

**167. Dediazonation of Arenediazonium Ions in Homogeneous
Solution. Part XII.
Solvent Effects in Competitive Heterolytic and Homolytic
Dediazoniations¹⁾²⁾**

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Summary

In heterolytic dediazoniations arenediazonium salts form aryl cations. The reaction rates are relatively slow; they depend only to a small extent on the solvent. It is shown that the solvents in which the heterolytic dediazonation mechanism is predominant have a low nucleophilicity, whereas in solvents of high nucleophilicity homolysis of arenediazonium salts, *i.e.* the formation of aryl radicals and related intermediates, is favoured. Under comparable conditions, homolytic rates are faster than the corresponding rates of heterolysis. Homolysis is strongly enhanced by addition of nucleophiles which form relatively stable radicals by electron transfer. The ability of additives to catalyze homolysis of arenediazonium salts can be explained using the concept of a *nucleofugic*³⁾ *homolytic leaving group*.

1. Introduction. - In thermal dediazoniations of arenediazonium salts in solution, *i.e.* in reactions in which these compounds release molecular nitrogen, a complex variety of mechanisms operates giving a wide range of products. *Table 1* summarizes some representative results from the extensive literature on this subject⁴⁾. Not only reactions with nucleophiles, including the solvent and the counter-ion of the diazonium salt (even if it is a very weak nucleophile such as BF_4^\ominus), but also hydrogen abstraction, polymerizations and complex reactions with the solvent, *e.g.* formation of phenols with dimethylsulfoxide (DMSO) as the only source of oxygen [10], are observed. Minor changes in the reaction conditions, *e.g.* the absence or presence of molecular oxygen [15], or a change in the substituent [9] [12] alter the nature of the products significantly, strongly indicating a change in mechanism.

¹⁾ Part XI: [1].

²⁾ Presented at the 26th IUPAC Congress in Tokyo, Japan, September 7, 1977.

³⁾ In the original proposal [32] we used the word *nucleofugal*. In keeping with a forthcoming proposal on nomenclature in physical organic chemistry by Commission III.2 (Physical Organic Chemistry) of IUPAC we now use the word *nucleofugic*.

⁴⁾ For a review, see [2].

Table 1. *Products of thermal dediazoniations (representative examples) X-C₆H₄-N₂[⊕]Y[⊖] → Products*

X	Solvent	Products	Yield	Ref.
H and others	H ₂ O/dilute H ₂ SO ₄	X-C ₆ H ₄ -OH	> 90%	[3]
<i>p</i> -Cl	H ₂ O (pH 9-11)	Polymers containing -O-, -NH-, -N=N-; Ar-Ar, Ar-NH-Ar etc.	-	[4]
H; <i>p</i> -Cl	CF ₃ CH ₂ OH	X-C ₆ H ₄ -OCH ₂ CF ₃ + X-C ₆ H ₄ -F ^{a)}	ca. 65% ca. 35%	[5]
H	CF ₃ CH ₂ OH/pyridine	C ₆ H ₆ , C ₆ H ₅ -C ₆ H ₅ , polymers etc.	-	[6]
2,4,6-(CH ₃) ₃	(CF ₃) ₂ CHOH	(CH ₃) ₃ C ₆ H ₂ OCH(CF ₃) ₂ (CH ₃) ₃ C ₆ H ₂ F	ca. 95% ca. 5%	[7]
2,4,6-Cl ₃	CF ₃ CH ₂ OH	Cl ₃ C ₆ H ₃	ca. 35%	[7]
2,4,6-Br ₃	CF ₃ CH ₂ OH	Br ₃ C ₆ H ₃	ca. 59%	[7]
H, <i>p</i> -Br	CH ₃ OH/0.1M TsOH/O ₂	X-C ₆ H ₄ -OCH ₃	92% (H) 72% (<i>p</i> -Br)	[8]
H	CH ₃ OH/0.1M TsOH/N ₂	C ₆ H ₅ -OCH ₃	88%	[8]
<i>p</i> -Br	CH ₃ OH/0.1M TsOH/N ₂	Br-C ₆ H ₄ -OCH ₃ + Br-C ₆ H ₅	73% 19%	[8]
H	CH ₃ OH/1.1M CH ₃ ONa/N ₂	C ₆ H ₆	64%	[8]
<i>p</i> -Br	CH ₃ OH/0.01M CH ₃ ONa/N ₂	Br-C ₆ H ₅	66%	[8]
<i>o</i> -CH ₃	(HF) _n /pyridine	<i>o</i> -CH ₃ -C ₆ H ₄ -F	100%	[9]
<i>o</i> -NO ₂	(HF) _n /pyridine	<i>m</i> -NO ₂ -C ₆ H ₄ -F	100%	[9]
<i>o</i> -CF ₃	(HF) _n /pyridine	<i>o/m/p</i> -CF ₃ -C ₆ H ₄ F	8/91/1	[9]
<i>p</i> -NO ₂	DMSO ^{b)}	NO ₂ -C ₆ H ₄ -OH	89%	[10]
H	DMSO	C ₆ H ₄ (OH)CH ₂ SCH ₃ + C ₆ H ₅ OH etc.	65%	[11]
<i>p</i> -NO ₂	DMSO/nitrobenzene	NO ₂ -C ₆ H ₄ -C ₆ H ₄ -NO ₂ (<i>o</i> > <i>p</i> > <i>m</i>)	63/27/10	[12]
H	DMSO/nitrobenzene	C ₆ H ₅ -C ₆ H ₄ -NO ₂ (<i>m</i> > <i>o</i> > <i>p</i>)	55/29/16	[12]
H and others	HMPT ^{c)}	X-C ₆ H ₅	82-93%	[13]

a) Product of reaction with tetrafluoroborate, see also *Swain et al.* [14].

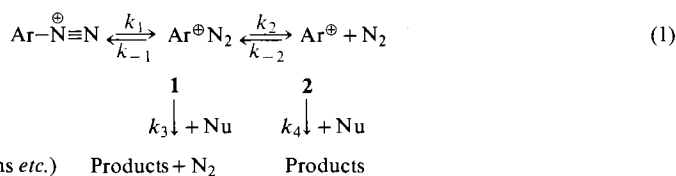
b) DMSO = dimethylsulfoxide.

c) HMPT = hexamethyl phosphoric acid triamide.

The purpose of the present investigation is to discuss critically the factors which govern the competition between heterolytic and homolytic dediazoniations. Although the detailed mechanism of some homolytic dediazoniations is not yet known, it is possible to elucidate the principle factors responsible for the occurrence of these two types of mechanism.

2. Heterolytic Dediazoniations. - Nearly 40 years ago it was proposed [16] that the first and rate-limiting step of the dediazonation of arenediazonium salts

in acidic aqueous solution is the heterolytic dissociation of the diazonium ion to give an aryl cation and molecular nitrogen, followed by rapid reaction with any nucleophile present. Recent work by *Swain et al.* [3] [14] [17] [18], who investigated substituent effects, primary ($C_6H_5-^{15}N\equiv N$) and secondary isotope effects ($C_6D_5N_2^+$), is consistent with a mechanism involving the phenyl cation as an intermediate. We have demonstrated [19] that the rate-limiting step is often, but not always, the formation of the aryl cation. In some cases, added nucleophiles increase the overall reaction rate by competing with the back reaction of the dissociation of ArN_2^+ into Ar^+ and N_2 . Later work [1] [7] demonstrated that the dediazonation kinetics in 2,2,2-trifluoroethanol (TFE) are not consistent with one intermediate (the aryl cation), but with at least 2 consecutive steady-state intermediates, the first being probably a tight ion-molecule pair between the phenyl cation and N_2 (**1**), while the second is the solvated phenyl cation (**2**), free from nitrogen (mechanism (1)).



In the above mechanism all rates except that with rate constant k_1 are fast and their ratios are such that the overall (measured) first-order rate constant (k) is not more than about 5 times

Table 2. Measured rate constants for the dediazonation of benzenediazonium tetrafluoroborate in various solvents at 25.0°

	$k \cdot 10^4$ $s^{-1a)}$	Ref.	$\epsilon^b)$	$n_D^{20c)}$	B ^{d)}	E ^{e)}	η (cp) ^{f)}
Dioxane	0.115	[3]	2.209	1.4224	-	-	1.087 (30)
3-Methylsulfolane	0.136	[3]	-	-	-	-	-
H ₂ SO ₄ (21M)	0.215	[3]	110	1.4290	-	-	24.5
CH ₂ Cl ₂	0.220	[3]	9.08	1.4246	23	2.7	0.393 (30)
CH ₃ COOH	0.226	[3]	6.15	1.3716	131	14.6	1.155
H ₃ PO ₄ (85%)	(0.245)	[19]	-	-	-	-	178.0 (100%)
CH ₃ NO ₂	0.29	[11]	38.57	1.3819	65	5.1	0.62
CH ₃ COCH ₃	(0.306)	[11]	20.74	1.3588	224	2.1	0.316
(CH ₃) ₂ NCHO	(0.316)	[11]	36.7	1.4272	291	2.6	0.796
CH ₃ CN	(0.329)	[11]	37.5	1.3416	160	5.2	0.345
CF ₃ COOH	(0.37)	[18]	8.2	1.2850	-	-	0.578
(CH ₃) ₂ SO	(0.416)	[11]	48.9	1.4783	362	3.2	1.98
H ₂ O	0.459	[3] [20]	80.1	1.3330	156	21.8	0.890
FSO ₃ H	0.465	[7]	-	-	-	-	1.56
F ₃ C-CHOH-CF ₃	0.792	[7]	16.70	-	-	-	-
F ₃ C-CH ₂ OH	0.807	[7]	26.67	-	-	-	-
C ₂ H ₅ OH	(0.82)	[21]	24.30	1.3614	235	11.6	1.003 (30)
CH ₃ OH	(0.91)	[21]	32.65	1.3286	218	14.9	0.547
H ₃ C-CHOH-CH ₃	(1.06)	[21]	18.3	1.3773	236	8.1	1.77 (30)

^{a)} Brackets: see text. ^{b)} Dielectric constant (from [22]). ^{c)} Refractive index (from [22]). ^{d)} *Koppel & Paju's* nucleophilicity parameter [23]. ^{e)} *Koppel & Paju's* electrophilicity parameter [24]. ^{f)} Viscosity (from [25]: at 25° unless otherwise indicated).

smaller than k_1 . Thus, as will be seen, the magnitude of the rate constant k serves as a useful basis for the purposes of discussion.

Representative data for the rates of the heterolytic dediazonation of the benzene diazonium ion at 25° in many solvents are given in *Table 2*, together with selected parameters describing certain solvent characteristics. Rate constants shown in brackets were calculated from literature data obtained at temperatures other than 25° and the reported activation energy.

Table 2 demonstrates that the solvent effect on heterolytic dediazonation rates is small, the slowest and fastest rate differing by a factor of 9 only. It is therefore unlikely that *one* generally recognizable solvent effect is correlated with these rates. This becomes clear by inspection of the last 5 columns of *Table 2*, in which some solvent properties which may influence the kinetics are listed; none of these parameters shows a simple correlation with the measured rate constant.

3. Homolytic dediazoniations. – The heterolytic dissociation of an arenediazonium ion to give an aryl cation and N_2 is a reaction likely to occur easily as the leaving group forms a very stable product, N_2 . In contrast, homolytic cleavage of the $C-N_\alpha$ -bond of a diazonium ion would yield no primary product of reasonable stability; the formation of a dinitrogen radical cation (N_2^{\oplus}) is definitely not an energetically favourable process. In many dediazoniations, however, it is possible to account for the nature of the products only with aryl radicals as intermediates. Therefore, mechanisms must exist in which aryl radicals are formed by processes other than the monomolecular homolytic cleavage of the $C-N_\alpha$ -bond of diazonium ions.

The formation of very complex products in some important homolytic dediazoniations, *e.g.* those carried out in water in the pH range 9–11 (*Table 1*), might be thought to preclude a discussion of solvent effects in the homolysis of solutions of diazonium salts. As will be seen, however, it is clear that in many thermal dediazoniations, the initial steps of these reactions are, in contrast to heterolytic dediazoniations, clearly correlated with solvent properties.

The basic principles underlying the factors which bring about a homolytic dediazonation can be recognized from a correlation of kinetic and product data in the literature. *Bunnett et al.* [8] investigated dediazoniations in methanol. The unsubstituted benzenediazonium tetrafluoroborate in the presence of 0.1M *p*-toluenesulfonic acid (TsOH) under N_2 yields 88% anisole, *i.e.* the product of heterolysis. In the absence of TsOH only 66% anisole together with 3% benzene, a product of homolysis, is formed. In a solution of 1.1M sodium methoxide in methanol benzene was the only product identified (besides polymers). Under analogous conditions the *p*-bromobenzenediazonium salt yields significantly more bromobenzene and significantly less *p*-bromoanisole (*Table 3*). Only under O_2 is the yield of this heterolytic reaction product dominant.

The function of O_2 is obviously to trap radical chain initiators. For both diazonium salts, the 3 experiments carried out under N_2 demonstrate that increasing concentrations of a nucleophile (CH_3O^\ominus) result in higher yields of homolytic products. The *p*-bromo derivative is the more electrophilic of the 2 diazonium ions and gives higher yields of the hydrogen abstraction product; with only

0.1M sodium methoxide the heterolytic product is not detectable whereas 1.1M of this additive was necessary to attain this situation with the less electrophilic unsubstituted benzenediazonium salt.

In a careful study of these dediazoniations in methanol, *Bunnett & Iijima* [15] showed that the homolytic rate was always 4 to 32 times larger than the heterolytic rate, the latter being essentially independent of additives and the atmosphere (N_2 , O_2 or Ar). One can therefore conclude that *nucleophilic additives* catalyse the homolytic reaction. This is corroborated by results from other investigations.

Table 3. *Products of dediazoniations in methanol*
(Data from *Bunnett et al.* [8].)

Substituent	Additives	Products (%)	
		Ar-H	Ar-OCH ₃
H	0.1M TsOH/O ₂	0	92
	0.1M TsOH/N ₂	0	88
	-/N ₂	3	66
	1.1M CH ₃ ONa/N ₂	64	0
<i>p</i> -Br	0.1M TsOH/O ₂	4	72
	0.1M TsOH/N ₂	73	19
	-/N ₂	82	5
	0.01M CH ₃ ONa/N ₂	66	0

1) Addition of pyridine to TFE in the dediazonation of benzenediazonium tetrafluoroborate increases the overall rate and yields products typical of homolytic decomposition [6]. In addition, the kinetics change from strictly first-order in pure TFE to a nonintegral order between 0 and 1 (depending on the pyridine concentration) indicating a chain reaction.

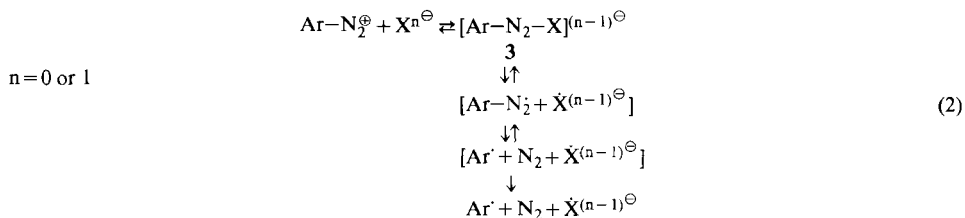
2) In water, the rate of dediazoniations increases if the pH is raised from 3 (or lower) to the range 8-11 [26] [27].

3) Nitrite ions in water and diphenylhydroxylamine in nitrobenzene or acetophenone are very effective catalysts for homolytic dediazoniations [28] [29].

It is difficult to compare these results on a quantitative basis as the reagents, solvents, temperatures *etc.* are very different. It seems clear, however, that the *nucleophilicity* of these additives is not the only factor responsible for their catalytic effect; catalysis by nitrite ions and diphenyl hydroxylamine is more effective than one would expect if only their basicities are considered.

The results are understandable on the basis of the general mechanism (2): $X^{n\ominus}$ is a nucleophile which adds to the β -nitrogen atom of the diazonium ion, *i.e.* to the electrophilic centre. The covalent azo compound **3** decomposes homolytically. This is probably a 2-step process as diazenyl radicals ($Ar-N=N\cdot$) have been detected in some cases [30]. The product is a radical pair and a N_2 molecule. The first step of this process is, of course, favoured by the nucleophilicity of $X^{n\ominus}$. The addition product **3** is very probably a steady-state intermediate; the rate of the overall process is, however, also dependent on the rate of the first of both radical-forming steps. If $X^{n\ominus}$ is a compound which easily loses an electron to form the radical $X^{(n-1)\ominus}$ - in other words, if $\dot{X}^{(n-1)\ominus}$ is a relatively stable

radical - the measured rate of the homolysis will be fast. Therefore nitrite ions and diphenylhydroxylamine are good catalysts because they form stable radicals, namely the NO₂ molecule and diphenylnitroxide.

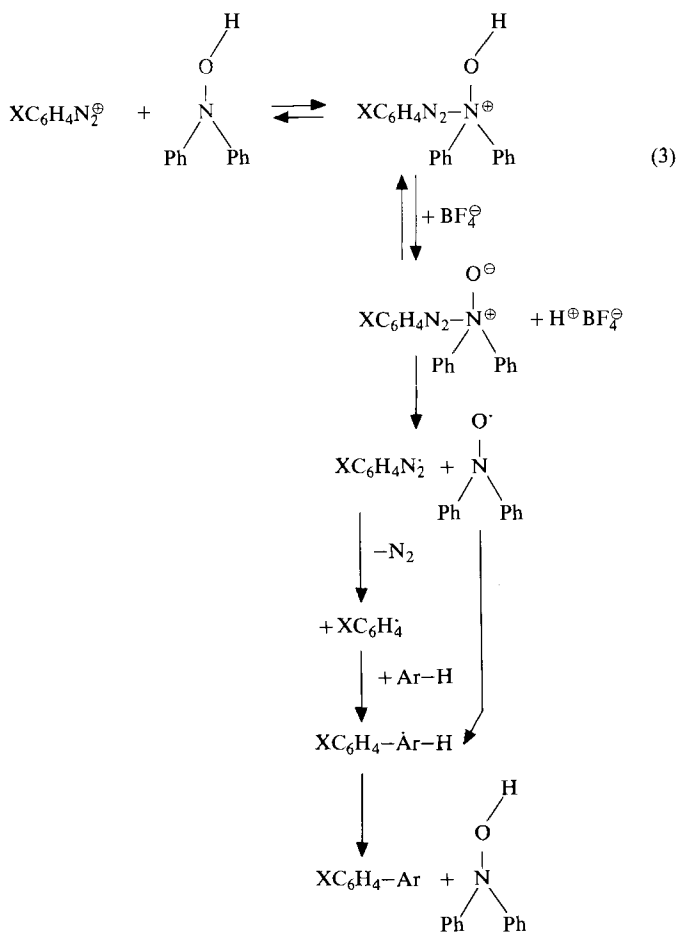


The following mechanism (3) explains why diphenylhydroxylamine can be used to catalyse the formation of biphenyl derivatives from arenediazonium salts and arenes in nitrobenzene or acetophenone [29]. In contrast to the classical *Gomberg-Bachmann* reaction and the version developed by *Hey* [31], the *Perkins* process works in homogeneous solution and therefore tends to give higher yields and to be more reliable. We have chosen [32] to call the type of catalysis postulated in mechanism (2), 'the concept of a nucleofugic³) homolytic leaving group' because X^{n⊖} must be a good nucleophile and, at the same time, a good homolytic leaving group. As the addition of a nucleophile to the diazonium ion is the first step in (2), the nucleophilicity is the *primary* condition for this mechanism⁵).

It is therefore likely that not only the additives to solutions of diazonium salts catalyze the homolytic dediazonation but also the solvent molecules if they are sufficiently nucleophilic. This can indeed be demonstrated by the nature of the products formed from arenediazonium salts in various solvents. In *Table 4* we list some solvents in which the products of dediazonation were investigated in detail. Products of heterolytic and homolytic intermediates are designated by C (cationic) and R (radical) for 4 characteristically substituted benzenediazonium salts. The last 2 columns contain the parameters which give the most reliable information on the nucleophilic character of the solvent for a wide range of solvents, namely *Koppel & Paju's* B values [23]⁶) and *Schleyer's* N_{BS} values [37].

Unfortunately neither B nor N_{BS} alone cover the full scale of solvent nucleophilicity because their method of measurement is not applicable to solvents of low nucleophilicity in the case of the former (see [38] [39]) and solvents of high nucleophilicity in the case of the latter. However, the 2 parameters overlap sufficiently. It can therefore be safely assumed that in *Table 4* the solvents are arranged in order of increasing nucleophilicity.

- 5) On the other hand, it is likely that particles such as transition metal ions and others which are good electron transfer reagents but poor nucleophiles act as catalysts in homolytic dediazonations by (free) electron transfer and not by primary formation of a (covalent) azo compound such as **3**. This has been demonstrated by *Becker et al.* [33].
- 6) In a preliminary publication [34] we did not use the B values of *Koppel & Paju* [23] which are based on the IR. spectrum of phenol in these solvents, but the older B values of *Koppel & Palm* [22] which relate to the stretching frequency of the OD bonds in CH₃OD. The latter have certain disadvantages which are indicated in the paper of *Koppel & Paju*. The DN (donor number) values of *Gutmann* [35] were also mentioned in [34]. As the DN values of CH₃OH and H₂O - important solvents for our discussion - are not known with sufficient accuracy [35] [36] we prefer to use *Koppel & Paju's* B parameters.



The columns showing the type of product demonstrate clearly that increasing nucleophilicity favours the formation of products of homolytic intermediates. A comparison of the products of the 4 substituted benzenediazonium salts also makes it clear that an increase in the electrophilicity of the diazonium ion favours homolytic dediazoniations in borderline solvents. On the other hand, as shown previously [32], there is no observable correlation between the electrophilicity of solvents and the ease of homolytic dediazoniations. The same is true for 'classical' solvent parameters such as polarity or polarisability.

In conclusion, it is very likely that the influence of solvents on the change from the 'basic', *i.e.* direct heterolytic, mechanism of dissociation of the C-Na bond in aromatic diazonium ions to homolytic dissociation can be accounted for by a mechanism analogous to (2). It involves an addition of a (nucleophilic) solvent molecule to the (electrophilic) β -nitrogen atom of the diazonio group, followed by a homolytic dissociation into a radical pair and N_2 . Evidence for such strong interaction of diazonium ions with nucleophilic solvents is also found in reactions

Table 4. Main products of dediazonation of substituted benzenediazonium salts in solvents of different nucleophilicity

Solvent	Products ^{a)}				Solvent parameters ^{b)}	
	<i>p</i> -NO ₂	<i>p</i> -Cl	H	<i>p</i> -OCH ₃	B	N _{BS}
HFIP	-	-	C	-	-	-3.93
TFE	C	C	C	C	-	-2.78
CH ₃ COOH	C	C	C	C	131	-2.05
H ₂ O (pH < 1)	C	C	C	C	156 ^{c)}	-0.26 ^{c)}
CH ₃ OH/O ₂ /0.1M TsOH	C/R	C	C	C	218 ^{c)}	+0.01 ^{c)}
CH ₃ OH/N ₂ /0.1M TsOH	R	C	C	C	218 ^{c)}	+0.01 ^{c)}
DMSO	R	-	C	-	362	-
HMPT	-	-	R	-	471	-
Pyridine	R	R	R	R	472	-

^{a)}C = heterolytic (cationic products); R = homolytic (radical products). ^{b)}B = [23], N_{BS} = [37]. ^{c)}Parameters for pure H₂O or CH₃OH, respectively.

of *p*-nitrobenzenediazonium ions in DMSO and in DMSO/benzene mixtures [10]: if the solvent is changed from DMSO to DMSO/benzene 2:1 or even 1:2, the UV. spectrum still shows the typical spectrum of the diazonium ion in pure DMSO which is significantly different from spectra in less nucleophilic solvents. In addition the rates of dediazoniations are practically the same if benzene is added to DMSO although the products change completely (*p*-nitrobiphenyl instead of *p*-nitrophenol).

Homolytic products in dediazoniations of unsubstituted benzenediazonium salts are thus expected in solvents which have a value of B [23] higher than *ca.* 400. This borderline value depends on the electrophilicity of the diazonium salt, *e.g.* it is shifted to *ca.* 190 for *p*-nitrobenzenediazonium salts.

4. Photolytic dediazoniations. - In the previous section we discussed exclusively thermal homolytic dediazoniations in the presence of compounds (solvent molecules and additives) which are potential nucleophiles. We did not discuss dediazoniations in the presence of good electron-transfer reagents such as transition metal ions (footnote 5) nor did we discuss photolytic dediazoniations. However, *Becker et al.* [40] recently discovered that some substituted benzenediazonium salts underwent predominant heterolytic decomposition in methanol or ethanol/acetonitrile if irradiated at 313 nm, the absorption maximum of the diazonium ion, but when light of wavelengths longer than 330 nm was used, mainly homolytic products were formed. They assumed that heterolytic photochemical dediazoniations start from the vibrational excited ground state and that excitation of a charge transfer state between electron donors and arenediazonium salts gives rise to electron transfer and therefore to homolytic dediazonation.

It is therefore interesting to see that relatively small changes in reaction conditions may also change the reaction mechanism significantly in photolytic dediazonation.

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