277. Dediazoniation of Arenediazonium Ions. Part XX. Secondary Deuterium Isotope Effects in Reactions of Benzenediazonium Tetrafluoroborate[1][2]

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(18.IX.81)

Summary

Secondary deuterium isotope effects were measured for the dediazoniation of [2,4,6-$^2H_3$]-benzenediazonium tetrafluoroborate ([$^2H_3$]-**1**), and were found to be $(k_H/k_{D_3})_s = 1.46$ in 2,2,2-trifluoroethanol (TFE) and 1.51 in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), respectively. These values are in agreement with the previously proposed rate determining formation of the phenyl cation *(Eqn. 1)*, and are similar to the results obtained by *Swain et al.* in other solvents. The N_α-N_β rearrangement *Eqn. 2)* of β-^{15}N labelled **1** was studied in TFE. The percent of rearrangement after 70% dediazoniation was found to be 8.18, which corresponds to a rate constant for the rearrangement $k_r = 4.02 \cdot 10^{-6}\,s^{-1}$. Thus the secondary deuterium isotope effect in the rearrangement in TFE $(k_H/k_{D_3})_r$ was calculated to be 1.42. The fact that the isotope effect in the rearrangement is, within experimental error, the same as that observed during dediazoniation, definitely excludes the formation of benzenespirodiazirine cation **3**, which has repeatedly been discussed as an intermediate in the rearrangement. The size of the deuterium isotope effect in the rearrangement is in accordance with the rearrangement proceeding via a phenyl cation/N_2 molecule pair (**2**).

Introduction. - The heterolytic dediazoniation of arenediazonium salts in 2,2,2-trifluoroethanol (TFE) and in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) proceeds *via* two intermediates, a tight aryl cation/N_2 molecule pair and a free aryl cation *(Eqn. 1)* [2-4]. The N_α-N_β rearrangement of the two N-atoms in the diazo group *(Eqn. 2)* that accompanies the dediazoniation occurs *via* the first intermediate [2] [3]. Concerning the structure of this intermediate, we proposed the phenyl cation/N_2 molecule pair (**2**) [2] [3], but the benzenespirodiazirine cation (**3**) has also been discussed [5].

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[1] Part XIX, see [1].

[2] Presented at the 1st European Symposium on Organic Chemistry, Cologne (Germany), August 1979.

0018-019X/81/8/2728-05$01.00/0

$$\begin{tikzcd}
Ar-\overset{+}{N_2} \arrow[r, shift left] & {[Ar^{+}N_2]} \arrow[l, shift left] \arrow[r, shift left] \arrow[rr, bend right=40, "\substack{+Nu\\ -N_2}"'] & Ar^{+} + N_2 \arrow[l, shift left] \arrow[r, "+Nu"] & \text{products}
\end{tikzcd} \qquad (1)$$

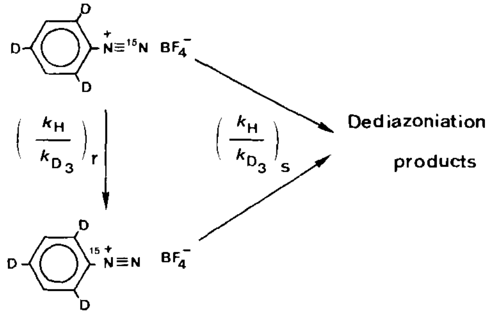
$$Ar-\overset{+}{N}\equiv{}^{15}N \longrightarrow Ar-{}^{15}\overset{+}{N}\equiv N \qquad (2)$$

2 **3**

Structures **2** and **3**

A differentiation between the two structures is possible from the comparison of the secondary deuterium isotope effects on the dediazoniation rate (k_s) with those on the rate of the N_α-N_β rearrangement (k_r) *(Scheme)*.

Scheme



If the deuterium isotope effect on the rearrangement rate $(k_H/k_{D_3})_r$ is larger than one, and is approximately equal to that on the rate of dediazoniation $(k_H/k_{D_3})_s$[3]), it can be concluded that the ion/molecule pair **2** is the more likely intermediate for the rearrangement reaction. On the other hand, an isotope effect in the rearrangement rate smaller, or equal to one would be an indication for the intermediacy of the benzenespirodiazirine cation **3**.

Results and discussion. – The solvolysis rates (k_s) for the dediazoniation of benzenediazonium tetrafluoroborate (**1**), and the [2,4,6-$^2H_3$]-compound ([$^2H_3$]-**1**) were measured in TFE and in HFIP *(Table 1)*.

The secondary deuterium isotope effect on the dediazoniation rate in both solvents is rather large, and comparable to the highest values observed in S_N1

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[3]) It could be argued that, owing to the ^{15}N-isotope effect, $(k_H/k_{D_3})_s$ for the rearranged ([$^2H_3$]-Ar-$^{15}\overset{+}{N}\equiv N$) and non-rearranged ([$^2H_3$]-Ar-$\overset{+}{N}\equiv{}^{15}N$) diazonium ion would differ. However, since the ^{15}N-isotope effect is very low [6], no complications arise.

Table 1. *Dediazoniation rate constants of benzenediazonium tetrafluoroborate* (**1**) *and [2,4,6-$^2H_3$]-benzenediazonium tetrafluoroborate [$^2H_3$]-***1**) *in TFE and HFIP* (25°, 1 atm N_2)

Solvent	k_s [a]) × 10^5 [s^{-1}]		$\left(\frac{k_H}{k_{D_3}}\right)_s$ [b])
	1	[$^2H_3$]-**1**	
CF_3CH_2OH	7.95 ± 0.14 [c])	5.45 ± 0.05 [c])	1.46 ± 0.03 [c])
$(CF_3)_2CHOH$	7.72 ± 0.25	5.10 ± 0.27	1.51 ± 0.09

[a]) Average of at least five measurements. [b]) The isotope effects are uncorrected. The deuterium content was found to be 97% $^2H_3$. [c]) Standard deviation.

solvolyses [7]. Very high secondary β-deuterium isotope effects ($k_H/k_{D_2} = 1.43$) have also been observed in the solvolysis of 1-phenylvinyl trifluoromethanesulfonate. The fact that isotope effects in vinyl systems in general are bigger than those observed in saturated systems was explained by a dihedral angle of 0° between the empty orbital and the β-H(D)-atoms, and by the shorter C,C-bond, both resulting in a larger overlap [8]. The same reasoning is applicable to the observed isotope effects in the solvolysis of benzene diazonium salts.

Similar values for the isotope effect on the dediazoniation rate ranging from 1.50 to 1.58 per three D, have been measured in aqueous H_2SO_4-solution, in CH_3COOH and in CH_2Cl_2 by *Swain et al.* [9]. They were attributed to substantial hyperconjugative stabilization of the positive charge to the *ortho* H-atoms in the transition state, and were considered as further evidence for the formation of a phenyl cation intermediate in dediazoniations [9].

The observed isotope effect changes very little in the different solvents used. The somewhat larger isotope effect[4]) in HFIP than in TFE may be due to the lower nucleophilicity [10] and the higher ionizing power [10] [11] of HFIP relative to TFE.

The N_α-N_β rearrangement of the β-^{15}N benzenediazonium tetrafluoroborate (β-^{15}N **1**) and the corresponding [2,4,6-$^2H_3$]-compound [$^2H_3$, β-^{15}N]-**1** was determined, and the isotope effect on the rate of rearrangement was calculated. The data are shown in *Table 2.*

The deuterium isotope effect on the rate of the rearrangement is practically the same as that on the rate of dediazoniation. The magnitude of the isotope effect indicates substantial hyperconjugative delocalization of the positive charge formed

Table 2. *Extent of N_α-N_β rearrangement of diazonium salts at 70% dediazoniation* (TFE, 25°, 1 atm N_2)

Substrate	% Rearrangement	k_r [a]) × 10^{-5} [s^{-1}]	$\left(\frac{k_H}{k_{D_3}}\right)_r$ [b])
β-^{15}N-**1**	7.96	0.572	
[$^2H_3$, β-^{15}N]-**1**	8.18	0.402	1.42

[a]) Calculated as described in [2], from the observed % of rearrangement and the dediazoniation rate k_s in *Table 1.* [b]) The isotope effect is uncorrected. The deuterium content was found to be 97% $^2H_3$.

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[4]) A statistical analysis of variance and an F-test led to the conclusion that the difference in magnitude of the isotope effects in TFE and in HFIP is significant only at a 82.6% confidence level, while the dediazoniation rates in TFE and in HFIP, and the rates for **1** and [$^2H_3$]-**1** differ significantly at 99.3% and 99.9% confidence level, respectively.

to the *ortho* H-atoms - a situation expected for the transition state immediately preceding the phenyl cation/N_2 molecule intermediate (**2**) where the *ortho* H,C-bonds are coplanar with the empty orbital. If the benzenespirodiazirine cation (**3**) were involved as an intermediate in the rearrangement, only a small inverse isotope effect $(k_H/k_{D_3}) \leqslant 1$ of inductive origine would be expected, since in the transition state preceding intermediate **3** the H,C-bonds are orthogonal to the π-orbitals where the positive charge is distributed. This expectation is borne out by the secondary deuterium isotope effect $(k_H/k_{D_3}) = 0.79$ [12] measured in the protodesilylation of trimethylphenylsilane, a model reaction that proceeds [13] through a σ-intermediate similar to **3**.

Recently, an *ab initio* study of benzenediazonium ions and of their N_α-N_β rearrangement was performed [14]. It was predicted that the rearrangement proceeds *via* an asymmetric transition state in which one of the N-atoms is weakly bound to a ring C-atom, and the other not at all. In order for this to be in agreement with the observed isotope effects on the rearrangement, the C,N-bond should be very weak indeed! In addition, a symmetric bridged structure which may be alternatively considered as a benzenespirodiazirine cation lying in a high-energy shallow potential well was predicted to be a metastable intermediate in this rearrangement [14]. Our experimentally observed isotope effects certainly exclude the benzenespirodiazirine cation (**3**) as a transition state in the rearrangement and, unless the *Hammond* postulate [15] is violated, **3** is also excluded as an intermediate. It is clear that calculations simulating the situation in the gas phase must be used with caution, if their results are to be applied to experiments carried out in solution.

The results of a CNDO/2 calculation of the benzenediazonium cation and of phenyl cation/N_2 molecule pairs in water [16], however, are in good agreement with the observed isotope effects and with the proposed mechanism [2-4] of heterolytic dediazoniation.

Conclusion. - The magnitude of the secondary deuterium isotope effect on the rate of the N_α-N_β rearrangement accompanying the dediazoniation of benzenediazonium ions indicates that the rearrangement proceeds through a phenyl cation/N_2 molecule pair intermediate (**2**). The benzenespirodiazirine cation (**3**) can definitely be excluded as an intermediate in the rearrangement reaction.

This work was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung*.

Experimental Part

Solvents and starting materials were purified, and the benzenediazonium tetrafluoroborate (**1**), β-^{15}N labelled **1** as well as the [2,4,6-$^2H_3$]-compounds were synthesized as described previously [2] [9]. The kinetic measurements and the determination of the extent of rearrangement were carried out as before [2] [3].

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