

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>16</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.

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(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

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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).

approximations to the rate constant, which is capable of high precision, has been described before.<sup>4</sup> The reactions followed a first-order course as long as the ratio of diazonium salt to thiocyanate ion did not become too small, and the values found are shown in Fig. 1, together with a curve calculated from eq. 1, in which (T)

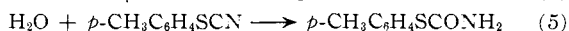
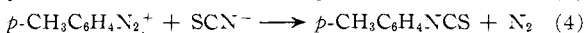
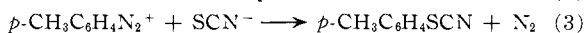
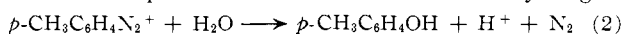
$$10^4 k_{app} = 1.572 + 0.064(T) - \frac{1}{10.35 + 93.1(T)} \quad (1)$$

represents the molar concentration of thiocyanate ion. The rates deviate from this expression with an average deviation of only 0.25%.<sup>5</sup>

The numbers in this equation are determined within about 5%, except the coefficient of (T) in the denominator. A value of 70 instead of 93 gives almost as good a fit, if the other numbers are slightly adjusted also.

The high precision of these rate constants also allowed a direct determination of the N<sup>15</sup> isotope effect, using a sample of *p*-toluenediazonium- $\alpha$ -N<sup>15</sup> fluoroborate prepared previously.<sup>3b</sup> The values obtained were  $k = 1.475 \times 10^{-4} \text{ sec.}^{-1}$  for normal diazonium salt and  $1.448 \times 10^{-4} \text{ sec.}^{-1}$  for the diazonium salt with the more than 99% N<sup>15</sup> label. This gives an isotope effect  $k_{14}/k_{15} = 1.019$  with an uncertainty in the neighborhood of 0.004. This is to our knowledge the only direct (noncompetitive) determination of a nitrogen kinetic isotope effect.

Yields were determined on the assumption that the only reactions taking place are those given by eq. 2, 3, 4, and 5, as suggested by the earlier work on the unsubstituted compound.<sup>2</sup> Of these reactions only 2 gives



acid, so the yield of *p*-cresol was determined by acid titration. *p*-Toluenediazonium bisulfate was here used as a source of the diazonium ion both to provide acid and to avoid the difficulties of titration associated with the ready hydrolysis of the fluoroborate ion. The isothiocyanate was determined gas chromatographically in three experiments. The principal limitation on the accuracy of the yield data is the purity of the diazonium bisulfate. A partial correction was made by running a portion of each sample to completion in the absence of thiocyanate and correcting the other phenol yields by this titer, assuming that the impurities were inert. All samples yielded from 98.5 to 99.5% of the theoretical amount of acid in this way. This correction is inadequate if some of the diazonium bisulfate has decomposed to *p*-tolyl hydrogen sulfate, which would hydrolyze to cresol and sulfuric acid, since even a completely decomposed sample would then assay 87% pure. Because of this error and some other less significant ones, the yields of cresol are not highly accurate; they are shown in Fig. 1. The *p*-tolyl isothiocyanate yields were 0.17% at 0.105 M SCN<sup>-</sup>, 3.2% at 0.659 M SCN<sup>-</sup>, and 8.2% at 3.01 M SCN<sup>-</sup>.

### Discussion

The sharp initial increase in rate with thiocyanate concentration and the sharp decrease in cresol yield at low thiocyanate concentration are difficult to explain with no intermediates or only one intermediate. Both

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

(5) If this accuracy can be routinely obtained, the measurement of rate for this reaction has potential application as a thermometer, since with the 29 kcal. activation energy, the associated temperature uncertainty is about 0.02°. The rate at (T) = 0 at our nominal temperature of 48.8° corresponds to a temperature of 48.9° if interpolated in the data of ref. 4, and 48.72° using the data of D. F. DeTar and A. R. Ballentine, *J. Am. Chem. Soc.*, **78**, 3916 (1956).

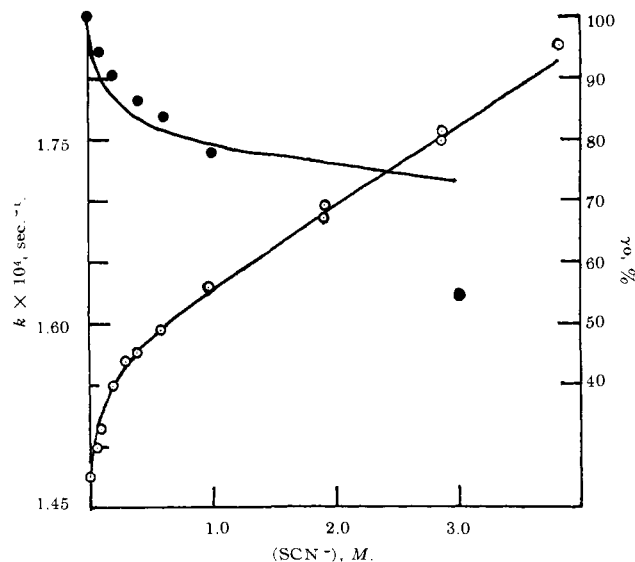
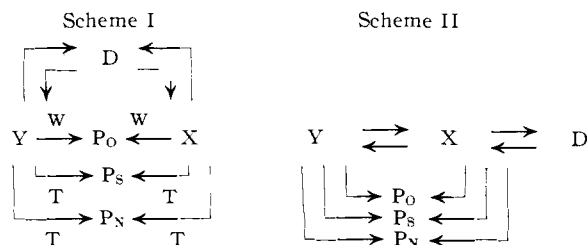


Fig. 1.—Apparent first-order rate constants, O, and *p*-cresol yields, ●, as a function of concentration of potassium thiocyanate in the decomposition of *p*-toluenediazonium ion in water at 48.8°. The rate curve is calculated from eq. 1; the yield curve is calculated from eq. 10, with the constants given in the text.

results are reasonable in terms of one of the two schemes presented below. In both schemes D represents the



diazonium salt, X and Y represent two intermediates, and P<sub>O</sub>, P<sub>S</sub>, and P<sub>N</sub> represent products in which the *p*-tolyl group is bonded to oxygen, sulfur, and nitrogen, respectively; W represents water and T thiocyanate ion. If in both schemes the reaction of X to give D is far faster than any other reaction of X, then we cannot distinguish return of Y to D directly or indirectly through X and the schemes are equivalent. We shall use Scheme I for convenience, recalling that II is as good.

Let us call the rate constant for the conversion of D into X,  $k_{XD}$ , and that for the conversion of X into P<sub>O</sub>,  $k_{XO}$ , etc., and combine (for the moment) the products P<sub>S</sub> and P<sub>N</sub> and write

$$P_S + P_N = P_T$$

and

$$k_{XS} + k_{XN} \equiv k_{XT}$$

$$k_{YS} + k_{YN} \equiv k_{YT}$$

Setting up the steady state in both X and Y, we can write eq. 6 and 7.

$$\frac{d(P_O)}{dt} = \frac{k_{XO}(W)k_{DX}(D)}{k_{XO}(W) + k_{XT}(T) + k_{XD}} + \frac{k_{YO}(W)k_{DY}(D)}{k_{YO}(W) + k_{YT}(T) + k_{YD}} \quad (6)$$

$$\frac{d(P_T)}{dt} = \frac{k_{XT}(T)k_{DX}(D)}{k_{XO}(W) + k_{XT}(T) + k_{XD}} + \frac{k_{XT}(T)k_{DY}(D)}{k_{YO}(W) + k_{YT}(T) + k_{YD}} \quad (7)$$

The sum of these two equations gives the total rate,  $-d(D)/dt$ , which we can also write as  $k_{app}(D)$ , where  $k_{app}$  is the observed apparent first-order rate constant (making only the very good assumption that (T) does not vary with time). Now a steady-state treatment

cannot give the rate constants for the reactions of an unstable intermediate; it only can give the relative rates of different paths. Let us write for these relative rates the constants  $c_{X_i} = k_{X_i}/k_{XO}$  and  $c_{Y_i} = k_{Y_i}/k_{YO}$ . Thus  $c_{YD}$  represents the relative rate constant for the conversion of Y to D compared to its reaction with water. We can write the new equation (8), derived by adding 6 and 7

$$k_{app} = \frac{k_{DX}(W) + k_{DX}c_{XT}(T)}{(W) + c_{XT}(T) + c_{XD}} + \frac{k_{DY}(W) + k_{DY}c_{YT}(T)}{(W) + c_{YT}(T) + c_{YD}} \quad (8)$$

If we make the further assumption that  $c_{XD}$  is far larger than  $c_{XT}(T)$  at all values of (T), then the denominator of the first term in 8 is approximately  $(W) + c_{XD}$  and we shall define the new constant  $c_D = k_{DX}/[(W) + c_{XD}]$  which then leads to eq. 9 by straightforward algebraic manipulation.

$$k_{app} = (W)c_D + k_{DY} + c_{XT}c_D(T) - \frac{1}{\frac{(W) + c_{YD}}{c_{YD}k_{DY}} + \frac{c_{YT}(T)}{c_{YD}k_{DY}}} \quad (9)$$

which contains the five unknown constants  $c_D$ ,  $k_{DY}$ ,  $c_{XT}$ ,  $c_{YT}$ , and  $c_{YD}$ , and is of the same form as the empirical eq. 1, which however contains only four constants. It is thus not possible to evaluate the constants in eq. 9 without further information.

Such information can be obtained from the yields sufficient to calculate the constants. This can be shown by dividing eq. 7 by eq. 6 to give eq. 10 after making the substitutions to include the  $c$  constants;  $Y_T$  and  $Y_O$  are the yields of tolyl thiocyanate + iso-

$$\frac{d(P_T)}{d(P_O)} = \frac{Y_T}{Y_O} = \frac{(T)}{(W)} \left[ \frac{c_D c_{XT} + \frac{k_{DY} c_{YT}}{(W) + c_{YT}(T) + c_{YD}}}{c_D + \frac{k_{DY}}{(W) + c_{YT}(T) + c_{YD}}} \right] \quad (10)$$

thiocyanate and *p*-cresol, respectively. The integration assumes that (T) and (W) are not time dependent and that no products are present at the beginning of the reaction. This equation allows, together with the rate data, the evaluation of all the constants; the calculated yield curve of Fig. 1 uses the set

$$\begin{aligned} c_{XT} &= 2.8(2.7-6.0); \quad c_D = 0.0228 \times \\ &\quad 10^{-4} \text{ l./mole sec. } (0.01-0.025) \\ c_{YD} &= 21 \text{ moles/l. } (6-38); \quad c_{YT} = 470(400-860) \\ k_{DY} &= 0.349 \times 10^{-4} \text{ sec.}^{-1} (0.24-1.0) \end{aligned}$$

The parenthetical numbers represent the extreme ranges of each of these constants using various rather less satisfactory fits to the data. It is clear that the agreement between the observed and the calculated *p*-cresol yields using these constants is far less than perfect. A somewhat better agreement could be made by sacrificing some of the agreement to the rate constants, but this is not worthwhile. In fact, the observed phenol yields are not exactly of the form calculated by eq. 10 even if all constants are quite arbitrary, using the assumption that  $(W) = 55.5 M$  (this assumption was used in calculating the yield curve in Fig. 1). The error in this assumption is substantial at high thiocyanate concentrations and is even worse if the several water molecules solvating the potassium ion are considered inert. A correction for this effect would reduce the calculated yields at high thiocyanate concentration and improve the agreement. No correction was made because the error introduced is probably smaller than that of neglecting salt effects on the various rate constants. The salt effects cannot be reliably estimated, so only qualitative agreement between any model and the experiment can be expected and it appears that the fit is adequate under these circumstances. A further possible source of discrepancy is that a reaction of either X or

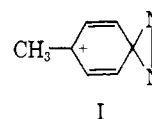
Y which is first order in thiocyanate ion may give cresol, for instance if water solvating the anion is more reactive than ordinary water.

It will be seen that the intermediate Y is quite selective in that it reacts with thiocyanate far more rapidly (even within the large uncertainty) than with water ( $c_{YT} = k_{YT}/k_{YO} = 470$ ), but X is very unselective ( $c_{XT} = 2.8$ ). An independent indication may be obtained from the mode of attachment of the thiocyanate. At low concentrations most of the thiocyanate containing materials are derived from Y, but at higher concentrations X contributes more extensively. Using the measured yields of tolyl isothiocyanate and tolyl thiocyanate yields calculated by difference (using interpolated values of cresol yields), the ratio  $Y_S:Y_N$  has the values 34 at  $(T) = 0.105 M$ , 4.4 at  $(T) = 0.66 M$ , and 4.5 at  $(T) = 3.0 M$ . While the minimum is clearly unreasonable, the markedly higher value at low (T) is clear and confirms the high selectivity of Y.

The rate of return from the intermediate X to D cannot be calculated; it is assumed to be large compared to other fates of X. The rate of return from Y to D is readily calculated; it is the amount that the rate falls below the linear asymptote of Fig. 1 or, alternatively, the magnitude of the negative term in eq. 1. At zero thiocyanate concentration it then has the value  $10^{-4}/10.35 = 0.0966 \times 10^{-4} \text{ sec.}^{-1}$ . Graphically, this is the difference between the observed rate at  $(SCN^-) = 0$  and that extrapolated from the linear portion of the curve of Fig. 1. From the previous work the rate of the isotopic turnaround reaction of  $N^{15}$ -labeled diazonium ion is 0.029 times the solvolysis rate =  $0.043 \times 10^{-4} \text{ sec.}^{-1}$ . We may then say that *the rate of return from Y is twice the rate of isotopic rearrangement*, within the experimental error of each determination. The correction of the isotopic rearrangement rate for the isotope effect now measured and previously ignored is trivial. Support for this view may also be obtained on the unsubstituted compound.

Using the rate data of ref. 2 on unsubstituted benzenediazonium ion, and making the reasonable assumption that all measured rates were on the essentially linear portion of a curve like that in Fig. 1, these then yield (by least squares) the extrapolated value at  $(SCN^-) = 0$  of  $4.16 \times 10^{-4} \text{ sec.}^{-1}$  if all the data are used, or  $4.25 \times 10^{-4}$  using only the presumably most reliable data (condition I, Table II in ref. 2). These exceed the observed rate by 0.08 and  $0.17 \times 10^{-4} \text{ sec.}^{-1}$ , respectively, and are therefore estimates of the return from an intermediate like Y. The isotopic rearrangement rate<sup>3</sup> is 1.4% of the solvolysis rate, or  $0.057 \times 10^{-4} \text{ sec.}^{-1}$ . This value is, within the far larger experimental error, again about one-half of the extent of return from the intermediate.

If Y returns half the time to an unrearranged diazonium ion, and half to the rearranged ion, Y most likely has two equivalent nitrogens, and these are not of the form of free molecular nitrogen. We propose the structure I for Y, in order to explain the rate and rearrangement data, and also the larger extent of rearrangement with the *p*-tolyl compound than the unsubstituted compound.



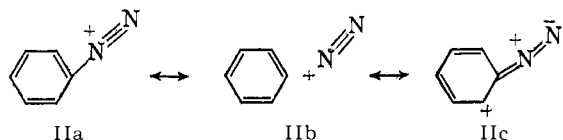
Some further consequences of this proposed structure for Y are being explored.

The nature of the intermediate X is in many ways more puzzling for X must have the following characteristics in order to explain the new kinetics and the

older observations: (1) It must return predominantly to the diazonium ion. (2) The two nitrogen atoms must maintain their identities (since all rearrangement is now attributed to Y). (3) It is highly unselective. (4) Arguments on the effect of structure on rates, formerly applied to support the intermediacy of aryl cations, must now be explicable in terms of a mechanism through X. (5) Since most of the reaction at  $\text{SCN}^- = 0$  goes through X, the significant isotope effect suggests a weakened C-N bond.

Of these, 1 and 3 are difficult to reconcile. If an intermediate is unselective, it has probably almost no activation energy for its bimolecular reactions, and therefore to say that the return reaction is far faster than these reactions of very low activation energy must be to say that it must have a very large Arrhenius pre-exponential factor, compared to the reactions of X with solvent or nucleophiles.

We suggest that X may be an excited state of the diazonium ion, probably a vibrational state having nearly all the activation energy in it, which can react by a properly oriented collision at the nitrogen-bearing carbon atom, but which will be deactivated by the large majority of collisions elsewhere on the molecule. The low selectivity follows naturally and the substituent effects can be reasonable if this excited state has a charge distribution similar to that in the aryl cation. With a highly bent diazonium salt such as II, the contributions of IIc and to a lesser extent IIa must be



markedly reduced because of the unfavorable bond angles. Only IIb is free from angle strain, so that the process of bending the C-N bond might reasonably make the molecule more like a phenyl cation. The arguments apply equally well to a linearly stretched molecule.

It should be noted that this argument for a two-step reaction *via* the intermediate X is entirely equivalent to 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. The original and still valid argument<sup>2</sup> for X was that it was unreasonable to propose a nucleophilic attack on the diazonium salt which was not markedly accelerated by the *p*-nitro group. It is clear that a transition state for a bimolecular nucleophilic attack in which the new bond is hardly present but the C-N bond is nearly totally broken would not be activated by the *p*-nitro group, so that this mechanism fits all requirements.

Figure 2 illustrates the relation between the two mechanisms. The solid curve shows the route through X. The first transition state contains the elements of the diazonium ion only, the second also contains a nucleophilic reagent, such as water or thiocyanate ion. From Hammond's postulate,<sup>6</sup> both transition states strongly resemble X. The dotted line shows the one-step reaction. The single transition state contains both the nucleophile and the diazonium ion, and it still closely resembles X in energy and structure, but X is now a hypothetical molecule rather than a real intermediate. We prefer to talk in terms of the intermediate X because the structural resemblance of the transition state and the weakly bonded X is clear.

The mechanism proposed, through X in which no carbonium ion need ever be formed and in which the transition state for the product determining step con-

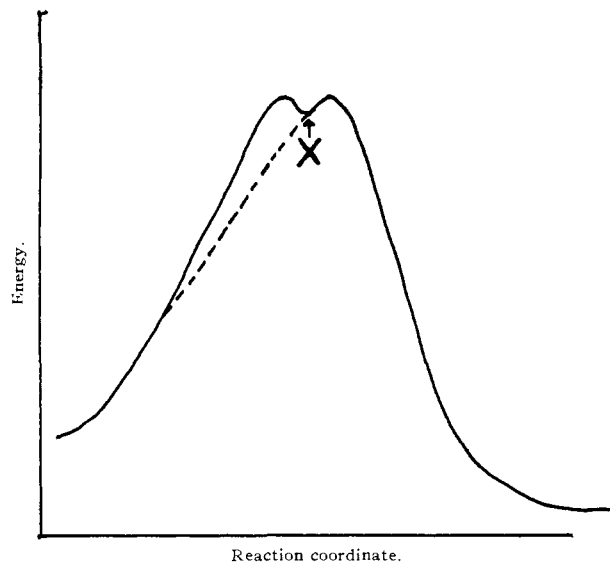


Fig. 2.—Energy-reaction coordinate plot for reaction through the perceptibly stable intermediate X (solid line), and for a one-step reaction of starting material (D) by way of a transition state closely resembling X, but containing the nucleophile.

tains a nucleophile and a nitrogen molecule on the same side of carbon, has possible application to the knotty problem of the aliphatic deamination reaction, in which it has been necessary to propose a carbonium ion intermediate different from that in solvolytic reactions to explain the reaction course.<sup>7</sup>

### Experimental

**Materials.**—*p*-Toluidine was diazotized conventionally in hydrochloric solution and the diazonium salt was precipitated as the fluoroborate with fluoroboric acid. It could be kept as a white crystalline solid for several weeks at about 0°. *p*-Toluidine was also diazotized in glacial acetic acid, methanol, and sulfuric acid with isoamyl nitrite; addition of ether precipitated *p*-toluenediazonium bisulfate, which was dissolved in acetic acid and acetone and reprecipitated with ether. The  $\alpha$ -N<sup>15</sup>-labeled diazonium salt was that described previously.<sup>3b</sup>

**Rates.**—The technique described previously<sup>4</sup> was used. A solution of about 0.4 g. of *p*-toluenediazonium fluoroborate was prepared in 50 ml. of water, 0.02 *M* in hydrochloric acid, and containing the desired amount of potassium thiocyanate. The solution was placed in the reaction vessel, wrapped with aluminum foil to exclude light, and cooled to ice temperature. Purified nitrogen, saturated with water, was passed in to remove oxygen through a bottom capillary tube used later for withdrawal of sample. The closed reaction vessel was then placed in the thermostat (at  $48.81 \pm 0.02^\circ$ , as read on an uncalibrated thermometer), and after 0.5 hr. a sample was forced through the bottom tube with slight nitrogen pressure. The first part of this sample, not all contained in the thermostat, was discarded, the later part was then cooled rapidly and a sample, of 20  $\lambda$ , was taken. Subsequent samples of 25, 50, 75, and 200  $\lambda$  were taken at times calculated on the basis of a guessed rate constant. The analysis and calculation of the rate constant was exactly as described before.<sup>4</sup> No rate constants are reported using a correction of more than 5% of the guessed rate constant, and in each case the reactions followed a first-order course accurately. However, curvature was observed in the presence of thiocyanate ion if the ratio of thiocyanate to diazonium salt was too large; we attribute this to a reaction between the diazonium salt and some hydrolysis product of the thiocyanate. There was therefore an upper limit on the thiocyanate concentration, and even the result at highest concentration in Fig. 1 may be slightly biased for this reason.

**Product Yields.**—About 0.4 g. of *p*-toluenediazonium bisulfate was dissolved in 50 ml. of freshly standardized potassium thiocyanate solution in an opaque glass vessel. It was cooled to 0°, flushed with nitrogen, then placed in the thermostat. Allowing 5 min. for warming up, it was then left long enough for 80% decomposition, calculated from eq. 1. Only 80% reaction was used to minimize error from thiocyanate hydrolysis. The cooled solution was then titrated with 0.1 *N* sodium hydroxide to a methyl

(6) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(7) Many aspects of this problem are summarized by H. Zollinger, "Diazo and Azo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961.

purple end point. A concurrent experiment, carried to completion but without thiocyanate, gave an assay on the diazonium salt, and there was between 98.5 and 99.5% of the calculated acid produced. The assay was applied in calculating the yield of acid (and hence of *p*-cresol). A minor source of error was the perceptible coupling of the diazonium salt with the indicator.

A gas chromatographic analysis for the other products was used. A solution of 1.239 g. of *p*-toluenediazonium bisulfate was dissolved in 150 ml. of potassium thiocyanate solution and cooled, degassed, and decomposed as before. After essentially complete reaction, the mixture was extracted with ether, the ether solution reduced in volume, and a measured amount of methyl benzoate added as an internal standard. A 1-m. column of 5% Carbo-

wax 1500 on Chromosorb P separated all the products and the yield of *p*-tolyl isothiocyanate was calculated from the area of its peak and that of the internal standard. *p*-Tolyl thiocyanate and *p*-cresol were also detected in the chromatogram, but were not measured quantitatively. They were identified by comparison of retention times with those of authentic samples. Tolyl thiocarbamate was not eluted from the column in a reasonable time, and the efficiency of extractions of *p*-cresol was not high, so the areas of the tolyl thiocyanate and the *p*-cresol peaks were not used.

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[CONTRIBUTION NO. 730 FROM THE DEPARTMENT OF CHEMISTRY, FORDHAM UNIVERSITY, NEW YORK, N. Y.]

## Heteropolar Ozonization of Aza-Aromatics and Their N-Oxides<sup>1-3</sup>

BY EMIL J. MORICONI AND FRANCIS A. SPANO

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The ozonization of four aza-aromatics [1-methyl- (12) and 3-methylisoquinoline (17), acridine (1), and phenanthridine (4)] and five aza-aromatic N-oxides [quinoline-1- (24), phenanthridine-5- (29), acridine-10- (32), isoquinoline-2- (42), and 3-methylisoquinoline-2-oxides (45)] are reported. Initial electrophilic ozone attack on 1, 4, 12, and 17 led to carbocyclic ring-cleaved carboxylic acids; simultaneous nucleophilic ozone attack at the C-atom adjacent to (4), or conjugated with (1), the aza-atom produced cyclic amides. Relative to isoquinoline, the methyl group in 12 and 17 deactivated the aza-aromatic ring to electrophilic ozone attack. Generally, initial nucleophilic ozone attack on aza-aromatic N-oxides led to cyclic hydroxamic acids and cleavage of the C=N aromatic bond (to nitroaldehydes) as primary products. With ozone as an electrophile, further ozonization of the former led to deoxygenated products, cyclic amides. Phthalic acid was also obtained from 42 and 45. In almost all cases, solvent effects were noted. N→O and C=O absorption frequencies of reactants and products are tabulated.

The low reactivity of the pyridine ring to ozone in the parent compound and its homologs,<sup>4,5</sup> of its N-oxide,<sup>5b</sup> and quinoline and its alkyl derivatives<sup>6,7</sup> is well documented. Although alkyl substituents on the pyridine nucleus effectively enhance its reaction rate with ozone,<sup>4a,8</sup> the rate is still considerably lower than for the corresponding benzene derivative, and the yields of ozonolysis products are little improved over the parent heterocycle. In quinoline and its derivatives, major attack seems to occur initially in the carbocyclic ring, followed by a slower attack at the 3,4-bond of the heterocyclic ring.

What is perhaps surprising is the unusual reactivity of isoquinoline to ozone. Ozonolysis of this aza-aromatic with excess ozone in glacial acetic acid containing trace amounts of water produced 3,4-pyridinedicarboxylic acid, and, after hydrogen peroxide oxidation, phthalic acid in almost equal amounts.<sup>9</sup> From a quantitative

measurement of isoquinoline absorption characteristics and of the ammonia formed on hydrolysis of the peroxidic ozonolysis products, Wibaut<sup>5b</sup> has reported that in this heterocyclic ring system, the aza-aromatic moiety reacted one and one-half times more rapidly than the benzenoid nucleus. In all aza-aromatics ozonized, however, it has been generally assumed that only C=C cleavage occurs in both carbocyclic and heterocyclic nuclei<sup>10</sup> and that the ammonia formed resulted from hydrolysis of the primary scission products, the acid amides.

In this paper we report on the ozonization of the aza-aromatics: acridine, phenanthridine, 1-methyl- and 3-methylisoquinoline, their N-oxides, and quinoline-1- and isoquinoline-2-oxide.

**Acridine (1) and Phenanthridine (4).**—Ozone reacted readily with acridine (1) in both methanol and methylene chloride solvents; with two molar ozone equivalents in methanol, followed by alkaline hydrogen peroxide oxidation, 1 gave ring-cleaved 2,3-quinolinedicarboxylic acid (acridinic acid) (2) in 73–75% yield and less than 0.1% of the oxygenated 9-acridanone (3); in methylene chloride, however, 60–62% of 2 and up to 2.5% of 3 were obtained. In both instances, 2–3% of 1 was also recovered.

Phenanthridine (4) did not react with ozone in methanol, and only sluggishly in methylene chloride. In the latter solvent, two molar equivalents ozone absorption followed by alkaline peroxide oxidation produced up

form at –40°. There is no doubt however that further oxidation of the peroxidic ozonolysis products with hydrogen peroxide in acetic acid solvent must be strongly accelerated by the equilibrium presence of peracetic acid. It is unfortunate that no product yields are reported in ref. 6b.

(10) This conclusion is based on a quantitative measurement of ozone uptake and ammonia formed,<sup>4a,6b</sup> and product isolation: 2,2,6-trimethylcyclohexanecarboxamide from 2-(2,2,6-trimethylcyclohexyl)-4,6-dimethylpyridine,<sup>11</sup> methylethylacetamide from 2-(*sec*-butyl)-4,5-dimethylpyridine,<sup>12</sup> and glyoxal, carbon dioxide, and hydrazine from pyrazole.<sup>13</sup> No nitrous or nitric acid was found on ozonolysis of the pyridine nucleus.<sup>4a</sup>

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(3) Presented in part at the Metropolitan Regional Meeting, American Chemical Society, New York, N. Y., Jan., 1962; at the 142nd National Meeting of the American Chemical Society, Org. Div., Atlantic City, N. J., Sept., 1962; and at the XIXth IUPAC Congress, London, July 15, 1963.

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