49. Dediazoniations of Arenediazonium Ions in Homogeneous Solution. Part XIV. ^{15}N-CIDNP. Investigation of the Reactions of Diazonium Ions in Weakly Alkaline Aqueous Solutions[1])

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Summary

^{15}N-CIDNP. spectra recorded during the reaction of diazonium cations with OH^- in weakly alkaline aqueous solutions show that the dediazoniation is at least *partially* homolytic. The polarizations observed for the diazonium and *trans*-diazotate ions can be explained by reaction proceeding *via* a cage involving diazenyl and diazotate radicals using *Kaptein*'s rules and simple intensity considerations.

1. Introduction. - For synthetic organic purposes, aqueous, weakly alkaline solutions are by far the most important media for reactions of aromatic diazonium salts. On the other hand, just under such conditions, the decomposition reactions of diazonium ions (dediazoniations) are extremely complex. At present, there are very few reliable data concerning products, catalysis, kinetics and mechanism of dediazoniations in these media. This is in contrast to the situation in organic solvents [2] where products and mechanisms have been identified, and ^{1}H- and ^{13}C-CIDNP. investigations carried out [3-5]. During the course of longer term research projects of our two groups, we thought it of interest to investigate for the first time the mechanism of these reactions in an aqueous medium using CIDNP.

^{1}H- and ^{13}C-CIDNP. results [2-4] demonstrate that dediazoniations of diazonium ions under basic conditions may follow a homolytic pathway in which the diazonium ion can be regenerated [4]. Detailed information on this reaction can be expected from ^{15}N-CIDNP. investigations as the involvement of the postulated [2-4] nitrogen-containing radicals should be directly detectable. Moreover, in the case of ^{15}N the CIDNP. effect is so pronounced that NMR. signals appear under conditions under which no regular ^{15}N-NMR. spectra would be obtained even with highly enriched compounds.

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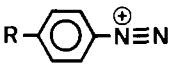
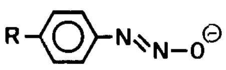
In the following we report on our investigations with 4-chlorobenzenediazonium tetrafluoroborate (**1a**-BF_4) and benzenediazonium tetrafluoroborate (**1b**-BF_4).



1a R = Cl
1b R = H



2a R = Cl
2b R = H

2. Results. - 2.1. *4-Chlorobenzenediazonium tetrafluoroborate* (**1a**-BF_4). When ^{15}N-NMR. spectra are recorded during the decomposition of ^{15}N-labeled **1a**-BF_4 in aqueous alkaline solutions (D_2O or H_2O) at 60° under Ar, signals of enhanced absorption (*A*) and emission (*E*) can be observed *(Fig. 1a-e)*. They can be attributed to the ^{15}N-nuclei in diazonium-ion **1a** and 4-chlorobenzene-*trans*-diazotate (**2a**) and to molecular nitrogen *(Table 1)*, as demonstrated by the reference NMR. spectra of **1a**, **2a** and N_2 [6].

As a consequence of the deuterium solvent effect [7] the equilibrium **1a** $\rightleftharpoons$ **2a** is more on the side of **2a** in H_2O; and thus the intensity of the CIDNP. signals of **2a** is larger in H_2O *(Fig. 1d)* than in D_2O *(Fig. 1a-c)*. With increasing temperature

Table 1. *CIDNP. signals in the reaction of* **1a**-BF_4 *with* OH^-/H_2O; ^{15}N*-chemical shifts of* **1a**, **2a** *and* N_2a)

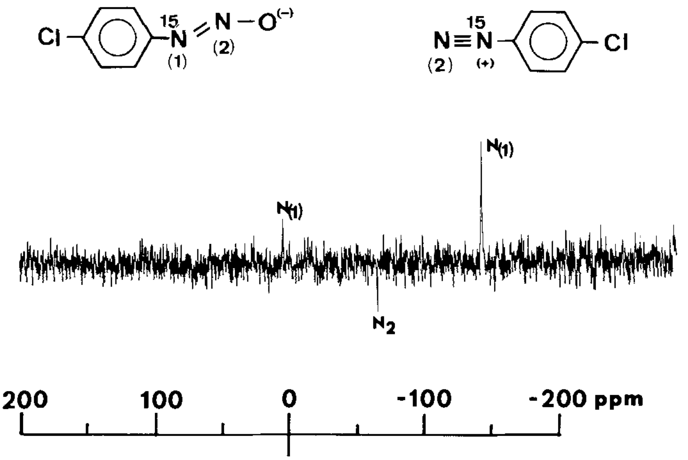
Reference	CIDNP. signals		
	4-Cl-C_6H_4-[$^{15}N^+(1)$]$\equiv$N(2)	4-Cl-C_6H_4-$N^+(1)\equiv$[$^{15}N(2)$]	4-Cl-C_6H_4-[$^{15}N^+(1)$]$\equiv$[$^{15}N(2)$]
1a: N(1) at −144.9	−144.5 (*A*)	-	−144.5 (*A*)
N(2) at −59.6	-	−58.4 (*E*)	−58.4 (*E*)
J(N(1),N(2))			*J*(N(1),N(2))
≤0.7 Hz			≤1 Hz
N_2b) −66.5	−66.3 (*E*)	−66.3 (*E*)	−66.3 (*E*)
2a: N(1) at +2.4	+2.4 (*A*)	-	+2.4 (*A*)
N(2) at +143.7	-	+148.4 (*E*)	+148.4 (*E*)
J(N(1),N(2))			*J*(N(1),N(2))
= 15.3 ± 0.5 Hz			= 14.7 ± 0.5 Hz

a) The CIDNP. and ^{15}N-chemical shifts are given in ppm relative to NO_3^- as internal standard (= 0 ppm). Positive values for signals at lower field relative to NO_3^-. *A* = enhanced absorption, *E* = emission.
b) From [6].

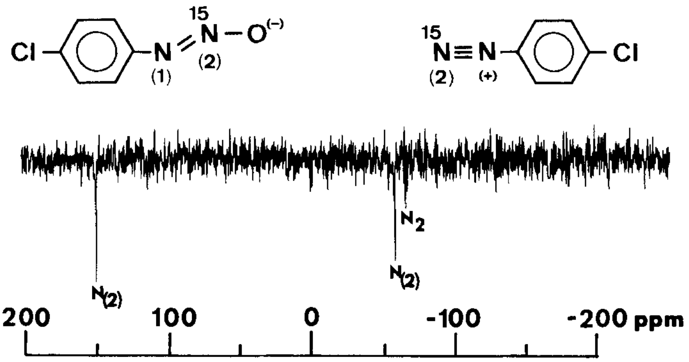
Table 2. *CIDNP. signals in the reaction of* **1b**-BF_4 *with* OH^-/CH_3OH *in aqueous solution*a)

Referenceb)	CIDNP. signals	
	C_6H_5-[$^{15}N^+(1)$]$\equiv$N(2)	C_6H_5-$N^+(1)\equiv$[$^{15}N(2)$]
1b N(1)	−142.3 (*A*)	-
N(2)	-	c)
N_2	−65.4 (*E*)	−65.4 (*E*)
2b N(1)	−14.6 (*A*)	-
N(2)	-	+144.9 (*E*)

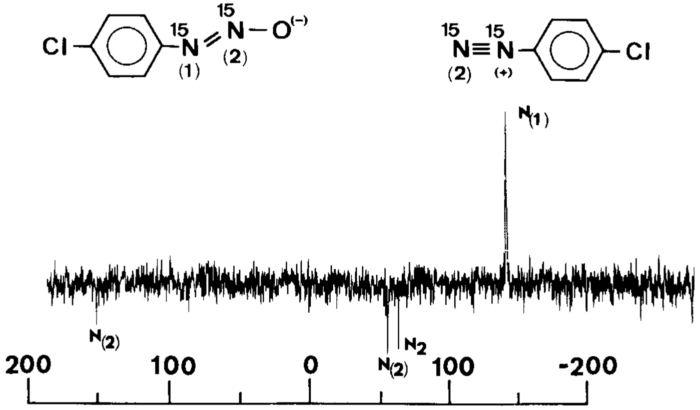
a) S. footnote a in *Table 1.*
b) From [6].
c) Reaction too fast to allow observation of signal.


Cl
15
N
(1)
N
(2)
O(-)
15
N≡N
(2)
(+)
Cl
N(1)
N(1)
N2
200
100
0
-100
-200 ppm

a)


Cl
N
(1)
15
N
(2)
O(-)
15
N≡N
(2)
(+)
Cl
N2
N(2)
N(2)
200
100
0
-100
-200 ppm

b)


Cl
15
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(1)
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(2)
O(-)
15 15
N≡N
(2)
(+)
Cl
N(1)
N(2)
N2
N(2)
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100
-200

c)

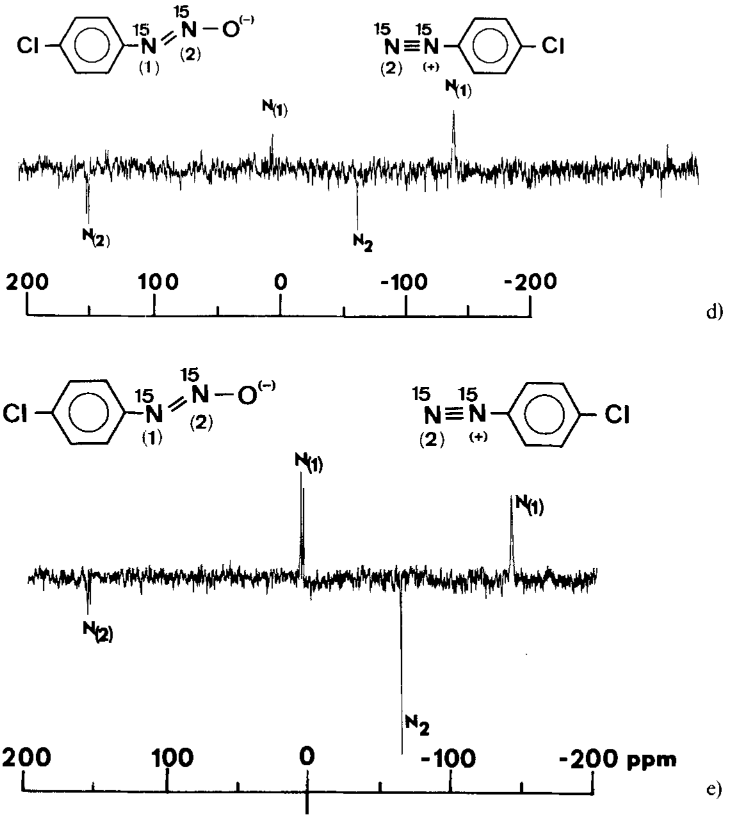


Fig. 1a-e. *^{15}N-CIDNP. spectra of 4-chlorobenzenediazonium salts*

a) [1-^{15}N]-**1a** in D_2O, pD = 9.7, 60°
b) [2-^{15}N]-**1a** in D_2O, pD = 9.7, 60°
c) [1,2-$^{15}N_2$]-**1a** in D_2O, pD = 9.7, 60°
d) [1,2-$^{15}N_2$]-**1a** in H_2O, pH = 9.4, 60°
e) [1,2-$^{15}N_2$]-**1a** in H_2O, pH = 9.7, 72°

the equilibrium is shifted further to the side of **2a**. Thus, the intensities of the signals of **2a** increase with increasing temperature *(Fig. 1e)* not only because of the higher rate of the radical reactions, but also because of the shift in equilibrium. In *Figures 1d* and *1e* coupling between the two N-nuclei can be easily observed in the doubly labeled *trans*-diazotate.

2.2. *Benzenediazonium tetrafluoroborate* (**1b**-BF_4). The reaction of **1b**-BF_4 in aqueous solution with NaOH/CH_3OH is similar to that of **1a**-BF_4. Higher concentrations were used and the pH dependence was not investigated. The CIDNP. results *(Table 2)*, however, correspond to those of the *p*-chloro derivative **1a**-BF_4.

Similar results were obtained for **1b** in acetonitrile with KOH/CH_3OH. In addition to CIDNP. signals corresponding to those in *Table 2* other emission and enhanced absorption signals were found at ~30 and ~100 ppm. Their origin will be investigated later.

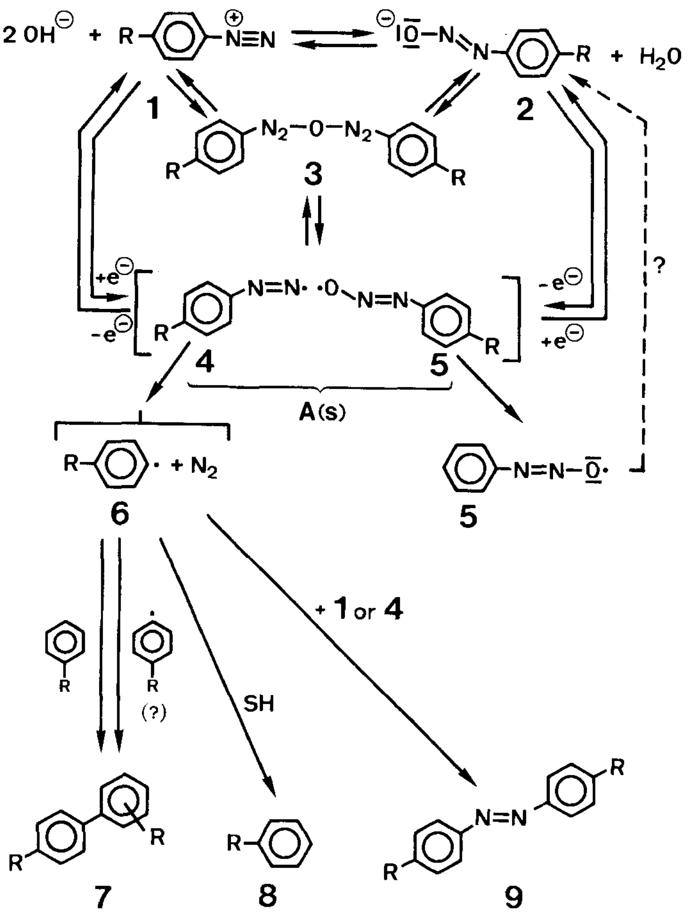
3. Discussion. - 3.1. *General mechanistic aspects of the homolytic dediazoniation of* **1**. As a plausible mechanism for the homolytic dediazoniation of **1** in aqueous solutions we have to consider one similar to the mechanism formulated by *Rüchardt et al.* [8] for the *Gomberg-Bachmann* reaction (*cf.* also [4]). A simplified presentation is given in *Scheme 1*.

A diazoanhydride **3** may be formed by reaction of diazonium ion **1** with *trans*-diazotate **2** [9] or its *cis*-isomer [10]. The configuration of **3** (*cis, cis; cis, trans; trans, trans*) is uncertain.

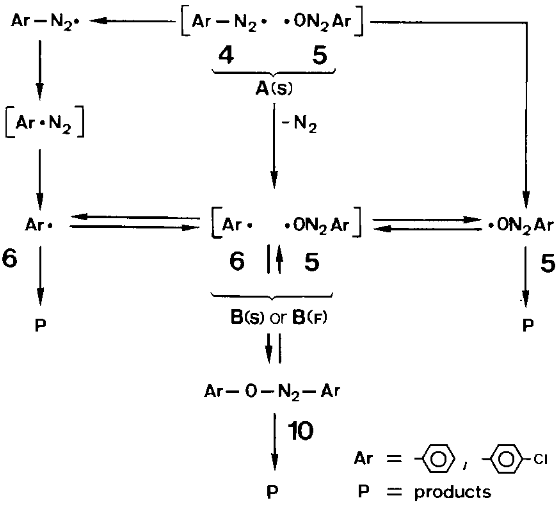
In the solid state, compounds such as **3** are relatively stable at room temperature ($t_{1/2}$ = 402 min at 19.5° [10]). Almost insoluble in water, **3** decomposes immediately when treated with organic solvents. The formation of a radical pair **A**(S), consisting of the diazenyl radical **4** and the diazotate radical **5**, in the singlet state (S), can be assumed. Alternatively, pair **A** might be formed *via* direct electron transfer from **2** to **1**, *i.e.* without **3** as an intermediate (for electron transfer to produce **4** from **1** in non-*Gomberg-Bachmann* reactions s. [11] and ref. cit. in [12]).

The diazenyl radical **4** escaped from the cage should mainly decay into molecular nitrogen and the aryl radical **6**. Saturation products of the latter, such as biaryls **7** (reaction with arene, perhaps even formed by dimerization), arenes **8**

Scheme 1



Scheme 2



(hydrogen abstraction) and azoarenes **9** (reaction with **1** or **4**) are indeed found [7]. This has been already demonstrated in earlier work [3] [4] for organic solvents.

For the existence of a radical pair [Ar· ·ON$_2$Ar] (**B**) *(Scheme 2)*, either formed by N$_2$-loss from diazenyl radical **4** within cage **A** (→ **B** (S)) or by diffusive encounter of the two radicals **4** and **5** (→ **B** (F)) no chemical evidence was found. The diazo ether **10**, the recombination product of pair **B**, should ionize in water and hence give the azo-coupling product of its two components [10]. Starting with **1a**, however, 2-hydroxy-5,4′-dichloroazobenzene and 4-chlorophenol were found only in traces. Moreover, their formation might well be explained by heterolytic dediazoniation of **1a**.

3.2. *General features of the ^{15}N-CIDNP. spectra.* The ^{15}N-CIDNP. experiments corroborate the results obtained previously [4] with ^{13}C-CIDNP. In particular they show that in the reaction of diazonium ions with OH$^-$ the diazonium ion **1** is regenerated. At least under the conditions mentioned in *Figure 1* (pH 9–10, Ar-atmosphere) the equilibrium between **1** and *trans*-diazotate **2** *(Scheme 1)* is fast ($t_{1/2} \approx 30$ s [7]) relative to the rate of relaxation of the ^{15}N nuclei ($T_1 = 200$–500 s) (*cf.* chap. 3.5). As a consequence polarization in **1** provokes also polarization in **2** and *vice versa.*

Further, it is of interest that the polarizations of the two ^{15}N nuclei N(1) and N(2) in **1** and also in **2** have opposite signs. In this respect they contradict the results and conclusions of *Bargon & Seifert* [12] (*cf.* also [13]) who proposed a symmetrical azobenzene cation radical as precursor, and also those of *Lippmaa et al.* [14], and, in part, those of *Bubnov et al.* [15] who found identical signs for both N-atoms in reactions of **1b** with phenolate. As *Porter et al.* [6] have suggested, the signal at −65.0 ppm in *Bubnov*'s paper [15] is probably due to polarized N$_2$ molecules. Finally, it is important to note that under our reaction conditions no exchange between the two N-atoms in **1** can be observed. This is in agreement with the results of *Rüchardt et al.* [13] showing that the intermediate azobenzene cation radical plays only a minor role in the scrambling of the N-atoms in **1**. The rearrangement of the two N-atoms appears only to occur under reaction conditions which favour heterolytic dediazoniations [16] [17]. An example is reported [17] where, in the presence of pyridine (which favours homolytic decomposition), very little rearrangement is observed.

3.3. *Deduction of the relevant radical pair.* Since all ^{15}N nuclei in **1** and **2** show polarization, at least one of the radicals in the pair responsible for polarization still contains both N-atoms and must be able to regenerate **1** and/or **2**. The appearance of polarized molecular nitrogen *(Fig. 1)* in all cases, combined with the evidence for an intermediate aryl radical **6** (*cf.* chap. 3.1), can only be explained by the existence of the diazenyl radical **4** in the relevant pair (*cf.* equ. 1)[2]. The intermediacy of a diazenyl radical in homolytic dediazoniations has been proposed many times (*cf. e.g.* [19] and ref. cit. in [12]). Evidence for its formation during homolytic dediazoniations in media other than aqueous solutions has been found according to ^1H- and ^{13}C-CIDNP. experiments [3] [4].

$$\underset{\mathbf{4}}{\mathrm{Ar{-}N{=}N^{\cdot}}} \rightarrow \underset{\mathbf{6}}{\mathrm{Ar^{\cdot}}} + \mathrm{N_2} \qquad (1)$$

According to chap. 3.1 the diazotate radical **5**, characterized by *Cadogan et al.* [20], would fit well into the role of the counter radical.

Since under our conditions **1** and **2** are in equilibrium, the radical pair responsible for the observed CIDNP. should be formed from these species. There are two reasonable pathways leading to such a radical pair (*Scheme 1*, chap. 3.1): (a) Direct electron transfer from **2** to **1**, and (b) Homolytic decomposition of the diazoanhydride **3**, formed in a pre-equilibrium from **1** and **2** (by analogy to the *Rüchardt* mechanism [8]). In both cases the same radical cage **A** (in the singlet state *S*) consisting of the diazenyl radical **4** and the *trans*-diazotate radical **5** would be formed. It is not possible to distinguish between these two possibilities by CIDNP.

The diazenyl radical **4** as well as the *trans*-diazotate radical **5** can form the diazonium-ion **1** and the *trans*-diazotate **2**, respectively, by the following mechanisms: (a) by disproportionation of the two radicals in the cage, (b) by recombination to the diazoanhydride **3** followed by heterolytic dissociation, and (c) *via* the escaped radicals **4** and **5**. The observed polarization of **1** and **2** should then appear as a superposition of the polarizations of the disproportionation/recombination as well as the escape products of both radicals in pair **A**.

Recombination and disproportionation have the same effect on the CIDNP. phenomenon (s. chap. 3.4). However, in the disproportionation case, **1** is always reformed from **4**, and **2** from **5** (with a subsequent 'scrambling' of the CIDNP. intensities due to the equilibrium $\mathbf{1} \rightleftharpoons \mathbf{2}$), whereas in the recombination case additional 'scrambling' may occur if the intermediate **3** is symmetric or prone to sym-

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[2] Formation of polarized N_2 from polarized diazonium-ion **1a** *via* heterolytic dediazoniation can be neglected; this reaction is far too slow ($t_{1/2} = 49$ h at 50° [18]) under our conditions. As mentioned in chap. 3.2, the participation of the azobenzene-cation radical in the relevant radical pair, as suggested by *Bargon et al.* [12], can also be ruled out.

metric heterolytic dissociation. This is not necessarily the case (*cf.* chap. 3.1), therefore, a 'memory effect' might exist: as in the disproportionation, **1** would be preferentially formed from the molecular fragment in **3** stemming from **4**, etc. Since we did not observe polarized ^{15}N-signals attributable to **3**[3]), we cannot rule out the disproportionation mechanism. We have now to discuss the possibility that a transfer of polarization to **1** and **2** *via* the escaped radicals **4** and **5** takes place. Formation of **1** as escape product of the diazenyl radical **4** is regarded as unlikely due to its short life time ($t_{1/2} \approx 10^{-6}$–10^{-9} s, in organic solvents) [21] [22]; it will mainly decay by C,N-bond dissociation (*cf.* equ. 1), forming polarized molecular nitrogen as escape product. This is supported by the strong CIDNP. signal of N_2, especially when it is considered that this gas will escape relatively fast from the solution. The diazotate radical **5** is a relatively persistent radical, since it can be detected by ESR. [20]. Not much is known about its reactivity, apart from its role in the *Gomberg-Bachmann* reaction [8] and the thermolysis of N-nitrosoacetanilides [20]. It will probably decay by dimerization (*cf.* the analogous iminoxy radicals [23]) leading to products incorporated in the 'diazo-tar' forming 50–60% of the products [7], as well as by H-abstraction and/or electron transfer from heterolytically and homolytically formed organic products, finally leading to **2**. Especially at the beginning of the reaction, the concentration of reaction products serving as hydrogen or electron donors will be very small under our conditions. Further, taking into account the relatively fast nuclear spin-lattice relaxation in radicals ($\tau = 10^{-4}$ s [24]), formation of **2** as escape product from **5** will make only a minor contribution to the polarization of **2** (respectively **1**). Therefore, polarization in **1** and **2** should mainly result from recombination/disproportionation in cage **A** (*cf. Scheme 1*).

3.4. *Application of* Kaptein*'s rules to the* ^{15}*N-CIDNP. spectra.* The theory underlying the CIDNP. effect is well established [24–27]. With *Kaptein*'s rules [24] qualitative predictions on the sign of the polarization Γ [enhanced absorption (A), emission (E)] of the ^{15}N-nuclei in the diamagnetic product of the radicals are possible:

$$\Gamma_{\text{net}}\,^{15}\text{N}(\text{i}) = -\{\mu \cdot \varepsilon \cdot \Delta g \cdot a_{^{15}\text{N}(\text{i})}\}^{4)} \qquad \begin{array}{l} \Gamma_{\text{net}} \text{ positive: enhanced absorption } (A) \\ \Gamma_{\text{net}} \text{ negative: emission } (E) \end{array} \qquad (2)$$

$\Gamma_{\text{net}}\,^{15}\text{N}(\text{i})$: Sign of the net polarization of the nucleus i in radical **4**
μ: + for triplet precursors or F-pairs
  – for singlet precursors
ε: + for products of recombination or disproportionation
  – for escape products
Δg: difference in the g-factors of the radicals in the radical pair (g_1–g_2)
$a_{^{15}\text{N}(\text{i})}$: hyperfine coupling constants of the ^{15}N-nuclei

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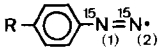
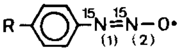
[3]) It is important to note that the classical *Gomberg-Bachmann* reaction (*cf.* [8]) takes place in a two phase system (water/aromatic hydrocarbon) where the diazoanhydrides have very probably a higher solubility and consequently a higher concentration in the *organic* phase. The reaction in our case, however, occurs in a homogeneous *aqueous* system, where the concentration of **3** should be small.

[4]) As the ^{15}N-nucleus has a negative gyromagnetic momentum, Γ has to be multiplied by -1 [6]. The radical pair **A** *(Scheme 1)* discussed here is formed by bond dissociation or electron transfer between diamagnetic ions, therefore μ is negative.

Table 3. *^{15}N Hyperfine-coupling constants*[a]) *and* g*-factors of the radicals* **4** *and* **5**

		$a_{N(1)}$	$a_{N(2)}$	g
	$[^{15}N(1)]=[^{15}N(2)]^{\cdot}$	− 19.4 G	− 9.1 G	2.0012 [21] 2.0010 [29]
	$[^{15}N(1)]=[^{15}N(2)]-O^{\cdot}$	+ 3.2 G	−43.1 G	2.0017 [20]

[a]) The values for ^{15}N were calculated from those for ^{14}N using equ. (3):

$$a_{^{15}N} = [(\mu/I)_{15}/(\mu/I)_{14}] \cdot a_{^{14}N}\ [33] \qquad (3)$$

As it is likely that radicals **4** and **5** are involved (*cf.* chap. 3.3), their hyperfine-coupling constants and g-factors must be known for the application of *Kaptein*'s rules. These magnetic properties of the diazenyl radical **4** have not yet been determined directly, as it was not possible to obtain the ESR. spectrum of this instable radical [6] [21] [22] (*cf.* also [28]). From CIDNP. investigations *Porter et al.* [21] estimated the g-value of the radical **4a** to be smaller than 2.0012, *Kasukhin et al.* [29] reported a g-value of 2.0010. For the hyperfine-coupling constants of **4**, one has to rely on calculations [12] [20] [29] [30]. They yield various values, but in all cases the same sign is found for both nitrogen nuclei, with $|a_{N(1)}| > |a_{N(2)}|$. These results are well supported by ^{15}N-CIDNP. studies of the thermolysis of arylazoalkanes [6]. In this investigation, the values of *Seifert & Gerhart* [30] were used.

For the magnetic properties of the diazotate radical **5** one has to rely on the ESR. measurements reported[5]) [20a]. The signs of the hyperfine-coupling constants are only obtainable from INDO-calculation [20b] (*cf. Table 3*). Because $|a_{N(1)}| \ll |a_{N(2)}|$, the sign of $a_{N(1)}$ is anhyhow of little influence.

The parameters given in *Table 3* refer to the unsubstituted radicals **4** and **5** (R = H). For the present qualitative discussion they can, however, also be used for the radicals with R = Cl.

The *Kaptein* rule for the net effect (2) can be directly applied only to the reaction with mono-labeled compounds. In the case of double-labeling, an *AB* system is observed for the diazotate **2**, because of coupling between $^{15}N(1)$ and $^{15}N(2)$. In the CIDNP. spectrum we therefore expect a multiplet-effect pattern. As *Figure 1e* shows, the two *A* and *B* lines are each of comparable intensity and of the same sign. As a consequence, we may apply *Kaptein*'s rule (see equ. 2) for the net effect here also, thus determining the sign of the sum of both *A* or *B* lines. This agrees completely with the results obtained from the CIDNP. of mono-labeled **2**.

Using the parameters of *Table 3* we derive the signs compiled in *Table 4* for the ^{15}N-nuclei of **1**, **2** and N_2.

If the polarization were based on the diazenyl radical **4** only, the same sign would be expected for the polarization of *both* N-atoms in **1** and **2**, irrespective of whether one assumes the formation of these species is a recombination, a disproportionation or an escape process. In reality, we observe alternate signs. The diazotate radical **5**, on the other hand, has two hyperfine-coupling constants with opposing

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[5]) It is rather surprising that the radical **5** with a g-value considerably smaller than that of the analoguous iminoxyradical $>C=N-O^{\cdot}$ [23] [31] [32] has not been further studied.

Table 4. *Application of* Kaptein's *rules to products of pair* **A**(S)

Product	N(i)	Signs of $^{A}\Gamma$	Sign of Γ	Absorption (A) or emission (E)	Corresponding *Figure*
$ArN_2^{\cdot}$	N(1),N(2)	$--+--$	+	*A*	*2a*
$ArN_2O^{\cdot}$	N(1)	$--+++$	+	*A*	*2b*
	N(2)	$--++-$	−	*E*	*2b*
$ArN_2O^{\cdot}$	N(1)	$---++$	−	*E*	*2c*
	N(2)	$---+-$	+	*A*	*2c*
$ArN_2^{\cdot}$ (respectively N_2)	N(1),N(2)	$-----$	−	*E*	-

signs, and enhanced absorption for N(1) and emission for N(2) are expected if the polarized recombination/disproportionation products are formed *via* **5**. This corresponds to the experimental results. In addition, however, the intensities of the signals should differ greatly due to the large difference in absolute magnitude of the hyperfine-coupling constant values. This is not the case.

In a special radical pair such as **A**(S), where polarized products can be formed from both radicals, we cannot describe the CIDNP. results solely in terms of *Kaptein*'s rules. Since we have to assume chemical exchange between **1** and **2** (*cf.* chap. 2.1) the total polarization *P* of the N-nuclei i in **1** and **2** is the sum 4 of *all* contributions⁶):

$$P^{\text{total}}_{^{15}\text{N}(i)} = {}^{A}P^{\text{rec./disp.}}_{ArN_2\cdot(i)} + {}^{A}P^{\text{rec./disp.}}_{ArN_2O\cdot(i)} + {}^{A}P^{\text{escape}}_{ArN_2O\cdot(i)} \qquad (4)$$

Since the polarization of a nucleus will be the higher with increasing hyperfine-coupling constant value, we can already see that in N(1) polarization from radical **4** (enhanced absorption), and in N(2) polarization from radical **5** (emission) will dominate *(cf. Table 4)*, provided that recombination/disproportionation prevail. This agrees well with the observed spectra.

The polarization of molecular nitrogen can be correctly predicted by *Kaptein*'s rules *(Table 4)*. Irrespective of whether one starts from a diazonium ion labeled at N(1) or N(2) or at both positions the signal has to be an emission signal, provided that N_2 is formed as an escape product of the diazenyl radical **4**. The experimental spectra confirm this view; consequently the identical sign (−) of the hyperfine-coupling constants of both N-atoms in **4** is again verified.

3.5. *Semiquantitative intensity considerations.* For a first estimation of the relative intensities of the four ^{15}N-signals in the products of recombination/disproportionation we assumed the T_1-values to be equal and the equilibrium **1**$\rightleftharpoons$**2** *(Scheme 1)* to be fast relative to the time necessary to obtain a spectrum. The relative intensities are then mainly a function of the position of the equilibrium and the hyperfine-coupling constant values a_i. The equilibrium ratio **1**/**2** was assumed to be 2:1. This corresponds to the position of the equilibrium at 60° in D_2O [7].

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[6] Contributions from the escaped diazenyl radical **4** and from pair **B** have been neglected. Justification for this is provided by the arguments given in chap. 3.1 and 3.3.

The population N_m of the energy level of a nucleus of fragment 1 with spin *m* as a function of the *a*-values according to the diffusion model is given by equ. 5 for 'short lived' and by equ. 6 for 'long lived' radicals[7]) [34] (*cf.* also [24] [35]):

$$N_m \sim \left(\Delta g \cdot H_o + \sum g_1 \cdot a_i \cdot m_i - \sum g_2 \cdot a_j \cdot m_j \right)^2 \tag{5}$$

$$N_m \sim \left(\Delta g \cdot H_o + \sum g_1 \cdot a_i \cdot m_i - \sum g_2 \cdot a_j \cdot m_j \right)^{1/2} \tag{6}$$

Second order effects have been neglected; the a_i are in field units. If the quadratic equ. 5 is used, the intensity I_{mn} of a transition m → n of a nucleus i on fragment 1 is proportional to the right hand side of equ. 7.

$$I_{mn} \sim N_m - N_n \sim a_i \left[\Delta g \cdot H_o + g_1 \sum_{j \neq i} a_j \cdot m_j - g_2 \sum a_k \cdot m_k \right] \tag{7}$$

In the case of radical pair **A** we have to consider a four spin system of ^{15}N-nuclei (the protons in the aryl rings can be neglected due to very small hyperfine-coupling constants). There are sixteen energy terms and eight transitions for every nucleus. If we further neglect the small coupling between two adjacent ^{15}N-nuclei, the eight transition intensities of every nucleus can be averaged; we obtain equ. 8.

$$I_{mn} \sim 4 a_i \left(\Delta g \cdot H_o \right) \sim a_i \tag{8}$$

That means that the relative intensities of the signals of the nuclei i are given by their relative hyperfine-coupling constants. Taking into account the sign of the eight transitions we obtain the absorption or emission mode of the signal of the corresponding nucleus: it is in agreement with the sign Γ calculated by *Kaptein*'s rule 2. On the other hand, if we apply the square root equ. 6 to our problem, the resulting signs of the signals do not always correspond to those determined according to equ. 2. As a consequence, the quadratic dependence 5 is used in this estimation. The estimated intensities for the doubly labeled compounds based on the a_i-values of *Table 3* are shown in *Figures 2* and *3*.

Figure 2a represents the relative intensities of the signals of N(1) and N(2) of **1** and **2**, if these recombination/disproportionation products were formed solely *via* **4**. Hence, all lines show enhanced absorption (*A*). The line intensities for N(1) and N(2) of **2** are each equally distributed on the corresponding doublet system (*cf.* chap. 3.4). Due to this and to the ratio **1**/**2** (= 2:1) the signals of the diazonium-ion **1** reveal the larger intensities.

Figure 2b shows the situation when **1** and **2** are recombination/disproportionation products of the diazotate radical **5** only. *Figure 2c* reproduces the extreme case of formation of **1** and **2** as escape products *via* **5**.

Since in the recombination/disproportionation process the amount of **1** and **2** formed from either **4** or **5** is the same, we have to add the corresponding intensities of *Figure 2a* and *2b* to give the real relative CIDNP. intensities. The result is shown

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[7]) Life time τ of the radicals relative to the reciprocal value of the expression in parenthesis of equ. 5 and 6, respectively [34].

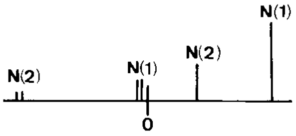

Fig. 2a

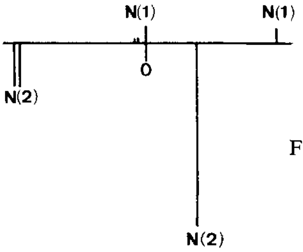

Fig. 2b

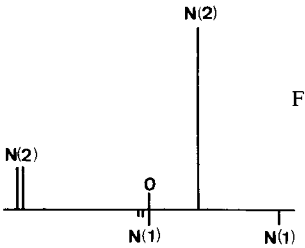

Fig. 2c

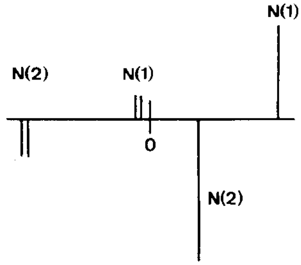

Fig. 3a

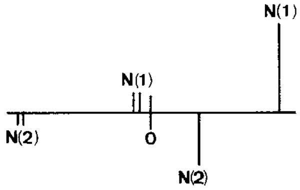

Fig. 3b

Fig. 2 and 3. *Schematic representation of calculated CIDNP. intensities* (see text). Signals of **1** upfield (right), signals of **2** downfield (left).

in *Figure 3a.* Apart from the too high intensity of the emission line of N(2) of the diazonium-ion **1** there is a relative good agreement with the experimental spectra if we take into account the manifold possibilities of errors which are discussed briefly below:

(a) the experimental spectra suffer from a bad signal-to-noise ratio; the signals of the diazonium ^{15}N-nuclei are broadened due to a hidden *AB*-coupling;

(b) we could not estimate the contribution of the escape products of the diazotate radical **5** to the polarization of **1** and **2**. Such a contribution would result in addition of a fraction of the intensities in *Figure 2c* to *Figure 3a.* This could, indeed, improve the calculated spectrum, as may be seen from *Figure 3b*, allowing for 50% of escape contribution. However, as has been stated in chap. 3.3 this amount seems to be too high;

(c) the relaxation times of the ^{15}N-nuclei in **1** and **2** (at 60–70°) are not known. However, as an approximation, we can use the values of acetonitrile ($CH_3C{\equiv}[^{15}N]$) for **1** and azoxybenzene [$C_6H_5[^{15}N]{=}N(O)C_6H_5$] for **2**. For 70° T_1-values of about 500 and 250 s, respectively, are reported by *Lippmaa* [36] for those compounds in the pure liquid phase. These values are larger than the time necessary for accumulating a spectrum (100 s) and, especially, much larger than the 'life time' of the polarization of the recombination/disproportionation products **1** and **2** from *an individual pair:* It is known [37] that with every pulse applied, part of the polarization is destroyed. Under our conditions, we can assume that about 10-20% of the polarization is lost with every pulse [38]. Since the pulse frequency is 1/s, after about 20 s the polarization of **1** and **2** generated from an individual pair would fall below 10%, therefore, the relative intensities should not be influenced significantly by the relaxation rates of the nuclei[8]);

(d) if chemical exchange occurs only through the equilibrium **1**$\rightleftharpoons$**2**, the assumption of complete chemical exchange is incorrect due to the fact that with every pulse applied part of the polarization from an individual pair is destroyed (for **1**$\rightleftharpoons$**2**: $\underset{\rightarrow}{t} = 15$ s; $\underset{\leftarrow}{t} = 60$ s; 60°, D_2O [7]; pulse frequency 1/s). Such a situation would result if we have disproportionation in pair **A** *(Scheme 1)* or recombination proceeding *via* an unsymmetrical diazoanhydride **3** (memory effect, *cf.* chap. 3.3). This would explain the fact that in the observed CIDNP. spectra the ratio of the relative signal intensities of N(1) and N(2) is different in **1** and **2**. However, a more detailed discussion requires computer simulations of the spectra, which is also necessary for an understanding of the lack of a multiplet effect in the CIDNP. spectra of **2**. Such investigations are currently under way [41];

(e) the data of *Table 3* may, in some cases, be erroneous. If this is so, apart from the obvious *direct* influence on the relative intensities, there is an *indirect* one. As discussed in chap. 3.5, we chose the quadratic dependence 5 of the intensities on the a_i due to the fact that the computed signs then obey *Kaptein*'s rules. If a sign or absolute value given in *Table 3* is wrong, this concordance might no longer be true.

Finally it should be stated that we can derive the life time of the diazenyl radical **4** from the quadratic dependence (*cf.* footnote 7) to be shorter than 10^{-7}-10^{-8} s. In organic solvents at room temperature $t_{1/2}$ is reported to be $\sim 10^{-6}$-10^{-9} s [21] [22] (*cf.* chap. 3.3). However, in aqueous solution at 60-70° (our experimental conditions) τ might be much shorter. Thus, we cannot rule out or support the quadratic dependence by life time considerations of the diazenyl radical **4**. For the same reason, reflecting on whether molecular nitrogen is formed 'inside' or 'outside' of a pair **A** (from **4**) actually is pointless. It has, anyhow, to be treated as escape product.

4. Conclusions. - As discussed in chap. 3.2-3.5 our ^{15}N-CIDNP. results on the homolytic dediazoniation of diazonium-ion **1** in weakly alkaline solutions are best explained by a recombination (*via* an intermediate diazoanhydride **3**) and/or disproportionation of diazenyl radical **4** and diazotate radical **5** in pair **A**(S) *(Scheme 1)*. However, they do not rule out other radical pairs, nor do they allow determination of the extent to which the homolytic pathway contributes to the total reaction.

Pair **A** may be either formed by electron transfer from diazotate **2** to diazonium-ion **1** or by homolytic N,O-bond cleavage in the diazoanhydride **3**. The mechanism

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[8]) In solution the T_1-values seem to be smaller, *e.g.* aldoximes $>C=[^{15}N]OH$: 30-50 s, 26°, acetone-d_6 [39]; acetonitrile ($CH_3C\equiv[^{15}N]$): 90 s, 26°, acetone-d_6 [39]; azobenzene ($C_6H_5[^{15}N]=NC_6H_5$): 72 s, 70°, chloroform-d_3 [40]. In such a case, they approach the 'life time' of the polarization and can not be neglected.

via the diazoanhydride **3** corresponds to the *Rüchardt* mechanism [8] of the *Gomberg-Bachmann* reaction which is also favoured by the product analysis [7].

After decades of sometimes frustrating work by many groups in the field of the very complex homolytic dediazoniations and several years after the first report of CIDNP. in diazonium reactions [3] [42] contours become now visible. Further insight will, however, require more sophisticated experimental work.

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Experimental Part

1. *Synthesis of [^{15}N]-compounds.* - *[^{15}N]-4-Chloroaniline.* The hydrochloride was synthesized by reduction with hydrazine hydrate and *Raney* nickel of [^{15}N]-4-chloronitrobenzene prepared by the method of *Paul* [43] (yield 88.3%). In the nitration of chlorobenzene [43] 99.9% ^{15}N-labeled nitric acid was employed and the reaction performed with a twofold excess of chlorobenzene.

[1-^{15}N]-, [2-^{15}N]- and [1,2-$^{15}N_2$]-4-Chlorobenzenediazonium tetrafluoroborate (**1a**-BF_4) were prepared by diazotization of 4-chloroaniline or [^{15}N]-4-chloroaniline with sodium nitrite or ^{15}N-labeled sodium nitrite in 50% aqueous HBF_4-solution. On warming 0.996 g (6 mmol) of 4-chloroaniline hydrochloride were dissolved in 7 ml of 50% aqueous HBF_4-solution. After cooling to 0° a solution of 420 mg (6 mmol) of sodium nitrite in 1.5 ml of water was added dropwise with stirring. After addition the solution was stirred for 15 min, cooled to −10°, quickly filtered through a cooled sintered glass funnel, and the white filtrate washed with ether. It was dissolved in 5 ml of dry CH_3CN (3 times distilled from P_2O_5), filtered to remove $NaBF_4$ and reprecipitated with ether. The procedure was repeated 3 times. The diazonium salt was dried at 0° under high vacuum and stored at −20° under argon (yield 61%, m.p. 134°).

*Sodium [1-^{15}N]- and [1,2-$^{15}N_2$]-4-chlorobenzene-*trans-*diazotate* (**2a**-Na) were prepared by nitrosation of 4-chlorophenylhydrazine with isopentyl nitrite according to the method of *Lewis & Hanson* [44]. 4-Chlorophenylhydrazine was obtained by reduction of 4-chlorobenzenediazonium chloride with sodium hydrogensulfite by the method of *Bullock* [45] (yield 50%).

[1-^{15}N]-, [2-^{15}N]- and [1,2-$^{15}N_2$]-Benzenediazonium tetrafluoroborates (**1b**-BF_4). A mixture of 1.0 g (10.7 mmol) of aniline or [^{15}N]-aniline in 5 ml of 20% HCl-solution was diazotized with 740 mg (10.7 mmol) of sodium nitrite or ^{15}N-labeled sodium nitrite in 6 ml of water with stirring. A solution of 1.8 g of $NaBF_4$ in 4.5 ml of water was then added. After 30 min the precipitated diazonium salt was collected by filtration. It was washed with ice cold saturated $NaBF_4$ solution (*ca.* 1 ml), methanol (*ca.* 1 ml) and ether (*ca.* 3 ml), and used directly for the CIDNP. experiments. Further purification involved drying over P_2O_5 under vacuum for 5 h, and crystallization from acetone or hot water (yield 770 mg, 36%). The total ^{15}N-content of the diazonium salts labeled at one of the two N-atoms was 50.6%: 98% of ^{15}N was in the position wanted, *i.e.* either in N(1) or in N(2).

2. *^{15}N-NMR. Spectra.* The CIDNP. spectra of **1a**-BF_4 *(Fig. 1, Table 1)* were obtained on a *Bruker* instrument HFX-90: 9.12 MHz; pulse width 10 µs; acquisition time 0.35 or 0.75 s; 100 scans; sweep width 6024 Hz; 1.47 Hz/data point; external reference: [^{15}N]H_4[^{15}N]O_3 in D_2O, $\delta([^{15}N]O_3^-) = 0.0$ ppm. The phase correction was performed with the parameters obtained for [^{15}N]H_4 ^{15}N]O_3 in D_2O under the same experimental conditions.

For each experiment, 80 mg (0.35 mmol) of [^{15}N]-4-chlorobenzenediazonium tetrafluoroborate were dissolved under argon in a 10-mm-NMR. tube in 4 ml of oxygen-free buffer solution (pD = 9.7, pH = 9.4) and thermostated for 1 min in the NMR. probe, preheated to the chosen temp.

Buffer solution: The buffer solutions ($I = 1.00$) were prepared by bubbling CO_2 through a solution of sodium carbonate (*Merck*, ultrapure) in D_2O or H_2O. The buffer solutions were carefully degassed by repeated freezing and thawing under high vacuum and stored under argon. The pD or the pH was measured before and after each experiment with a specially designed microelectrode from *Metrohm*.

The reference spectra of **1a**-BF_4 were recorded with a *Bruker* instrument HFX-90: pulse angle 20°; acquisition time 1.6 s; 3000 scans; sweep width 6024 Hz; the reference spectra of **2a**-Na were taken with a *Bruker* instrument WH-450 (400 MHz): pulse angle 25°; acquisition time 0.87 s; 50 scans.

For recording the spectra of **1b**-BF_4 with single ^{15}N-labeling *(Table 2)* a *Varian*-XL-100 spectrometer with external fluorine lock was used: 10.14 MHz; pulse width 10–50 μs; acquisition time 0.67 s; 50–100 scans; sweep width 6151 Hz; 1.52 Hz/data point. [^{15}N]-Aniline was used as reference; the ppm values were determined using $\delta([^{15}N]O_3^-) = 0.0$ ppm (δ(aniline) $= -320.0$ ppm). The spectra were recorded with and without proton broad band decoupling; no difference was observed.

In a rotating NMR. tube ($d = 10$ mm) 0.3–0.7 ml of a solution of **1a**-BF_4 in water were decomposed by addition of 12–15 drops of a saturated solution of NaOH in methanol by means of a glass capillary. A rigorous reaction occurred with production of nitrogen.

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