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STUDY OF THE MECHANISM OF THE INTERACTION OF NITROSOARYLS WITH HYDRAZOIC ACID WITH THE AID OF N^{15}

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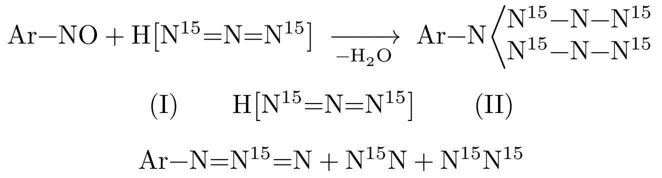
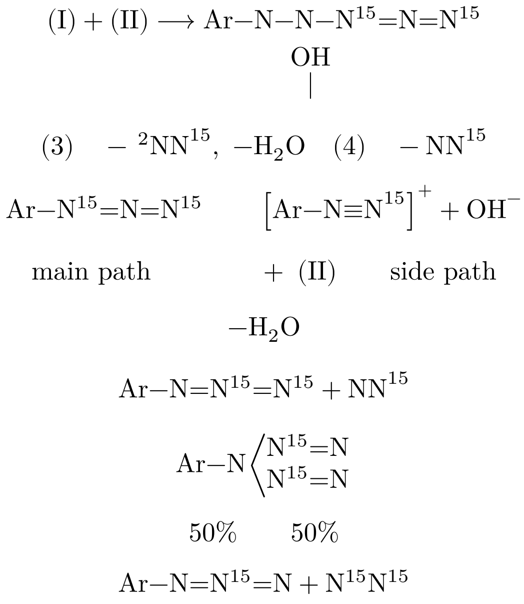
The mechanisms of formation and reactions of triazo compounds have until recently been little studied. Only recently, in the work of Clusius and co-workers, have a number of important questions in this field been resolved. In particular, the linear structure of the azido group and the nonequivalence of the nitrogen atoms composing it have been precisely established (1). Knowledge of this, in turn, facilitates the study of the mechanism of reactions and formation of azides. A new method for preparing aryl azides has recently been published (2). Aromatic nitroso compounds react with hydrazoic acid on gentle heating and smoothly form aryl azides with liberation of elemental nitrogen

$$\mathrm{ArNO} + 2\mathrm{HNNN} \rightarrow \mathrm{ArNNN} + 2\mathrm{N_2} + \mathrm{H_2O}. \qquad (1)$$

The authors of the cited work confine themselves to the supposition that diazohydroxide is formed as an intermediate. They give no experimental evidence for this assumption. Thus, the mechanism of this reaction is unclear. Three mechanisms may be proposed, differing in the arrangement of the initial nitrogen atoms in the reaction products. It is obvious that the use of the nitrogen isotope N^{15} permits the correct reaction path to be determined here.



$$\begin{array}{c} \mathrm{Ar{-}NO} + \mathrm{H[N^{15}{=}N{=}N^{15}]} \xrightarrow[-\mathrm{H_2O}]{} \mathrm{Ar{-}N}\left\langle \begin{matrix} \mathrm{N^{15}{-}N{-}N^{15}} \\ \mathrm{N^{15}{-}N{-}N^{15}} \end{matrix} \right. \\ \mathrm{(I)} \qquad \mathrm{H[N^{15}{=}N{=}N^{15}]} \qquad \mathrm{(II)} \\ \mathrm{Ar{-}N{=}N^{15}{=}N} + \mathrm{N^{15}N} + \mathrm{N^{15}N^{15}} \end{array} \qquad (2)$$



$$(I) + (II) \longrightarrow Ar{-}\underset{\displaystyle OH}{\underset{|}{N}}{-}N{-}N^{15}{=}N{=}N^{15}$$

$$(3) \quad -\,^{2}NN^{15},\ -H_2O \quad (4) \quad -\,NN^{15}$$

$$Ar{-}N^{15}{=}N{=}N^{15} \qquad \left[Ar{-}N{\equiv}N^{15}\right]^{+} + OH^{-}$$

main path + (II) side path

$$-H_2O$$

$$Ar{-}N{=}N^{15}{=}N^{15} + NN^{15}$$

$$Ar{-}N\left\langle\begin{matrix}N^{15}{=}N\\ N^{15}{=}N\end{matrix}\right.$$

50% 50%

$$Ar{-}N{=}N^{15}{=}N + N^{15}N^{15}$$

If hydrazoic acid $HN^{15}NN^{15}$ is used, then the distribution of N^{15} in the reaction products will correspond to schemes (2)–(4).

In mechanism (4), the second stage, according to Clusius (3), has a branched character, and the expected results can be calculated on the basis of the data obtained by him.

The reactions were carried out with hydrazoic acid labeled with N^{15} in the terminal nitrogen atoms. Carbon dioxide was passed through the reaction vessel containing a solution of the nitroso compound in alcohol. After complete removal of the air, a solution of HN_3 in chloroform was poured in, the flask was gently heated, and the nitrogen evolved was collected over a solution of caustic potash, transferred into evacuated ampoules, and analyzed in a mass spectrometer. The aryl azides were isolated in pure form and, by reduction with zinc dust and hydrochloric acid, converted into amine and ammonia (4)

$$Ar \underset{a}{-} N = \underset{b}{N} = \underset{c}{N} + 4H_2 \rightarrow \underset{a}{ArNH_2} + \underset{b,c}{2NH_3} \qquad (5)$$

The reaction products were separated, converted into elemental nitrogen, and analyzed in a mass spectrometer. The results of the analyses are summarized in Table 1.

Table 1

Experiment No.	N^{15} content in the starting substances (%)	Found: Ar—N=N[illegible] a	Found: ArNH$_2$, NH$_3$, b, c	Found: NN	Calculated by mechanisms (2), (3), (4): Ar—N=N[illegible] a	Calculated by mechanisms (2), (3), (4): ArNH$_2$, NH$_3$, b, c	Calculated by mechanisms (2), (3), (4): NN
1	n-NO$_2$· Ph· NO(0.37) (0.37)H[N=N=N](4.95) (0.37) (4.95)	0.40	4.86	3.10	0.37(2)4.95[illegible]	[illegible]	[illegible]82.662.73
2	n-CH$_3$· CO· NH· Ph· NO(0.37) (0.37)H[N=N=N](4.95) (0.37) (4.95)	0.39	4.72	3.00	0.37(2)4.95[illegible]	[illegible]	[illegible]82.662.80
3	n-Cl· Ph· NO(0.37)H[N=N=N](4.27) (0.37) (4.27)	–	3.9	2.50	–	2.32(2)2.32[illegible]	[illegible]2.47
4	n-(CH$_3$)$_2$N· Ph· NO(0.37) (0.37)H[N=N=N](4.27) (0.37) (4.27)	–	–	2.55	–	–	3.30(2)2.32(3)2.58(4)

Upon reduction of n-nitrophenyl azide and n-acetamidophenyl azide, ammonia and n-phenylenediamine are obtained. Analysis of the latter gives the total N^{15} content in both nitrogen atoms. Since one amino group, originating from the substituent in the nitroso compound and not participating in the reaction, obviously cannot contain an excess of N^{15}, Table 1 gives the recalculated N^{15} content in one amino group corresponding to the nitrogen from the C—N bond of the azido group.

The calculated values according to mechanism 4 were obtained on the basis of the results of Clusius' s work $^{(3)}$. Of the substances investigated by us, a calculation according to Clusius can be made only for n-nitrophenyl azide. In the remaining cases the comparison was made with the results for analogous compounds. Thus, n-chlorophenyl azide was compared with n-bromophenyl azide, and n-dimethylaminophenyl azide with n-ethoxyphenyl azide. For n-acetamidophenyl azide, the ratio of the reaction paths was first calculated from the analysis of ammonia, and then, for this ratio, the N^{15} content in nitrogen was calculated.

To check the absence of side reactions involving evolution of nitrogen, samples of it for mass-spectrometric analysis were taken at the beginning and at the end of the experiment. The isotopic composition of the nitrogen remained practically constant during the reaction.

In the amine obtained upon reduction of the aryl azide, there is no excess of N^{15}. Consequently, in the azide the nitrogen nearest to the nucleus is light. In am-

in the ammonia obtained from the other two N atoms of the azide, the content of N^{15} nearly reaches the initial concentration. Consequently, both these atoms are heavy and originate from the terminal nitrogen atoms of the azide ion. The isotopic structure of the aryl azide therefore corresponds to

$$\mathrm{Ar} = \underset{1}{\mathrm{N}} = \underset{2}{\mathrm{N}^{15}} = \underset{2}{\mathrm{N}^{15}}.$$

An azide of this structure can be obtained only according to scheme 4. The somewhat lower content of N^{15} than in the initial nitrogen is explained by the reaction proceeding in the second stage by a branched mechanism, in which an azide of the structure $\mathrm{Ar} - \underset{1}{\mathrm{N}} = \underset{2}{\mathrm{N}^{15}} = \underset{3}{\mathrm{N}}$ is partially formed. Thus, the isotopic composition of the middle N atom in the azide group exactly corresponds to the isotopic composition of the terminal nitrogen atoms in the azide ion. The terminal N atom contains a smaller amount of N^{15}, which can be calculated if the degree of branching of the reaction for the corresponding substituent is known.

The content of N^{15} in the nitrogen in some of the experiments does not fully agree with the calculated value. This is still difficult to explain.

From the isotopic composition of the products, the share of both reaction pathways in the second stage of the process was calculated. These values are given in Table 2 and compared with the branching of the reactions of diazo compounds (having the same or similar substituents) with hydrazoic acid according to Clusius.

The calculation was carried out according to the formulas:

$$k = 2x - 100;$$

$$l = 2(100 - x),$$

where k is the fraction of the main reaction in percent, x is the fraction of the main product in percent, and l is the fraction of the side reaction in percent. The percentage of the main product (x) was calculated, for example, from the ammonia for n-acetamidophenyl azide from the equation:

Initial nitroso compound	Share of reaction pathway in %, main, with formation of linear pentazene	Share of reaction pathway in %, side, with formation of cyclic pentazene
n-NO_2 PhNO [1]	92(92)	8(8)
n-$CH_3CONHPhNO$ [1]	80–	20–
n-ClPhNO [1]	62(71) [3]	38(29)

Initial nitroso compound	Share of reaction pathway in %, main, with formation of linear pentazene	Share of reaction pathway in %, side, with formation of cyclic pentazene
n-$(CH_3)_2NPhNO$ [2]	53(47) [4]	47(53)

[1] Calculated from the composition of ammonia. [2] Calculated from the composition of nitrogen. [3] Clusius' s data for n-$BrPhN_2^+$. [4] Clusius' s data for n-$C_2H_5OPhN_2^+$.

$$4.95x + \frac{4.95 + 0.37}{2}(1 - x) = 4.72.$$

Taking the errors of the mass-spectrometric determination to be up to 3% relative, the errors in the fractions of the reaction pathways may be estimated at ±10%. Clusius' s data are apparently accurate to ±4%. Taking also the difference in substituents into account, the values and the order of the figures may be considered sufficiently close.

As is seen from Table 2, the degree of participation of the main reaction increases with increasing electrophilicity of the substituent. In the same direction, substituents affect the activity of diazocations in coupling. This analogy is understandable, since both reactions include electrophilic attack by the diazocation, through a terminal nitrogen atom, on the second reacting molecule. In the diazo reaction, the first stage—the formation of linear or cyclic pentazene—is rate-determining. In the reaction of nitroso compounds with hydrazoic acid, the diazo reaction is the second stage and proceeds much faster than the first —the formation of the diazocation. This follows from work ([9]), where it was shown that, when the amount of hydrazoic ···

of hydrazoic acid (less than 2 moles per 1 mole of the nitroso compound), no intermediate product is detected, and the expected amount of final products and a portion of unchanged nitroso compound are obtained.

The reaction rate increases from n-nitrosodimethylaniline to n-nitrosonitrobenzene, i.e., it depends on substituents in the same way as the rate of the diazo reaction studied by Clusius. Although the slow stages of these reactions are different, such an analogy was to be expected, since formation of the diazo compound should be promoted by an increase in the positive charge on the nitrogen of the nitroso group caused by electrophilic substituents.

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Note: Figure translations are in progress. See original paper for figures.