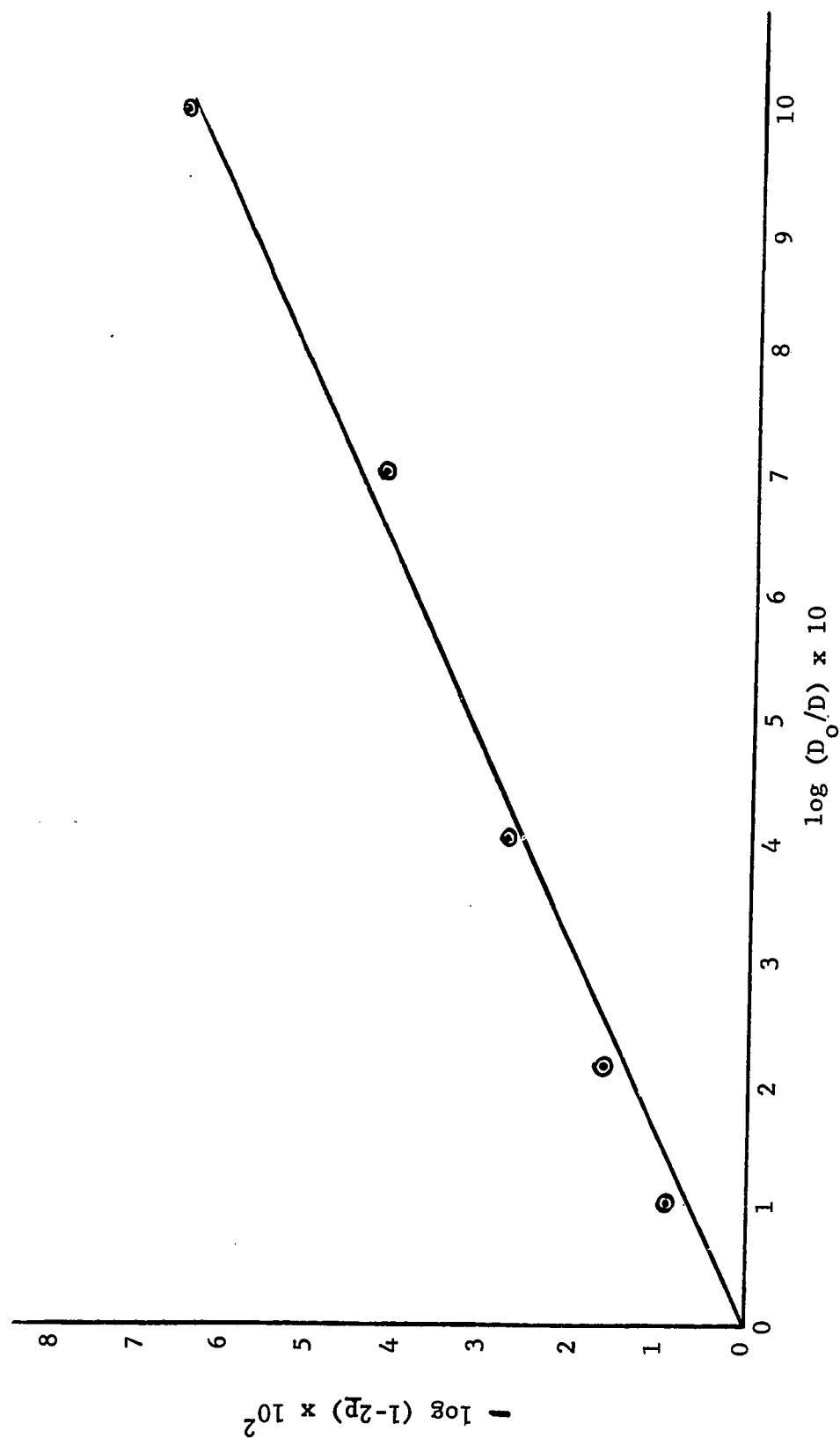


Figure 6. The Extent of Rearrangement of p-Toluenediazonium- α - ^{15}N Ion as a Function of the Solvolysis Reaction at 48.8°C. From Eq. 22.

processes is therefore believed to be less than 1.7 kcal. This value should only be considered as an upper limit for the difference in activation energies.

The Effect of Substituents on the Turnaround Reaction. The substituent effect on the turnaround reaction of benzenediazonium- α - ^{15}N fluoborate was investigated. The most striking feature of this study is that although the relative rates of solvolysis (calculated at 50°C) vary over a range of 3×10^4 , the values of $k_{\text{rearr}}/k_{\text{solv}}$ vary only over a total range of three. Table V shows the relationship of the turnaround reaction to the solvolysis reaction. From this table and more clearly from Fig. 7, it is obvious that both reactions have almost identical substituent effects.

Table V
The Relationship of the Turnaround Reaction
to the Solvolysis Reaction

Substituent	$k_{\text{rearr}}/k_{\text{solv}}$	Relative Rates of Solvolysis at 50°C	Relative Rates of Rearrangement at 50°C	E_{ACT} Solvolysis	Ref.
m-Methyl	0.018	27,200	12,900	25.61 kcal	(5)
Hydrogen	0.014	8900	3290	27.1	(5)
p-Methyl	0.029	1000	765	29.2	(5)
p-Chloro	0.023	18	10.8	31.6	(35)
p-Methoxy	0.038	1	1	32.5	(35)

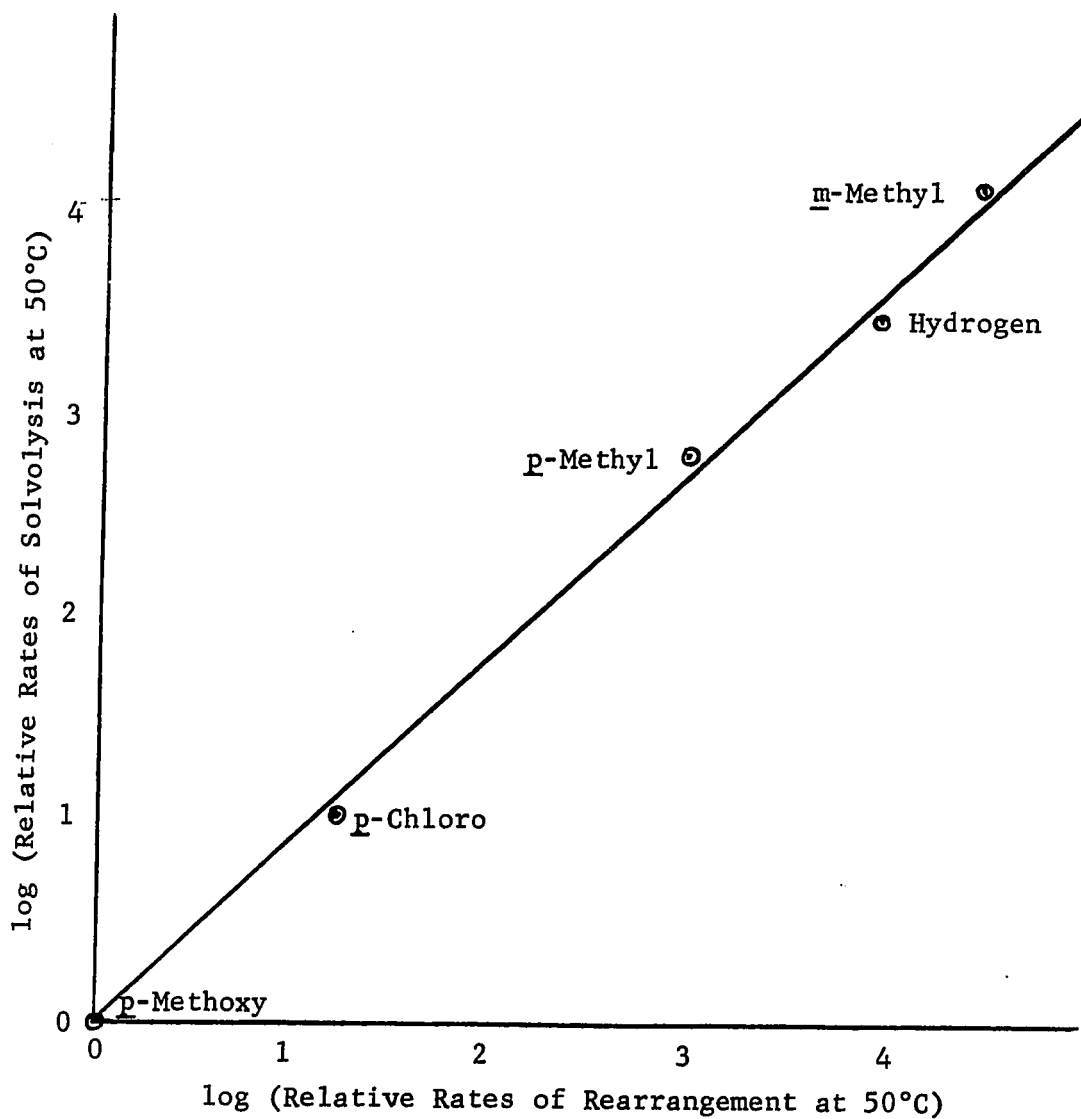


Figure 7. The Relationship of the Turnaround Reaction to the Solvolysis Reaction.

An attempt was made to fit the rate of rearrangement to the migratory aptitude of the aryl group. The order of migratory aptitude as measured for the acid catalyzed pinacol rearrangement is p -methoxy \rangle p -methyl \rangle m -methyl \rangle hydrogen \rangle p -chloro (25). The order of the relative rates of rearrangement for the labeled diazonium salts is m -methyl \rangle hydrogen \rangle p -methyl \rangle p -chloro \rangle p -methoxy. From the observed order of the rates of rearrangement it is obvious that migratory aptitude is not the proper explanation for the turnaround reaction.

From Table V it can be seen that the relative rates of turnaround are in the same order as the E_{ACT} for the solvolysis reaction. This is not unreasonable, since it has been shown that the energy of activation for the turnaround reaction is close to the energy of activation for the solvolysis reaction for p -toluenediazonium- α - ^{15}N fluoborate and benzenediazonium- α - ^{15}N fluoborate.

From the study of the five α - ^{15}N labeled diazonium salts it can be concluded that the substituent effects for the rearrangement reaction and the solvolysis reaction are almost identical. This indicates that the intermediates (or transition-state structures) for the two reactions closely resemble the phenyl cation (8,20).

The Photolysis of Labeled Diazonium Salts. A comparison of the yield of aryl chlorides obtained from both the photolytic and thermal decomposition of several benzenediazonium fluoborates suggests that the two processes have a similar mechanism. Although the shapes of the yield curves are almost identical, slightly higher yields of p -chlorotoluene and p -dichlorobenzene are obtained photochemically than thermally,

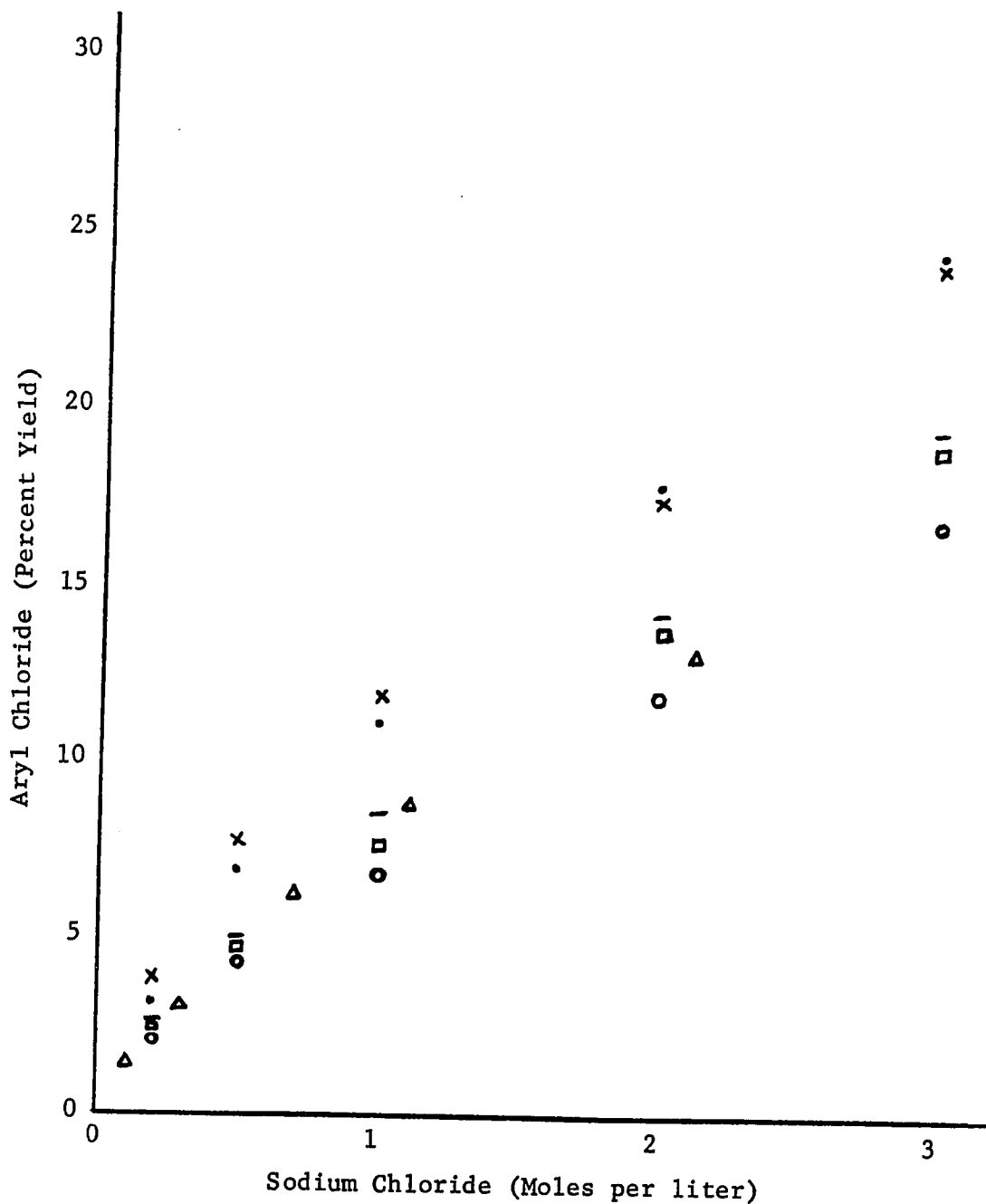


Figure 8. Aryl Chloride Yields from the Photolytic and Thermal Decompositions of Benzenediazonium Fluoborates in Aqueous Sodium Chloride Solutions.

(Photolytic Runs: • p-Methyl, X p-Chloro, — Hydrogen;

Thermal Runs: Δ Hydrogen*, \square p-Chloro, \circ p-Methyl)

* Ref 9

The difference in yield does not appear to arise from experimental error. The photochemical yield of *p*-chlorotoluene was essentially the same when the decomposition of *p*-toluenediazonium ion was carried out at pH7 or in strong acid.

Although the yields are slightly different, there remains enough similarity between the photochemical process and the thermal process to warrant a further comparison.

The partial photolysis of two labeled diazonium salts resulted in rearranged diazonium ion. For *p*-toluenediazonium- α -¹⁵N fluoborate, the amount of rearranged diazonium ion produced was three times larger photochemically than thermally. For *p*-methoxybenzenediazonium- α -¹⁵N fluoborate, the photochemical rearrangement was 1.5 times larger than the thermal rearrangement. The observed turnaround for *p*-methoxybenzenediazonium- α -¹⁵N ion might be low since the reaction was not ideally first order, Fig. 5. Deviations of this type would cause the observed turnaround to be less than that actually produced.

Although the intermediates for the two processes appear to be similar from yield data, they are definitely not identical. Apparently the mechanisms are different and the turnaround reaction is more important photochemically than thermally.

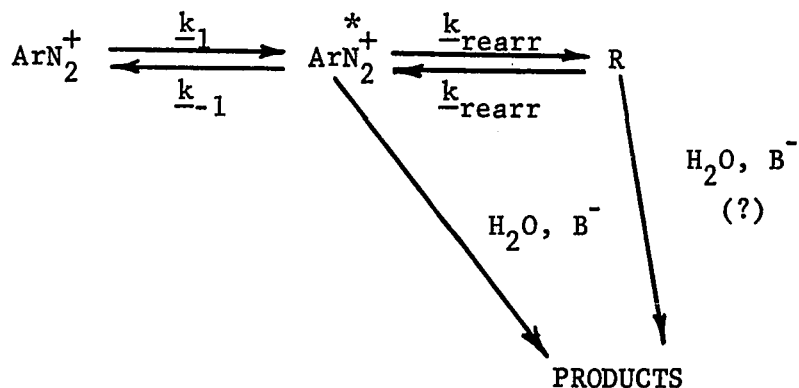
The Mechanism of the Turnaround Reaction

Any mechanism which is proposed for the turnaround reaction must account for the following experimentally observed facts: the turnaround reaction is an intramolecular, first-order process which accompanies the first-order solvolysis; the extent of rearrangement is unaffected by the addition of potassium bromide; the activation energy of the turnaround reaction is very similar to that of the solvolysis process; the substituent effect for the turnaround reaction is very similar to that of the solvolysis reaction and is suggestive of an intermediate which closely resembles the phenyl cation; and the turnaround intermediate, R, is not identical to the intermediate, ArN_2^{*+} , which is responsible for the acceleration in the rate of disappearance of diazonium ion observed in aqueous thiocyanate solutions. Two plausible mechanisms are consistent with these facts.

In these mechanisms, the solvolysis reaction is pictured as proceeding via a two-step process. The first step is formation of the intermediate ArN_2^{*+} . The second step is the reaction of ArN_2^{*+} with solvent or some other nucleophile. The solvolysis reaction can be explained equally well by a one-step bimolecular reaction ". . . provided that the transition state has very little new bond character, and very little of the old C-N bond either"(20). If the solvolysis reaction does not involve the intermediate ArN_2^{*+} , Mechanism I becomes meaningless. Mechanism II, however, fits for either case.

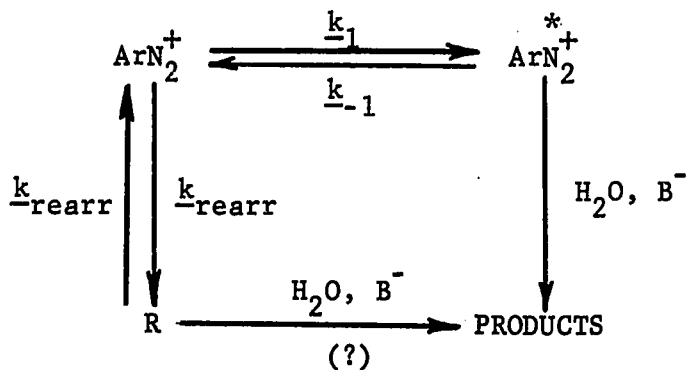
In Mechanism I, R is formed by a subsequent reaction of ArN_2^{+*} .

Mechanism I



In Mechanism II, R is formed by an independent route from ArN_2^{+*} .

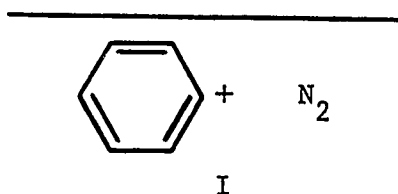
Mechanism II



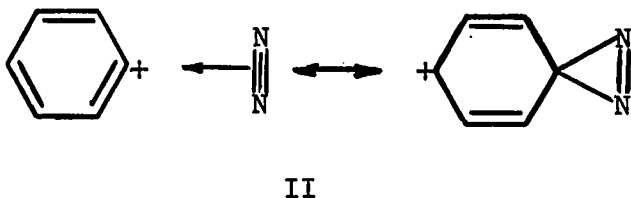
It is not known whether R in either mechanism reacts with a nucleophile such as H_2O or B^- to form product, or if the only fate of R is return to diazonium ion. If R does react with a nucleophile, it demonstrates the same selectivity as the intermediate ArN_2^{+*} , since the addition of potassium bromide does not affect the rate of rearrangement.

In neither of the two mechanisms is it necessary that R be a discrete intermediate. Most probably R is a transition-state in which the nitrogens are equivalent.

Two reasonable intermediates or transition-state structures can be proposed for R. One is the charged-caged pair, I, suggested by Lewis and Cooper (8). The nitrogen of this charged-caged pair cannot



exchange with nitrogen dissolved in the reaction mixture, since the extent of rearrangement is unaffected by the concentration of nitrogen-29 dissolved in the solution. A second possibility is that the carbon-nitrogen bond becomes stretched and/or bent until the two nitrogens lose their identity. There is still the presence of a weak carbon-nitrogen bond, but no longer is it directed at only one nitrogen. This structure, which can be represented by II, was also proposed by Lewis and Cooper (8).



It is reasonable that a properly oriented collision would deactivate R and cause it to revert to diazonium ion. Since the nitrogens have become equivalent, rearranged diazonium ion will be produced 50% of the time.

Figure 9 shows energy-reaction coordinate plots for the two mechanisms. These plots show R as a transition state rather than as a discrete intermediate.

It should be pointed out that Mechanisms I and II resemble those originally proposed by Lewis and Insole, with the exception that the intermediate R is not highly selective (if it reacts at all with nucleophiles). A steady-state approximation in R will lead to the prediction that the rate of rearrangement will be slightly suppressed if the rate of solvolysis is speeded up by the addition of nucleophiles. However, this suppression will be small compared to that which was predicted by the two-intermediates mechanism.

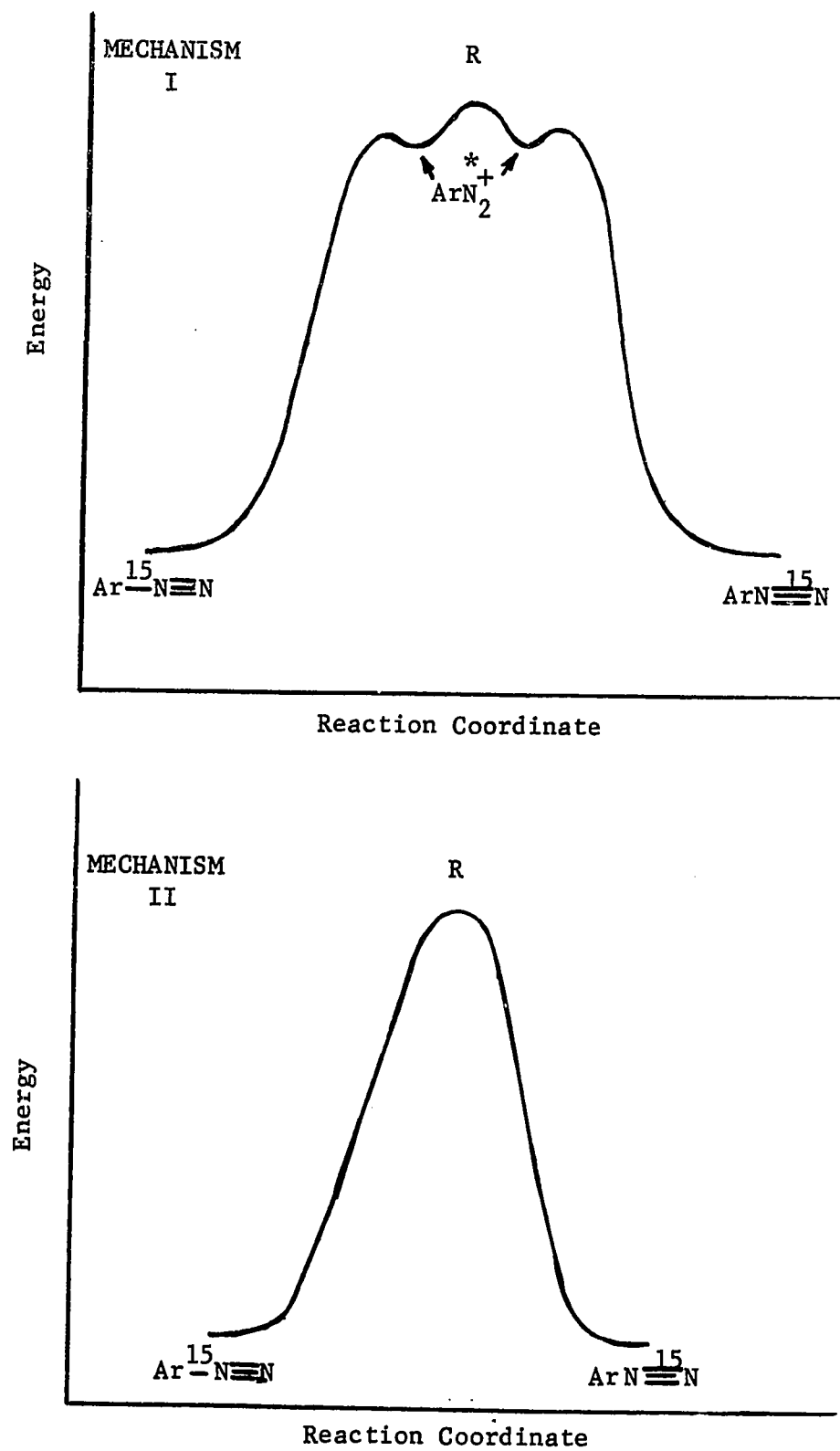


Figure 9. Energy-Reaction Coordinate Plots for the Formation of R in Mechanisms I and II.

REFERENCES

- 1) W.A. Waters, J. Chem. Soc., 266 (1942).
- 2) Edward S. Lewis, J. Am. Chem. Soc., 80, 1371 (1958).
- 3) H.A.H. Pray, J. Phys. Chem., 30, 1417 (1926).
- 4) J.S. Petrus Blumberger, Rec. Trav. Chim., 49, 259 (1930).
- 5) D.F. DeTar and A.R. Ballentine, J. Am. Chem. Soc., 78, 3916 (1956).
- 6) J.C. Cain, Ber., 38, 2511 (1905).
- 7) H.A.H. Pray, J. Phys. Chem., 30, 1477 (1926).
- 8) E.S. Lewis and J.E. Cooper, J. Am. Chem. Soc., 84, 3847 (1962).
- 9) L.D. Hartung, Ph.D. Thesis, Rice University (June, 1966).
- 10) H. Zollinger, "Azo and Diazo Chemistry," trans. by H.E. Nursten, Interscience Publishers, Inc., New York (1961), p 139.
- 11) Jack Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York (1962), p 66.
- 12) K. Clusius and M. Hoch, Helv. Chim. Acta, 33, 2122 (1950).
- 13) E.S. Lewis and J.M. Insole, J. Am. Chem. Soc., 85, 122 (1963).
- 14) E.S. Lewis and J.M. Insole, J. Am. Chem. Soc., 86, 32 (1964).
- 15) K. Clusius and H. Hürzeler, Helv. Chim. Acta, 37, 798 (1954).
- 16) R. Huisgen and I. Ugi, Ber., 90, 2914 (1957).
- 17) I. Ugi, "Pentazoles," in "Advances in Heterocyclic Chemistry," Vol. 3, ed. by A.R. Katritzky, Academic Press (1964).
- 18) I. Ugi, H. Perlinger, and L. Behringer, Ber., 91, 2330 (1958).
- 19) A. Gutmann, Z. Anal. Chem., 66, 241 (1925).
- 20) E.S. Lewis and J.M. Insole, J. Am. Chem. Soc., 86, 34 (1964).
- 21) E.S. Lewis and J.M. Insole, unpublished data.
- 22) H. Kich and W. Haaf, Angew. Chem., 70, 311 (1958).

- 23) G. Stork and M. Bersohn, J. Am. Chem. Soc., 82, 1261 (1960).
- 24) L.L. Brown and J.S. Drury, J. Chem. Phys., 43, 1688 (1965).
- 25) E.S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart, and Winston, New York (1959), p 607.
- 26) W.E. Lee, J.G. Calvert, and E.W. Malmberg, J. Am. Chem. Soc., 83, 1928 (1961).
- 27) C.D. Hodgman, ed., "Handbook of Chemistry and Physics," The Chemical Rubber Publishing Co., Cleveland (1960).
- 28) A.H. Blatt, ed., "Organic Syntheses," Collective Volume 2, John Wiley and Sons, Inc., New York (1948), p 44.
- 29) G. Harris, ed., "Dictionary of Organic Compounds," Oxford University Press (1965).
- 30) I. Ugi, H. Perlinger, and L. Behringer, Ber., 92, 1865 (1959).
- 31) Milton P. Hanson, Ph.D. Thesis, Rice University (1964), p 72.
- 32) R.L. Shriner, R.C. Fuson, and D.Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York (1958), 4th Ed., p 279.
- 33) E.S. Lewis, J.L. Kinsey, and R.R. Johnson, J. Am. Chem. Soc., 78, 4294 (1956).
- 34) Reference 11, p 160.
- 35) M.L. Crossley, R.H. Kienle, and C.H. Benbrook, J. Am. Chem. Soc., 62, 1400 (1940).