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152. Dediazoniation of Arenediazonium Ions in Homogeneous Solution. Part VIII¹). Reaction Kinetics and Products in Dimethyl Sulfoxide

by **Yoji Hirose, George H. Wahl, jr.**²) and **Heinrich Zollinger**
Technisch-Chemisches Laboratorium, Eidgenössische Technische Hochschule Zürich

(27. III. 76)

Summary. p-Nitrobenzenediazonium tetrafluoroborate dissolved in dimethylsulfoxide (DMSO) at 50° forms *p*-nitrophenol in 88–90% yield. The phenolic oxygen atom originates exclusively from the oxygen atom of DMSO as demonstrated by the use of ^{18}O-labelled DMSO. The first-order rate of dediazoniation is the same under N_2 as it is in the presence of air. The rate is little influenced by the addition of benzene or iodobenzene. However, the products formed in the presence of these additives are significantly different. UV. spectra and the reactivity of diazonium salt solutions in DMSO when mixed with reagents in aqueous solution demonstrate that a relatively stable charge-transfer complex is formed between the diazonium ion and DMSO. The product analyses and the kinetic and spectral results of dediazoniation in DMSO with and without additives are consistent with a mechanism in which the rate-limiting step is the formation of a *p*-nitrophenyl radical from the charge-transfer complex. *p*-Nitrophenol and the products with benzene and iodobenzene are formed in subsequent fast competition steps. In the presence of small amounts of pyridine the dediazoniation is much faster and follows a different kinetic law. Pyridine effectively competes with DMSO in the reaction with diazonium ions.

1. Introduction. – Some years ago we investigated arylations of benzene and nitrobenzene with arenediazonium salts in dimethyl sulfoxide (DMSO) as solvent [2]. Products and other experimental evidence indicated a heterolytic arylation if benzenediazonium ion was used as arylating reagent, but a homolytic mechanism with *p*-nitrobenzenediazonium ion. We [3] as well as other research groups, *e.g. Ritchie et al.* [4] are interested in interactions of solvents with diazonium ions on a more general basis. Since reaction products of *p*-nitrobenzenediazonium tetrafluoroborate

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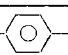
¹) Part VII: See [1].

²) On leave from the Department of Chemistry, North Carolina State University, Raleigh, N.C. 27607, U.S.A.

with DMSO were detected in our previous work, we investigated the reactions of this diazonium salt with DMSO in the absence of benzene or other aromatic substrates. In the present paper we describe product analyses, the kinetics of the dediazoniation and experiments with scavengers. Particular attention was given to the question of the homolytic nature of dediazoniation and of the intermediacy of addition complexes of the diazonium ion with solvent molecules.

2. Results. – 2.1. *Reaction products.* The reaction products of *p*-nitrobenzenediazonium tetrafluoroborate dissolved in DMSO at 50° were analysed after complete dediazoniation with the help of various separation processes (see Exper. Part). The results of six experiments are given in Table 1. In addition, at high concentration (0.4 M) of diazonium salt traces of *p,p'*-dinitrodiphenyl and *p,p'*-dinitroazobenzene were found.

Table 1. *Dediazoniation products of* p-*nitrobenzenediazonium tetrafluoroborate in DMSO at 50°*

Concentration	Yield (%) (Ar = O_2N––)						
M	Ar—OH	Ar—H	Ar—F	Ar—$SOCH_3$	Ar—CH_2SOCH_3	Ar—SCH_3	CH_3SCH_3
1.7×10^{-2}	89	0.5	<0.1	<0.1	<0.1	Trace	0.1
2.0×10^{-2}	90	1	<0.1	<0.1	<0.1	0	4.9
2.0×10^{-2}	88	2	<0.1	<0.1	<0.1	Trace	3.8
40×10^{-2}	10	10	0.7	<0.1	<0.1	<0.1	<5 [b]
40×10^{-2}	[a]	11	0.5	Trace	<0.1	Trace	<2 [b]
40×10^{-2}	10	6	0.1	Trace	<0.1	Trace	[a]

[a] Not determined.

[b] Gravimetric determination (not quantitative), see Experimental Part.

Table 1 demonstrates that in dilute solutions *p*-nitrophenol is the main product. For material balance reasons and as a basis for mechanistic interpretation of our results it was important to determine the origin of the phenolic oxygen atom. DMSO, air and/or traces of water or other oxygen containing compounds might be the oxygen donator. Therefore ^{18}O-DMSO (26.2 ± 0.2% ^{18}O) was synthesized and used as solvent for the dediazoniation. The *p*-nitrophenol obtained also had an ^{18}O-content of 26.2%, showing that DMSO is indeed the oxygen source.

The yield of *p*-nitrophenol decreases substantially from 89 ± 2% to 10% as the initial concentration of the diazonium salt is increased to 0.4 M. At this twenty fold higher concentration large quantities of polymeric diazo tars are formed. This observation and the by-products formed will be discussed later in this paper.

We also measured the rate of dediazoniation and the products formed in DMSO containing low concentrations of iodobenzene. The latter is known as a scavenger

Table 2. *Dediazoniation products of* p-*nitrobenzenediazonium tetrafluoroborate in DMSO in the presence of iodobenzene at 50°* ([iodobenzene]/[diazonium salt] 1:1)

	Yield (%)		
Concentration	*p*-Nitroiodobenzene	*p*-Nitrophenol	Nitrobenzene
1.7×10^{-2}	1–2	16–18	4–5
8.4×10^{-2}	6–14	16–27	8
42.0×10^{-2}	19–20	23–24	[a]

[a] Not determined.

for aryl radicals [5]. The results are given in Table 2. The most noteworthy findings are a large decrease in the yield of *p*-nitrophenol, an increased yield of diazo tars (not isolated) and of nitrobenzene relative to dediazoniation in pure DMSO. The formation of *p*-nitro-iodobenzene, a product typical of a reaction involving *p*-nitrophenyl radicals³) is especially significant. Its formation seems to be favored by higher concentration of iodobenzene and/or diazonium salt.

2.2. *Kinetics of dediazoniation.* The rate of *p*-nitrophenol formation was determined at 50° by measuring the increase in optical density at 317 nm, the maximum of the absorption band of *p*-nitrophenol. The reaction showed first-order kinetics. The data are given in Table 3.

Table 3. *Rates of dediazoniation of* p-*nitrobenzenediazonium tetrafluoroborate in various systems* ($[ArN_2^{\oplus}\ BF_4^{\ominus}]_0 = 10^{-2}$ M; T = 50.0°)

Solvent	Additives	Conditions	Range of Completion Measured	Rate Constant
DMSO	–	N_2; glass	93	$3.0 \times 10^{-5}\ s^{-1}$
DMSO	–	N_2; Teflon	93	$3.0 \times 10^{-5}\ s^{-1}$
DMSO	–	N_2; glass	95	$2.8 \times 10^{-5}\ s^{-1}$
DMSO	–	Air; Teflon	95	$2.8 \times 10^{-5}\ s^{-1}$
DMSO	–	Air; Teflon	95	$3.0 \times 10^{-5}\ s^{-1}$
DMSO	–	Air; glass	95	$2.9 \times 10^{-5}\ s^{-1}$
DMSO/C_6H_6 2:1 a)	–	N_2; glass	93	$2.9 \times 10^{-5}\ s^{-1}$
DMSO/C_6H_6 1:2 a)	–	N_2; glass	97	$3.7 \times 10^{-5}\ s^{-1}$
DMSO	10^{-2} M C_6H_6I	N_2; Teflon	95	$3.0 \times 10^{-5}\ s^{-1}$
DMSO	0.00528 M C_5H_5N	N_2; glass	95	0.0178 $M^{-1}\ s^{-1}$
DMSO	0.0106 M C_5H_5N	N_2; glass	90	0.0785 $M^{-1}\ s^{-1}$
DMSO	0.0528 M C_5H_5N	N_2; glass	90	0.566 $M^{-1}\ s^{-1}$
H_2O	0.1 N HCl	Air; glass	90	$0.35 \times 10^{-5}\ s^{-1}$

a) *v/v*.

Within experimental error the rate is the same under nitrogen and under air and is not influenced by the material of the vessel (glass or Teflon). The rate is about eight times higher than that observed in acidic water at the same temperature.

The rates of all dediazoniations given in Table 3, without and in presence of additives, *i.e.* when *p*-nitrophenol was not the sole major product, were measured by determining the concentration of diazonium ions in aliquot samples by diazo coupling with 2-naphthol-3,6-disulfonic acid and colorimetry of the azo compound formed. Although the addition of benzene to the system changes the ratio of products significantly the rate changes only slightly. The main product in DMSO/benzene mixtures containing 33 and 67% (*v/v*) benzene is the arylation product *p*-nitrobiphenyl. It is noteworthy that in the presence of benzene good first-order kinetics are obtained up to 93 to 97% completion. This is also the case for the experiments in the presence of a small concentration of iodobenzene mentioned in Table 2.

In contrast to all these experiments, very small additions of pyridine (0.00528 to 0.0528 M) change the kinetics qualitatively and quantitatively. With pyridine a

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³) The reproducibility of the yields in presence of iodobenzene is poor. We did not investigate the reasons of the poor reproducibility since these yields have only qualitative importance for this work.

plot of the reciprocal optical density versus time is linear up to at least 90% completion of the reaction, indicating second-order kinetics. The rate of dediazoniation is strongly increased by pyridine. The half life in pure DMSO (398 minutes) is decreased to 93, 21 and 2.9 minutes, in the presence of 0.00528 M, 0.0106 M and 0.0528 M pyridine respectively. The initial rates of the reactions with these three concentrations of pyridine indicate an order of reaction of 1.3 for pyridine.

2.3. *Ultraviolet spectra of diazonium salt solutions.* As observed already by *Koller* [6], solutions of *p*-nitrobenzenediazonium salts are yellowish in DMSO but colorless in water. Electronic spectra of this and other diazonium salts in DMSO and in water do not differ very much with respect to wavelength and extinction coefficient of the maxima of the bands (Table 4). However, all spectra in DMSO show a broad shoulder on the long wavelength side of the highest wavelength absorption band. This shoulder is even present in mixtures of DMSO with large proportions of benzene (volume ratio DMSO to benzene 1:1, 1:2 and 1:4). Examples are given in Figure 1.

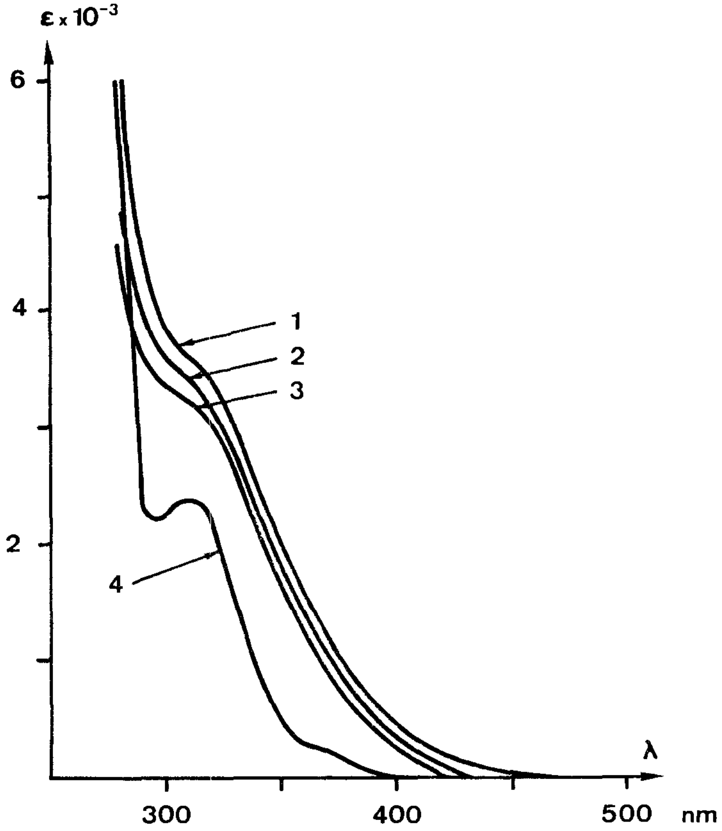


Fig. 1. *Electronic spectra of* p-*nitrobenzene diazonium tetrafluoroborate in DMSO* (spectrum 1), *in DMSO/benzene mixtures* (1:1 and 1:4, spectra 2 and 3, respectively) *and in 0.1* N *aqueous HCl*

2.4. *Reactivity of DMSO solutions of diazonium salts with aqueous solutions.* The spectra described in Section 2.3. of this paper suggest molecular complex formation

Table 4. *Longest wavelength absorption bands of diazonium salt solutions*

Diazonium salt	Absorption band				Reference
	in water		in DMSO		
	λ (nm)	log ε	λ	log ε	
C_6H_5–$N_2^{\oplus}$ $BF_4^{\ominus}$	290	3.29	290	3.54	[7]
p-Cl–C_6H_4–$N_2^{\oplus}$ $BF_4^{\ominus}$	280	4.21	350 (sh)	3.35	[8]
p-NO_2–C_6H_4–$N_2^{\oplus}$ $BF_4^{\ominus}$	259	4.22	<275	<4.0	[6] [7]
	308	3.39	317 (sh)	3.57	

(sh): Shoulder.

between diazonium ions (or ion pairs) and DMSO molecules. Further information was obtained by a semiquantitative determination of the reactivity of solutions of *p*-nitrobenzenediazonium tetrafluoroborate in DMSO relative to aqueous solutions in two reactions which are typical of heterolytic and homolytic mechanisms in diazo chemistry, namely a diazo coupling reaction and a dediazoniation under alkaline conditions.

For the diazo coupling reaction 0.1 ml each of 10^{-2} M solutions of diazonium salt in DMSO and in water respectively were added to a large excess of 2-naphthol-3,6-disulfonic acid in 5 ml of an aqueous $NaHCO_3$ solution. The formation of the azo compound was followed spectrophotometrically. After 30 minutes the aqueous reaction in DMSO solution produced only a 30% yield. That reaction required approximately five hours to reach completion.

The dediazoniation reaction in alkaline aqueous solution was studied by two different methods. In one experiment a solution of *p*-nitrobenzene diazonium tetrafluoroborate in 1 ml DMSO was added to an aqueous solution of $NaHCO_3$ (50 ml). In the second experiment the diazonium salt was dissolved in a solution of $NaHCO_3$ in a mixture of 1 ml DMSO and 50 ml water. Therefore both solutions had the same pH-value and the same composition of DMSO, water, $NaHCO_3$ and diazonium salt. The solution of the second experiment had a UV. spectrum ($\lambda_{max} = 333$ nm, log $\varepsilon = 4.18$) which coincided within experimental error to that of the ***trans*** (*anti*)-diazotate [9], whereas the spectrum of the first experiment was slightly different ($\lambda_{max} = 340$ nm, log $\varepsilon = 4.22$). The disappearance of the diazo compound took about 45 hours at room temperature in the first experiment, but only 15 hours in the second.

3. Discussion. – Both homolytic and heterolytic dediazoniations have been observed [10]. Small changes in the reactants, solvent, additives, *etc.*, may change the mechanism drastically. A striking example is *Bunnett's* observation [11] that either heterolytic or homolytic methoxy-dediazoniation of some arene diazonium ions can occur in acidic methanol depending on the presence or absence, respectively, of oxygen.

The straight-forward first-order kinetics of our hydroxydediazoniation in DMSO and the absence of an oxygen effect on the rate and product ratio suggest a heterolytic mechanism. However, a fair number of radical reactions which exhibit simple kinetics and which are not influenced by oxygen are also known.

On the other hand some of our additional observations are hardly compatible with a heterolytic mechanism or even exclude it completely: The rate is not influenced by large additions of benzene to the system. The competitive arylation which takes place under these conditions is, as we have previously shown [2], clearly a homolytic reaction. This conclusion is substantiated by experiments with small additions of iodobenzene which also do not change the rate but which change the product distribution drastically. Moreover, *p*-nitro-iodobenzene, a typical quenching product from radical intermediates, is formed.

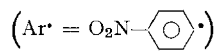
All by-products found (Table 1) may be explained as the result of a radical mechanism. In particular the (polymeric) diazo tars are compatible only with a radical mechanism. Nitrobenzene is known to be formed easily from *p*-nitrophenyl radicals in non-aromatic solvents free of halogen substituents. *p*-Nitrofluorobenzene may be formed by either a homo- or a heterolytic process. *p*-Nitrophenyl methyl sulfoxide is probably not formed from the respective sulfide (which we also find) since sulfide added to the system at 50° is not oxidized within 40 hours. Sodium, potassium and radical anions can decompose DMSO by a one electron transfer mechanism [12] [13]. Therefore homolytic substitution on the methyl group in DMSO by *p*-nitrophenyl radicals is feasible. The same is possible for the formation of *p*-nitrophenyl methyl sulfide based on observations of methyl substitutions in dimethyl sulfide by radicals [12]. *Kenney* [14] found that methyl mercaptan is formed from DMSO by acid catalysed thermolysis. If methyl mercaptan is an intermediate in our system, it may be the source for formation of nitrobenzene and *p*-nitrophenyl methyl sulfide by reactions (1) and (2) and/or (3).

$$Ar^{\bullet} + CH_3SH \rightarrow Ar{-}H + CH_3S^{\bullet} \qquad (1)$$

$$Ar^{\bullet} + CH_3S^{\bullet} \rightarrow Ar{-}S{-}CH_3 \qquad (2)$$

$$Ar{-}N_2^{\oplus} + CH_3SH \rightarrow Ar{-}N_2S{-}CH_3 + H^{\oplus} \qquad (3a)^{4)}$$

$$Ar{-}N_2{-}S{-}CH_3 \rightarrow [Ar \cdot N_2 \cdot SCH_3] \rightarrow Ar{-}S{-}CH_3 + N_2 \qquad (3b)^{4)}$$



For the formation of *p*-nitrobenzyl methyl sulfoxide a reaction of *p*-nitrophenyl radicals with DMSO or a combination with $CH_3{-}SO_2{-}CH_2 \cdot$ radicals seems reasonable. The formation of $CH_3{-}SO_2{-}CH_2^{\ominus}$ anions as a source for homolytic or heterolytic reactions with diazonium ions or aryl cations, respectively, appears very unlikely.

p,p'-Dinitrodiphenyl is an obvious product of the combination of two *p*-nitrophenyl radicals. Alternatively it could be formed by attack on nitrobenzene by *p*-nitrophenyl radicals. Azo compounds have been identified as by-products in a variety of homolytic reactions of diazonium salts. Thus the occurrence of traces of *p,p'*-dinitroazobenzene is not unexpected.

The major problem which we were not able to answer completely is the fate of the rest of the DMSO molecule which is the source of the oxygen atom in the main product, *p*-nitrophenol. Stoichiometry (4) suggests that the other product formed is a methyl methylene sulfonium cation (**1**). Although the methyl methylene sulfo-

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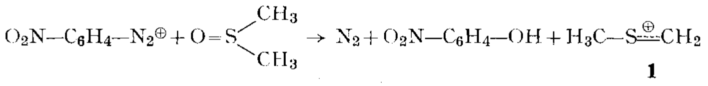
[4] Reaction (3a)–(3b) was recently investigated by *Zijp* & *Bogaert* [15].

nium cation (**1**) has been postulated as a steady-state intermediate in a number of cases [16] [17], equation (4) is too simple to be useful to interpret our results.



$$O_2N{-}C_6H_4{-}N_2^{\oplus} + O{=}S\begin{matrix}CH_3\\CH_3\end{matrix} \rightarrow N_2 + O_2N{-}C_6H_4{-}OH + \underset{\mathbf{1}}{H_3C{-}\overset{\oplus}{S}{=}CH_2} \qquad (4)$$

Dimethylsulfide which we found as a by-product is known to be formed in reaction (5) studied by *Rätz et al.* [16]. The methyl chloromethyl sulfide has an obvious relation to a methyl methylene sulfonium/chloride ion pair. As we could not detect the other products of reaction (5), we do not see positive evidence for the formation of **1** in our system.

$$\begin{array}{c} CH_3{-}S{-}CH_2{-}Cl + 3\ (CH_3)_2SO \\ \downarrow \\ CH_3{-}SO_2{-}S{-}CH_3 + (CH_3)_3S^{\oplus}Cl^{\ominus} + CH_2O + CH_3{-}S{-}CH_3 \end{array} \qquad (5)$$

All these partly ambiguous arguments for or against a homolytic or heterolytic dediazoniation are drawn from products formed in rather small quantities. They may in fact be due only to side reactions of the diazonium ion. Much more conclusive is the significant change in product distribution when small amounts of iodobenzene are added. The high yield of *p*-nitrophenol (88–90%) drops very large. The formation of *p*-nitroiodobenzene and diazo tars is consistent with the presence of *p*-nitrophenyl radicals. As iodobenzene is a radical scavenger, but does not initiate the formation of radicals, we conclude that it is highly probable that *p*-nitrobenzenediazonium ions also form these radicals in the absence of iodobenzene. The *hydroxy-dediazoniation of this diazonium ion in DMSO* is therefore likely to involve the *formation of* p-*nitrophenyl radicals.*

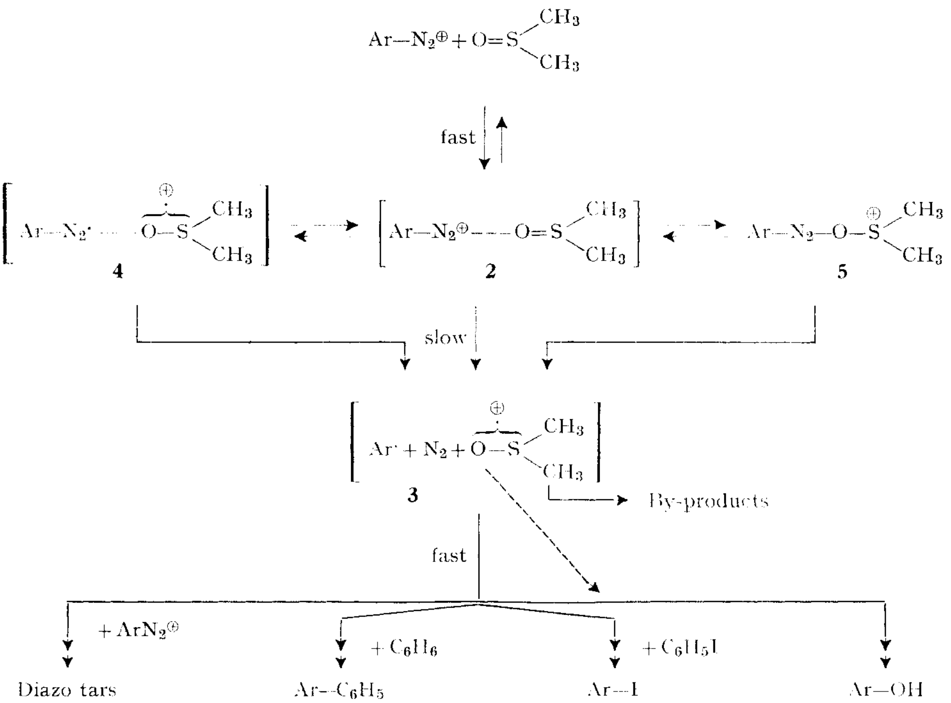
The kinetic results (Section 2.2.) are consistent with a mechanism in which the formation of the aryl radical occurs in the rate-determining step. The coupling of this radical with an oxygen donor is a subsequent fast step. This conclusion originates from the observation (Table 3) that the rate in the presence of iodobenzene and benzene – the latter even in large proportions relative to DMSO – is practically invariant, although the products formed are very different. The products are, however, still compatible with an aryl radical intermediate.

The UV. spectra indicate the formation of a charge-transfer complex between the diazonium ion and DMSO. Our observations on the decreased reactivity of DMSO solutions of diazonium ions with reagents in aqueous solution (section 2.4.) are consistent with the assumption that such a complex has a relatively high stability. It is formed rapidly, but dissociates slowly back to reagents. DMSO is a good electron donor. Measurements of the equilibrium of $SbCl_5$ with various electron donors [18] demonstrate that DMSO is almost as good a donor as pyridine.

That replacement of one and even two thirds of the solvent DMSO by benzene changes the rate only very little supports our postulate brought forward on other evidence [2] that in DMSO/benzene mixtures, the diazonium ion (or ion pair) is solvated by a solvent sphere containing essentially only DMSO. This conclusion is consistent with the UV. spectra in mixtures of DMSO and benzene which differ very little from the spectrum in pure DMSO even if the solvent contains 80% (vol) benzene.

All these experimental data are explained by the mechanism described by *Scheme 1*.

Scheme 1



The rapidly formed charge-transfer complex **2** decomposes slowly in the rate-limiting step into a nitrogen molecule, a *p*-nitrophenyl radical and a dimethylsulfoxide radical cation. We have no evidence that the back reaction of this radical step takes place. In analogy with the homolytic decomposition of azoalkanes, it is not likely that N_2 diffuses out of **3** and that *p*-nitrophenol or its precursors are formed by recombination of the two radicals in a cage. Such a mechanism could not explain our observation that all the subsequent reactions, *i.e.* the formation of *p*-nitrophenol, of *p*-nitrobiphenyl (in the presence of benzene), of *p*-nitro-iodobenzene (in the presence of iodobenzene) and of diazo tars proceed with the same overall rate. They all must be competitive parallel reactions *after* the rate-limiting step. Therefore no conclusions are possible about their detailed mechanisms.

In *Scheme 1* we include also two hypothetical intermediates **4** and **5**. In the charge-transfer complex **2** charge is transferred from DMSO to the diazonium ion in the excited state only. Transfer of one electron in the ground state leads to **4** and, if it is combined with formation of an N–O σ-bond, to **5**. This ion corresponds to covalent derivatives of diazonium ions like diazoamino compounds. We have no experimental evidence for or against **4** and **5**, but we think that they should be considered. Aryldiazine radical (Ar–N=N·) formation by electron transfer from an electron donor to a diazonium ion is proposed by several authors, particularly by *Becker et al.* [19].

It was mentioned above that in complex formation with $SbCl_5$, DMSO is less effective than pyridine. This higher nucleophilicity of pyridine explains the much higher rate and the change in kinetic order of the solution of the diazonium salt in DMSO containing some pyridine. In addition, the pyridine-diazonium ion complex has the advantage that the pyridine radical cation is a better nucleofugal homolytic leaving group⁵) than the DMSO radical cation, *i.e.*, the radical cation in formula **3**. This property of pyridine has been demonstrated in other papers of this series [20] for dediazoniation in 2,2,2-trifluoroethanol.

The decreased yield of *p*-nitrophenol and the large amount of diazo tars formed in dediazoniation in DMSO at higher concentrations of diazonium ions (see Table 1) can be understood on the basis of *Scheme 1*. For radical chain reactions of diazonium ions propagation steps are feasible in which an aryl or aryldiazine radical ($Ar^{\cdot}$ or $Ar–N_2^{\cdot}$) reacts with a diazonium ion. At higher concentrations of diazonium ions their equilibrium concentration in the first step of *Scheme 1* is higher and favors any second order reaction of radicals formed in steady state concentrations.

This investigation was supported by the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung* (project No. 2.722.72).

4. Experimental Part⁶)

4.1. *Chemicals used.* – *DMSO* (*Merck*, Spectroscopy grade) was distilled in the presence of CaH_2 (60°, 5 Torr). Immediately before use it was degassed for 2 h i.v. ^{18}O-*DMSO* ($M = 80$) was synthesized from dimethylsulfide, Br_2 and $H_2{}^{18}O$ (*Stohler* Isotope Chemicals, ^{18}O *ca.* 60%, diluted with natural abundance water *ca.* 1:1) following a published procedure for $DMS^{18}O$ [21]. The product was purified by GC., using a 2 m × 2 mm column packed with 10% FFAP (*Varian* Aerograph) on Chromosorb W (80/100, acid washed) at 140° with 120 ml/min He. ^{18}O-analysis was made by mass spectrometric evaluation of the intensities (I) of the peaks at $M = 80$ (relative to 78) and 65 (63) ($= M - CH_3$):

$$\left.\begin{array}{l} \%\ ^{18}O = \dfrac{100\ I_{80}}{I_{80} + I_{78}} = 26.0 \\[2ex] \%\ ^{18}O = \dfrac{100\ I_{65}}{I_{65} + I_{63}} = 26.5 \end{array}\right\}\ \text{mean value: } 26.25\%$$

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⁵) A nucleofugal homolytic leaving group is defined [10] as the group $X\cdot$ or $X\cdot^{\oplus}$ which leaves, besides N_2 and an aryl radical, the intermediate $Ar–N_2–X$ or $Ar–N_2–X^{\oplus}$, respectively, formed by addition of a nucleophile $X^{\ominus}$ or X to an arene diazonium ion. The effectiveness of these groups is influenced by their nucleophilicity in the addition step and in the ease with which they form a radical. A very good combination of these two properties is present in the nitrite ion which forms nitrogen dioxide (NO_2) as a leaving group.

⁶) Abreviations: i.V. = in vacuo, RT. = room temperature, TLC. = thin layer chromatography.

p-*Nitrobenzene diazonium tetrafluoroborate:* See [22].

^{18}O-p-*Nitrophenol. M.*p. 114°; $M = 141$. Determination of ^{18}O content from MS.-peak intensities at $M = 141$ (139) and $M = 111$ (109); ($= M - NO$):

$$\left.\begin{aligned} \%\ ^{18}O &= \frac{100\ I_{141}}{I_{141} + I_{139}} = 26.3 \\ \%\ ^{18}O &= \frac{100\ I_{111}}{I_{111} + I_{109}} = 26.0 \end{aligned}\right\}\ \text{mean value: } 26.15\%$$

All other chemicals were either purified commercial products or synthesized as described in the literature; see [7].

4.2. *Determination of reaction products.* With the exception of dimethylsulfide, it is difficult to determine the products by GC. in the presence of DMSO. We separated them therefore from DMSO by the following two methods: a) For the separation of volatile and water-insoluble products, the DMSO solution (25 ml) was diluted with 100 ml water and extracted with 2 × 100 ml ether. The ether extract was washed with water, dried (Na_2SO_4) and the main part of the ether evaporated. The residue was diluted with acetone to 1.0 ml and injected into the gas chromatograph. b) Less volatile and water-soluble products were obtained by distilling DMSO from the reaction mixture (50°; 2 Torr). The residue was diluted with acetone and analysed as above. In experiments which gave high yields of *p*-nitrophenol the residues were first separated by TLC. (Kieselgel *Merck* F 254, benzene/acetone mixture as eluent). GC.: 2 to 6 m × 2 mm columns sacked with 10% Silicone SE 30 (*Varian* Aerograph) or 10% Apiezon L (*Apiezol Products Ltd.*) both on Chromosorb W (80/100, acid washed) at 90–220° with 12–35 ml/min He. Dimethylsulfide was determined directly from the reaction mixture by GC. using the stationary phase described above for the purification of ^{18}O-DMSO, but using a 6 m column at 90°. A gravimetric method (precipitation of the complex $2(CH_3)_2S \cdot 3HgCl_2$) [7] does not give quantitative results. The figures in Table 1 for the two experiments with $[ArN_2^{\oplus}\ BF_4^{\ominus}] = 0.4\ M$ were obtained by this method.

4.3. *Kinetic measurements.* Kinetic measurements were made by running the reaction in a thermostated glass or Teflon vessel equipped with a magnetic stirrer and thermometer and closed with a gas balloon (N_2 or air). DMSO (20 ml) was introduced and then the solid diazonium salt was added (t = 0). At various times, samples of 0.17 ml were taken and added to a solution of 0.02 *M* 2-naphthol-3,6-disulfonic acid in 5 ml of a saturated aqueous solution of $NaHCO_3$. The mixture was kept at 0.5° for two h and another 10 h at RT. The solution was acidified by adding 5 ml 1 N HCl and diluted with water to 50 ml. The absorbance was measured at 488 nm, *i.e.* at λ_{max} of 1-(4′-nitrophenylazo)-2-naphthol-3,6-disulfonic acid. The absorbance values were evaluated in the usual way using a linear regression program on a *Hewlett-Packard* table computer. The reproducibility of the kinetic results is good. It was found, however, that with another quality of DMSO, purified in the same way as described above, all rate constants were higher by 10 to 12 percent.

The reaction order with respect to pyridine was determined from the initial rates (v_0) of the experiments, assuming second order kinetic with respect to the diazonium ion. With the help of the equation $v_0 = k_0[Ar{-}N_2^{\oplus}]_0^2$ log v_0 was plotted against log[C_5H_5N]. That plot yielded a slope of 1.30 (correlation coefficient r = 0.959) indicating an (overall) kinetic order of 1.3 with respect to pyridine.

4.4. *Reaction of diazonium salt solutions with a solution of 2-naphthol-3,6-disulfonic acid.* A sample of *p*-nitrobenzene diazonium tetrafluoroborate (47 mg) was dissolved either in DMSO or in water (0.01 M). An aliquot (0.1 ml) of the solution was added at RT. to 5 ml of an aqueous 0.02 M solution of 2-naphthol-3,6-disulfonic acid, saturated with $NaHCO_3$ (pH = 9.3). The formation of the azo compound was followed spectrophotometrically in both batches as described in Section 4.3.

4.5. *Decomposition of* p-*nitrobenzene-diazonium tetrafluoroborate in mixtures of alkaline water and DMSO.* A sample of diazonium salt (2.37 mg) was mixed with 1 ml DMSO and 50 ml saturated aqueous $NaHCO_3$ in two ways. In one experiment the diazonium salt was dissolved in

DMSO, this solution was added to an aqueous $NaHCO_3$ solution. In the other experiment DMSO and the aqueous $NaHCO_3$ solution were mixed and the diazonium salt was dissolved in the mixture. Initial concentrations were the same (1.96×10^{-4} *M*) in each case. The decomposition was followed by taking spectra in the range of 250 to 500 nm immediately after mixing, after 2, 5, 22 and 90 h. The initial maximum at 340 nm, $\log \varepsilon = 4.22$ (first experiment) decreased and was replaced gradually by a new maximum at 395 nm ($\log \varepsilon = 3.21$). In the second experiment the initial maximum was slightly different ($\lambda = 333$ nm, $\log \varepsilon = 4.18$), but the final spectrum was practically identical with that of the first experiment ($\lambda = 395$ nm, $\log \varepsilon = 3.26$). All spectra are published elsewhere [7].

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