

and 3817 cm.<sup>-1</sup>),<sup>10</sup> it is possible to calculate  $k_H/k_D$  ratios for two extreme cases: (1) where the hydride ion from the tributyltin hydride is unbonded in the transition state, and (2) where the bond between the two participating hydrogens is complete in the transition state.<sup>10</sup> For case 1  $k_H/k_D = 4.1$ , while for case 2  $k_H/k_D$  is 0.9. The data would argue for a transition state then in which the bond between the participating hydrogens was almost completely formed, one in which the transition state resembled product. Dessy and Paulik have indicated that the function of assistor is to weaken the M-X bond, which in this case yields a more hydridic hydrogen. The observation that the assisted reaction has a higher  $k_H/k_D$  ratio is consistent with this argument, since the transition state would be expected to occur earlier along the reaction coordinate, where the bond between the proton and incipient hydride ion was not as complete.

Finally, the point should be made that such nucleo-

philic assistance is not found in reactions run in protic solvent, where the halide ion is strongly hydrogen bonded.<sup>17</sup>

**Acknowledgment.**—The authors wish to thank the Sloan Foundation (R. E. D.), the Diamond Alkali Co., and Texaco Corp. for fellowship support, and to acknowledge the support of the National Science Foundation (NSFG-14182), the Petroleum Research Fund (PRF-1080-A4), the Army Research Office (Durham) (ARO 31-124), the U. S. Office of Scientific Research (AFOSR-49-638-824), and the National Institutes of Health (NSPH-RG-9022). We wish to thank Mr. D. Vordenburg (U. S. Industrial Chemicals Co.) for the mass spectrometry analyses.

(17) H. G. Kuivila and P. L. Levins [*J. Am. Chem. Soc.*, **86**, 23 (1964)] have investigated the acid- and base-catalyzed solvolysis of tributyltin hydride in *methanol* and found that no assistance was provided by halide ion. This is completely consistent with the feeling that nucleophilic assistance in organometal reactions will be observable only when solvents which do not coordinate with, and therefore mitigate the effect of, anions are employed.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WILLIAM MARSH RICE UNIVERSITY, HOUSTON, TEXAS]

## The Reactions of Diazonium Salts with Nucleophiles. X. A Tracer Demonstration of the Reversible Step in Diazonium Ion Hydrolysis<sup>1</sup>

BY EDWARD S. LEWIS AND JOAN M. INSOLE

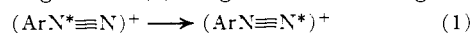
RECEIVED JUNE 24, 1963

The rearrangement  $\text{ArN}^{+15}\equiv\text{N} \rightarrow \text{ArN}^{+15}\equiv\text{N}^{15}$  is shown to accompany the hydrolysis of diazonium salts at a rate slower than the solvolysis by a factor of 0.014 for  $\text{Ar} = \text{C}_6\text{H}_5$ , and a factor of 0.029 for  $\text{Ar} = p\text{-CH}_3\text{C}_6\text{H}_4$ . A degradation to determine the position of  $\text{N}^{15}$  label in  $\text{ArN}_2^+$  is described. It is shown that the extent of rearrangement is not simply correlated with the previously observed acceleration of the decomposition in the presence of thiocyanate. A relation between nitrogen fixation and this reaction is shown to be improbable.

### Introduction

The solvolysis of aromatic diazonium salts was believed to pass through an intermediate aryl cation, which then reacts very rapidly with solvent or other nucleophiles; the evidence for this mechanism has been frequently presented.<sup>2</sup> Recently, the mechanism was modified by the inclusion of an initial reversible step to account for the small increase in rate on adding thiocyanate ion.<sup>3</sup> The structure of this reversibly-formed intermediate was the subject of speculation; the high reactivity suggests an intermediate of energy content close to that of the transition state for the slow step, and thus a structure resembling the phenyl cation.

In view of the fact that the carbon-nitrogen bond must therefore be nearly, if not completely, broken in this intermediate, there was a chance that when the diazonium salt was re-formed, the new bond might be formed to the other nitrogen atom. In other words, the isotopic rearrangement (1) might occur through the



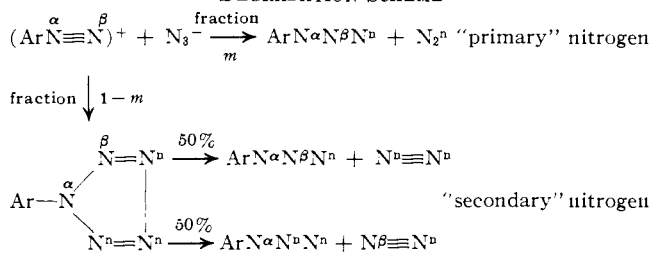
same intermediate responsible for the rate acceleration by thiocyanate. A search for this reaction in benzenediazonium and *p*-toluenediazonium salts is presented here.

### Results and Discussion

Aniline- $\text{N}^{15}$  was prepared from ammonium- $\text{N}^{15}$  chloride *via* benzamide and the Hoffman reaction. On diazotization with normal nitrite, it yielded benzenediazonium- $\alpha\text{-N}^{15}$  ion, isolated as the fluoroborate. The degradation of the diazonium salt was based upon the reaction with azide ion, as elucidated by the work

of Clusius<sup>4</sup> and Huisgen and Ugi.<sup>5</sup> It is shown in Chart I. Reaction at  $-27^{\circ}$  in aqueous ethanol solution between the diazonium salt and the azide gave "primary" nitrogen (derived from the azide ion only) of normal isotopic abundance. On warming, the "secondary" nitrogen (derived from the decomposition of phenylpentazole) was evolved and collected for analysis. The phenyl azide from both paths was reduced to aniline and nitrogen gas, which was also collected for analysis.

CHART I  
DEGRADATION SCHEME



Let us define the terms

$m$ , the fraction of "primary" nitrogen  
 $f_{\text{S}}$ , the atom fraction of  $\text{N}^{15}$  in the "secondary" nitrogen  
 $f_{\text{A}}$ , the atom fraction of  $\text{N}^{15}$  in nitrogen from reduction of aryl azide  
 $f_{\text{D}}$ , the atom fraction of  $\text{N}^{15}$  in the  $\alpha$ -position of the diazonium salt  
 $f_{\text{N}}$  = natural abundance of  $\text{N}^{15}$   
 $p$ , the fraction of molecules of diazonium salt which have undergone the turnaround reaction 1

It is then easy to derive two equations, 2 and 3, assuming no isotope effect in the cleavage of the aryl-pentazole.

(1) A portion of this paper was published in preliminary form: J. M. Insole and E. S. Lewis, *J. Am. Chem. Soc.*, **85**, 122 (1963); part IX is ref. 3.

(2) For example, E. S. Lewis, *ibid.*, **80**, 1371 (1958).

(3) E. S. Lewis and J. E. Cooper, *ibid.*, **84**, 3847 (1962).

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

(5) R. Huisgen and I. Ugi, *Chem. Ber.*, **90**, 2914 (1957).

$$p = 4(f_B - f_N)(1 - f_N)/(f_D - f_N) \quad (2)$$

$$p = \frac{4(f_A - f_N)(1 - f_N)}{(m + 1)(f_D - f_N)} \quad (3)$$

For  $m$  we used literature values since our experiments were not designed to determine this fraction. We used  $m = 0.70$  for benzenediazonium ion and  $m = 0.62$  for  $p$ -toluenediazonium ion. For  $f_D$ , the manufacturer's analysis on ammonium chloride, 0.993, was taken; we could only show that it was nearly unity. The value  $f_N = 0.0037$  was taken.

Table I shows the experimental results and the values of  $p$  calculated from them.

TABLE I

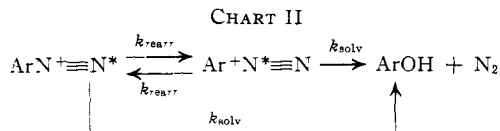
THE EXTENT OF REARRANGEMENT OF  $\alpha$ -N<sup>15</sup> DIAZONIUM SALTS

Aryl group	Fract. decomposed,	$f_B$ ,	$f_A$	$p_{eq. 1}$	$p_{eq. 2}$
	%	$\times 10^2$	$\times 10^2$	$\times 10^2$	$\times 10^2$
C <sub>6</sub> H <sub>5</sub>	0	0.40	0.37	0.1 <sup>a</sup>	0 <sup>a</sup>
C <sub>6</sub> H <sub>5</sub>	80 <sup>b</sup>	.91	1.22	2.17	2.02
C <sub>6</sub> H <sub>5</sub>	80 <sup>c</sup>	.93	1.33	2.25	2.27
C <sub>6</sub> H <sub>5</sub>	100	50.0 <sup>d</sup>	..	..	..
$p$ -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	0	0.74	0.38	0.4 <sup>a</sup>	0.04 <sup>a</sup>
$p$ -CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub>	80 <sup>e</sup>	1.58	2.11	4.87	4.33

<sup>a</sup> These values are believed to be zero within experimental error. The unusually high value of  $f_B$  for the  $p$ -tolyl compound is not confirmed by the  $f_A$  value. We can offer no explanation for this value, but believe that the assumption is tenable that no significant turnaround occurs before solvolysis. <sup>b</sup> Decomposition at 35°. <sup>c</sup> Decomposition at 50°. <sup>d</sup> This is the atom per cent N<sup>15</sup> in the gas from the decomposition of the diazonium salt. It confirms the extensive N<sup>15</sup> labeling. <sup>e</sup> Decomposition at 48.5°.

Inspection of the values of  $p$  in the table shows clearly that reaction 1, the turnaround reaction, does occur, and that it occurs principally, and possibly exclusively, with solvolysis.

If it may be assumed that this turnaround reaction is a kinetically first-order process accompanying the first-order solvolysis according to Chart II, and that



isotope effects can be neglected, the concentrations of the rearranged and unrearranged materials are given by expressions 4 and 5.<sup>6</sup> The data from the table then yield for benzenediazonium ion  $k_{\text{rearr}}/k_{\text{solv}} = 0.014$

$$[\text{ArN}^+\equiv\text{N}^*] = \frac{A_0}{2} [e^{-k_{\text{solv}}t} - e^{-(k_{\text{solv}} + 2k_{\text{rearr}})t}] \quad (4)$$

$$[\text{Ar}^+\text{N}^*\equiv\text{N}] = \frac{A_0}{2} [e^{-k_{\text{solv}}t} + e^{-(k_{\text{solv}} + 2k_{\text{rearr}})t}] \quad (5)$$

and for  $p$ -toluenediazonium ion  $k_{\text{rearr}}/k_{\text{solv}} = 0.029$ .

The existence of the isotopic rearrangement reaction is qualitative confirmation of the reversible step proposed previously,<sup>3</sup> but it is instructive to compare quantitatively the extent of rearrangement and the extent of rate acceleration by thiocyanate ion. It is clear that the amount of reversal from the intermediate proposed originally can be not less than (and probably is much greater than) the maximum increase in rate on adding thiocyanate. This rate increase is about 20% of the solvolysis rate, which is larger than twice the rate of isotopic rearrangement (1.4% of the solvolysis rate). We may conclude that if there is a single inter-

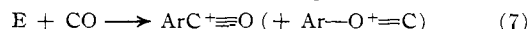
mediate responsible both for the relatively large acceleration by thiocyanate ion and for the small amount of isotopic turnaround, it cannot have equivalent nitrogens. It is possible that the turnaround is a subsequent infrequent reaction of the single intermediate responsible for the acceleration by thiocyanate, or that there is an independent route for the turnaround. Since it has been shown that the intermediate responsible for the thiocyanate acceleration is highly unselective, the first alternative is questionable. Further evidence on this problem is forthcoming.

Even if there is an independent route for the turnaround reaction, it cannot be very different from the solvolysis route. Thus the negligible temperature dependence of  $k_{\text{rearr}}/k_{\text{solv}}$  shown in the table indicates a similar heat of activation. The effect of the  $p$ -methyl substituent reduces the rate of solvolysis by a factor of 9.4<sup>7</sup> (at 44°), and that of rearrangement by a factor of 4.5, again showing the similarity but not the identity of the reactions.

The possibility that the isotopic rearrangement is the result of a reaction of free molecular nitrogen with some highly energetic and unselective electrophilic species, E (such as the aryl cation), by reaction 6, was considered.



Such a reaction might be a model for the crucial step in the natural nitrogen fixation process, and is not absurd, since the intermediate is known to be unselective. It is clear that this question can be attacked by the use of nitrogen tracers, but it was difficult to design an experiment using a practical amount of N<sup>15</sup> that might be expected to give a clear answer with our analytical methods. However, if reaction 6 occurs, then reaction 7 with the more powerful, but isoelectronic, nucleophile carbon monoxide should also occur. The principal isolated product of reaction 7 should be ArCO<sub>2</sub>H. Carbon monoxide is known to react analogously with more stable carbonium ions. Under 700 p.s.i. of carbon monoxide, the almost total decomposition of benzene-



diazonium fluoroborate led to no detectable amount of benzoic acid, so we believe that neither 6 nor 7 is a significant reaction and that there is no reason to believe that there is any close analogy to nitrogen fixation.

## Experimental

**Benzamide-N<sup>15</sup>.**—The reaction of benzoyl chloride with 2.0 g. of ammonium chloride (99.3% N<sup>15</sup>) in the presence of sodium hydroxide and chloroform yielded benzamide-N<sup>15</sup> in 79% yield.

**Aniline-N<sup>15</sup> Hydrochloride.**—Benzamide-N<sup>15</sup> was dissolved in sodium hypochlorite solution at ca. 10°. The solution was heated rapidly to 95° and, after 30 min. at this temperature, was steam distilled. The oily distillate was extracted with ether and the extract was dried over sodium sulfate. Aniline-N<sup>15</sup> hydrochloride, precipitated from the ethereal solution with dry hydrogen chloride, was isolated in 59% yield.

**Benzenediazonium- $\alpha$ -N<sup>15</sup> Fluoroborate.**—Aniline-N<sup>15</sup> hydrochloride was diazotized in hydrochloric acid solution at 0°. The addition of fluoroboric acid precipitated the diazonium fluoroborate in 71% yield.

**$p$ -Toluamide-N<sup>15</sup>** was prepared from  $p$ -toluyl chloride and ammonium chloride-N<sup>15</sup>.

**$p$ -Toluidine-N<sup>15</sup>.**— $p$ -Toluamide-N<sup>15</sup> (4.5 g.) was dissolved in an ice-cold, aqueous solution of sodium hypobromite (prepared by adding 7 g. of bromine to an ice-cold solution of 36 g. of sodium hydroxide in 180 ml. of water) and the solution was steam distilled. The distillate was filtered, and the solid product was washed with water and dried. The yield of  $p$ -toluidine-N<sup>15</sup> was 1.5 g. (42%).

**$p$ -Toluenediazonium- $\alpha$ -N<sup>15</sup> Fluoroborate.**— $p$ -Toluidine-N<sup>15</sup> was diazotized in hydrochloric acid solution and precipitated as the fluoroborate in 41% yield.

**Apparatus.**—The reaction of the aryldiazonium salts with azide, the reduction of the resulting arylazides with arsenite, and

(6) Although this scheme is identical with that attacked by E. S. Lewis and M. D. Johnson, *J. Am. Chem. Soc.*, **82**, 5399 (1960), the identity of the rate constants makes that solution unsatisfactory. The same approach can give the expressions used here, except that the  $B$  matrix cannot have a unit

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

the collection of the samples of nitrogen gas for analysis were carried out in a high vacuum apparatus.

The reaction vessel, was a 50-ml. round-bottomed flask connected by a side arm to another vessel of about 5-ml. capacity. The side arm and the smaller vessel were constructed in such a way that, when this vessel was rotated 180° about the connecting ground glass joint, the contents of the vessel emptied into the reaction flask. Samples of nitrogen gas generated in the reaction flask were conducted through a liquid nitrogen-cooled trap into a collection vessel, of about 10-ml. capacity, by a Toepler pump. This collection vessel was constructed with a narrow, thin-walled neck to facilitate sealing. The samples of nitrogen collected in this way were analyzed mass spectrometrically. The vacuum line was evacuated by an oil diffusion pump backed up by a mechanical pump. Another mechanical pump was used for evacuating the reaction flask during the preliminary degassing of its contents, in order that this degassing procedure should not contaminate the whole vacuum line. Final degassing was accomplished by opening the reaction flask to the high vacuum line.

**Decomposition and Reaction of Benzenediazonium- $\alpha$ -N<sup>15</sup> Fluoroborate with Azide.**—Eighty per cent of the benzenediazonium- $\alpha$ -N<sup>15</sup> fluoroborate was decomposed by heating a solution of it (0.2 g. in 10 ml. of deionized water) at 35° for 130 min. (or at 50° for 17 min.).<sup>8</sup> The solution was then cooled to 0°, and sufficient bromine was added to convert the phenol produced during the decomposition into tribromophenol, which precipitated as a white solid. This was removed by filtration and washed with 3 ml. of ice-cold water. The filtrate and washings, containing the residual 0.04 g. of diazonium salt, and 10 ml. of ethanol were poured into the reaction flask of the high vacuum apparatus. A solution of sodium azide (0.04 g., a threefold excess) in 2 ml. of aqueous ethanol (5 volumes of water to 1 of ethanol) was poured into the side vessel, and both solutions were frozen in a freezing mixture of acetone-Dry Ice. The solutions were separately degassed by repeatedly freezing, pumping out, and thawing. The azide solution was added to the diazonium solution and the temperature was maintained at ca. -27° for 75 min. The solution was frozen, and the "primary" nitrogen was removed using the mechanical pump (except in one experiment when it was collected for analysis to confirm that it contained only natural abundance of N<sup>16</sup>). The solution was degassed by thawing, freezing, and pumping out three times, keeping the temperature below 0°. Finally, the solution was frozen, and the reaction flask was left open to the vacuum line for 15 min. The reaction flask was isolated from the vacuum line and the solution was warmed to 0°. The temperature of the solution was allowed to rise to room temperature while the "secondary" nitrogen was being evolved (about 2 hr.). The solution was again frozen, the nitrogen was conducted into the collection vessel by the method previously described, and the vessel was sealed.

(8) E. A. Moelwyn-Hughes and P. Johnson, *Trans. Faraday Soc.*, **36**, 948 (1940).

**Decomposition and Reaction of *p*-Toluenediazonium- $\alpha$ -N<sup>15</sup> Fluoroborate with Azide.**—A solution of the diazonium salt (0.165 g.) in water (10 ml.) was heated at 48.5° for 195 min. to bring about 80% decomposition.<sup>9</sup> The solution was cooled and extracted with ether to remove the *p*-cresol. Dissolved ether was removed by bubbling air, under reduced pressure, through the combined aqueous solution and washings (3 ml.) for 15 min. During the reaction with azide and the collection of the "secondary" nitrogen, there were no essential differences between the procedure used for this compound and that used for the benzenediazonium salt as described above.

**Reduction of the Aryl Azides with Arsenite.**—The aryl azide solution remaining in the flask after the reaction of the arylidiazonium salt with sodium azide, and a solution of arsenite (0.34 g. of arsenic trioxide and 0.6 g. of potassium hydroxide in 2 ml. of 5:1 aqueous ethanol) in the side vessel were degassed in the usual way. After the final 15-min. degassing, the solutions were warmed to room temperature and the arsenite solution was added to the aryl azide solution. When the evolution of nitrogen had ceased (after ca. 4 hr.), the solution was warmed to 50° to ensure completion of the reaction and was then frozen. The nitrogen was collected for analysis. An independent control showed that sodium azide did not yield nitrogen with arsenite under these conditions.

The above experiments were repeated without the initial 80% decomposition, to show that substantial isotopic rearrangement was occurring only during solvolysis of the diazonium salts.

In a separate experiment, the nitrogen evolved during the solvolysis of benzenediazonium- $\alpha$ -N<sup>15</sup> fluoroborate was collected for analysis, using the techniques described above, in order to show that N<sup>15</sup> was present in the diazonium salt to the expected extent.

**Decomposition of Benzenediazonium Fluoroborate in Presence of Carbon Monoxide.**—A solution of 1 g. of benzenediazonium fluoroborate in 25 ml. of water was allowed to decompose at room temperature under 700 p.s.i. of carbon monoxide (in a steel bomb with a glass liner). After 19 hr. (>90%, but <95% decomposition),<sup>7,8,10</sup> solid sodium bicarbonate was added to dissolve any benzoic acid, and the solution was extracted with ether to remove the phenol. The aqueous layer was acidified and again extracted with ether. On evaporation of this ethereal extract, no benzoic acid was detected.

**Acknowledgment.**—We thank the Robert A. Welch Foundation for support of this work and for a post-doctoral fellowship to J. M. I. We also express our gratitude to Dr. E. G. Carlson and his co-workers at the Shell Oil Co., who performed the mass spectrometric analyses, without which this work could not have been done.

(9) E. S. Lewis, J. L. Kinsey, and R. R. Johnson, *J. Am. Chem. Soc.*, **78**, 4294 (1956); J. E. Taylor and T. J. Feltis, *ibid.*, **74**, 1331 (1952).

(10) K. R. Brower, *ibid.*, **82**, 4535 (1960).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RICE UNIVERSITY, HOUSTON, TEXAS]

## Intermediates in the Hydrolysis of *p*-Toluenediazonium Ion<sup>1</sup>

BY EDWARD S. LEWIS AND JOAN M. INSOLE

RECEIVED JUNE 24, 1963

Thiocyanate ion accelerates the decomposition of *p*-toluenediazonium ion in aqueous acid, but not linearly. The first increase in rate is almost saturated with 0.6 M SCN<sup>-</sup>, a second larger increase is linear up to 3 M SCN<sup>-</sup>. These rates and more qualitatively the products suggest two intermediates, X and Y; X mostly reverts to the diazonium ion and is apparently identical with the unselective intermediate previously identified as the aryl cation. It may also be related to the intermediates in aliphatic deamination; Y is far more selective and its return to diazonium ion is quantitatively correlated with the isotopic rearrangement previously reported. It is isomeric with the diazonium ion and is believed to have the spirocyclic structure I. The isotope effect for *p*-toluenediazonium- $\alpha$ -N<sup>15</sup> ion,  $k_{14}/k_{15} = 1.019$ , is reported.

### Introduction

The increase in the rate of hydrolysis of benzenediazonium ion by added thiocyanate ion was taken as evidence that an intermediate was formed reversibly.<sup>2</sup> The possibility that this intermediate had the carbon-nitrogen bond already broken was suggested, but not demonstrated, by the observation that both benzenediazonium and *p*-toluenediazonium ions showed a mixing of isotopic label on the two nitrogens in the diazo-

nium salt accompanying hydrolysis.<sup>3</sup> In this paper we attack the problem of the quantitative relation between the extent of isotopic rearrangement and the effect of thiocyanate ion on hydrolysis rate of *p*-toluenediazonium ion.

### Results

The rates of decomposition were conveniently followed by measuring the concentration of unreacted diazonium salt by coupling. The method of successive

(1) The Reaction of Diazonium Salts with Nucleophiles. XI.

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

(3) (a) J. M. Insole and E. S. Lewis, *ibid.*, **85**, 122 (1963); (b) E. S. Lewis and J. M. Insole, *ibid.*, **86**, 32 (1964).