

Arenediazonium *o*-Benzenedisulfonimides: Some Kinetics of Azo Coupling Reactions with Naphthols

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Kinetic investigation of azo coupling reactions between naphthols and 4-methoxy- and 4-nitrobenzenediazonium *o*-benzenedisulfonimides has been carried out for comparison with the related benzenediazonium tetrafluoroborates. The data clearly indicate that the two kinds of diazonium salts show very similar reactivities. This fact emphasizes that arenediazonium *o*-benzenedisulfonimides, which are very stable, may be used as alternatives to the more usual diazonium salts. The azo coupling reactions between 4-nitro-

and 4-methoxybenzenediazonium salts and 1-bromo-2-naphthol, performed with equimolecular amounts of both reagents, showed the unexpected formation of large amounts of 1-bromo-4-nitrobenzene and 1-bromo-4-methoxybenzene. Some mechanistic implications of this behaviour are discussed.

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Introduction

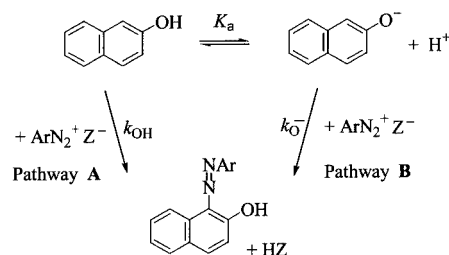
The reactivity of arenediazonium ions has for a long time^[1] been a subject of mechanistic research into the two commonly encountered kinds of reactions: those involving elimination of nitrogen (dediazonation reactions) and those featuring retention of nitrogen, such as azo coupling reactions.

The low stability of arenediazonium salts has been a limiting factor to quantitative investigations of their chemical properties, and the usual preparative procedures involve the preparation of arenediazonium salts immediately prior to their use. The obtaining of arenediazonium tetrafluoroborates, which may be stored and are commercially available in some cases, produced an improvement in such quantitative investigations. Recently, the synthesis of other stable arenediazonium salts, such as arenediazonium *o*-benzenedisulfonimides^[2] and trifluoroacetates^[3] has been reported. In particular, the simple method used for the preparation and isolation of dry arenediazonium *o*-benzenedisulfonimides has recently allowed the production of quite a large number of arenediazonium ions with exceptional stability and high grades of purity, and these salts have been successfully used in a number of synthetic reactions.^[4–6]

The arenediazonium azo coupling reaction with aromatic substrates was first reported by P. Griess in 1861 and became very popular for the preparation of azo dyes.^[7–9]

Arenediazonium ion is a weak electrophilic reagent and the azo coupling reaction necessitates a very electron-rich aromatic partner.

Azo coupling with naphthols is strongly affected by the pH of the reaction mixture: the reactivity of the naphtholate ion, for example, is about 10¹⁰ times higher^[10,11] than that of the undissociated naphthol, $k_{\text{O}^-} \gg k_{\text{OH}}$ in Scheme 1.



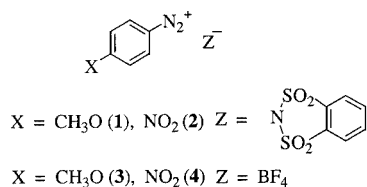
Scheme 1

There is a pH region with a maximum coupling rate for each diazo cation and coupling partner.^[7,10]

With the aim of investigating the reactivity of these salts and examining the importance of the unusual counter-ion (*o*-benzenedisulfonimide anion) we performed a kinetic study of the azo coupling reactions between naphthols and *p*-methoxy- (**1**) and *p*-nitrobenzenediazonium (**2**) *o*-benzenedisulfonimides (Scheme 2).

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Scheme 2

A comparison with the reactivity of the related tetrafluoroborates **3** and **4** was carried out.

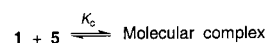
Three naphthols were used: 2-naphthol (**5**), sodium 1-naphthol-4-sulfonate (**6**) and 1-bromo-2-naphthol (**7**).

Results and Discussion

Scheme 1 describes the two main reaction pathways conventionally used for obtaining azo dyes. As reported in the literature,^[10,11] the reactions of naphtholate salts are very fast. In a strongly basic medium, obtained by addition of NaOH or 1,4-diazabicyclo[2.2.2]octane (DABCO) to methanol, methanol/water mixtures or acetonitrile, reactions between arenediazonium salts and naphthol derivatives are too fast for kinetic data to be obtained by the usual procedures (i.e., without the use of particular apparatus such as a stopped-flow system). Exploratory data in dimethyl sulfoxide showed kinetic behaviour parallel to that in methanol.

Zollinger reported^[12] the formation of molecular complexes (probably charge-transfer complexes) between naphthols and diazonium salts (Scheme 3). In methanol/water (2:1), by conventional UV/Vis spectrophotometric inspection of the reaction mixtures at zero reaction time,^[13] we observed extra absorbance values, indicating the presence of a donor/acceptor-like interaction, ($K_c = 92 \text{ mol dm}^{-3}$, see Exp. Sect.). In acetonitrile, though, under the experimental conditions given in Table 2, no extra absorbance arising from the presence of possible molecular complexes was observed.

As reported in Table 4 in the Exp. Sect., no differences between the ¹H NMR spectra of compounds **2** and **4** were observed in [D₄]methanol and [D₃]acetonitrile. This is an

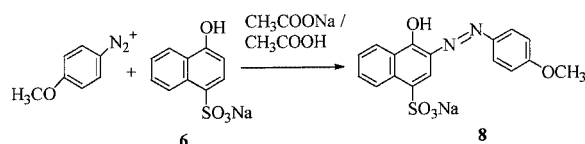


Scheme 3

indication that the proton signals are unaffected by the change in the anionic component of the diazonium salt. In addition, the ¹H NMR signals of **1** are unaffected by the addition of 2-naphthol (see Table 4). Under our experimental conditions, the NMR spectroscopic data do not show any interactions between **1** and **5**.

Reaction in Buffered Medium and in the Presence of Acids

Comparison between *p*-methoxybenzenediazonium *o*-benzenedisulfonimide (**1**) and the corresponding tetrafluoroborate **3** with naphtholate ion was also performed in buffered aqueous solution^[11] (see the Exp. Sect.) for the reaction shown in Scheme 4.



Scheme 4

The k_{O^-} values (in $\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$) were 1.82×10^5 and 1.93×10^5 for **1** and **3**, respectively. Not only are both salts qualitatively identical (they afford the same reaction product), but they are also very similar from a quantitative point of view.

In agreement with the data in Table 1, when an acid is initially added to the reaction mixture, the rate of formation of azo dye is depressed because it depresses the amount of naphtholate ion arising from the spontaneous dissociation of naphthol. The appearance of the dye follows a regular first order kinetic law ($[\text{naphthol}]_0 \gg [\text{diazonium salt}]_0$). For example, in the initial presence of *p*-toluenesulfonic acid (**9**), $k_{\text{obsd.}}$ ($\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$) decreases linearly as the initial amount of the acid is increased. Equation (1) is derived from Scheme 1, under the condition that $[\text{H}^+] \gg K_a$.

$$k_{\text{obsd.}} = k_{\text{O}^-} K_a / [\text{H}^+] + k_{\text{OH}} \quad (1)$$

Table 1. Reactions between arenediazonium salts and naphthols (ArOH) at 20 °C in the presence of variable initial concentration of acids

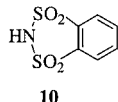
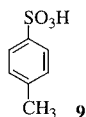
Entry	ArN ₂ ⁺ Z [−]	ArOH	Acid ^[a]	Solvent	k_{OH} ^[b] ($\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$)	$k_{\text{O}^-} K_a$ ^[b]	k_{O^-} ($\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$)	$n^{\text{o}[c]}$	$R^{[d]}$
1	1	6	9	CH ₃ OH/H ₂ O ^[e]	$3.8 \cdot 10^{-6} \pm 3 \cdot 10^{-5}$	$(1.06 \pm 0.04) \cdot 10^{-6}$	$1.57 \cdot 10^4$ ^[f]	6	0.997
2	3	6	9	CH ₃ OH/H ₂ O ^[e]	$(1.1 \pm 0.4) \cdot 10^{-4}$	$(8.11 \pm 0.4) \cdot 10^{-7}$	$1.20 \cdot 10^4$ ^[f]	7	0.993
3	1	5	9	CH ₃ OH/H ₂ O ^[e]	$2.1 \cdot 10^{-6} \pm 1 \cdot 10^{-5}$	$(4.37 \pm 0.2) \cdot 10^{-7}$	$7.95 \cdot 10^5$ ^[f]	7	0.993
4	1	5	10	CH ₃ OH/H ₂ O ^[e]	$(5.0 \pm 2) \cdot 10^{-3}$	$(7.04 \pm 0.4) \cdot 10^{-7}$	$1.28 \cdot 10^4$ ^[f]	4	0.997
5	2	5	9	CH ₃ OH	$(2.7 \pm 0.3) \cdot 10^{-3}$	$(9.38 \pm 0.2) \cdot 10^{-6}$	5.90×10^8 ^[g]	5	0.999
6	2	5	10	CH ₃ OH	$(5.2 \pm 2) \cdot 10^{-2}$	$(1.54 \pm 0.1) \cdot 10^{-5}$	9.75×10^8 ^[g]	5	0.992
7	4	5	10	CH ₃ OH	$(1.4 \pm 3) \cdot 10^{-2}$	$(1.78 \pm 0.1) \cdot 10^{-5}$	1.13×10^9 ^[g]	7	0.983

^[a] [Acid]₀ values were from 2×10^{-4} to $2 \times 10^{-3} \text{ mol dm}^{-3}$. ^[b] Errors are standard deviations. ^[c] Number of points. ^[d] Correlation coefficient. ^[e] CH₃OH/H₂O (2:1 by vol.). ^[f] pK_a values of **5** and **6** = 11.26 and 10.17, respectively, obtained by procedures described in ref.^[15]. ^[g] pK_a = 13.8, ref.^[14]

The plot of $k_{\text{obsd.}}$ against $1/[\text{H}^+]$ is a straight line, the intercept of this plot is the rate of the undissociated naphthol (k_{OH} in $\text{s}^{-1} \text{mol}^{-1} \text{dm}^3$), and the slope is $(k_{\text{O}^-} - K_a)$, where K_a is the dissociation constant of the three naphthols used and k_{O^-} refers to the rate of the reaction of the diazonium salt toward the naphtholate ion.

k_{O^-} and k_{OH} values are reported in Table 1 together with some relevant statistical parameters.

Table 1 also reports data obtained by using the acid related to the particular counter-ion used here, *o*-benzenedisulfonimide (**10**, see Exp. Sect.).



In these cases too, the plot of $k_{\text{obsd.}}$ against $1/[\text{H}^+]$ is linear and Equation (1) may be used to calculate k_{O^-} and k_{OH} values.

In some cases, k_{OH} values (reported in Table 1) are of only low significance because the calculated errors (such as standard deviation) are larger than the intercept values (entries 1, 3 and 7 in Table 1). However, some comparisons are worthy of consideration. In methanol, the kinetics depend only little on the acid used, even when the acid is that related to the counter-ion of salts **1** and **3** (entries 5 and 6) at least toward the naphtholate ion. This is an indication that the anionic part of the acid (and also the anionic moiety of the diazonium salt) is of little importance under these experimental conditions.

Reactions Carried out in "Neutral Medium"

The reaction of undissociated naphthol (in "neutral" medium, without external addition of bases or acids) is slow and in some cases does not follow simple kinetic laws. In fact, the reactions between **1** and **5**, carried out in methanol/water (2:1 by volume) mixtures, show strong autoinhibition. The reaction rate expressed by the usual first order equation, $k_{\text{obsd.}} = \ln(A_{\infty} - A_t)/t$ (where A_{∞} is the absorbance at "infinite" reaction time and A_t is the absorbance value at time t), decreases as the reaction proceeds, as reported in Table 2.

Under these experimental conditions, the reaction does not achieve complete conversion of diazo salt into azo dye, but stops at a variable percentage of conversion, probably depending on the $[\text{diazonium salt}]_0/[\text{naphthol}]_0$ ratio, where $[\]_0$ means the initial concentration of the reagent. The reaction achieves stable absorbance values after long reaction times (about 1 week), but kinetic data are difficult to repro-

duce. In this case, and in other similar reactions carried out under "neutral conditions", A_{∞} is experimentally evaluated by addition of base (NaOH, DABCO) to monitored solutions (see Exp. Sect.).

Some interesting considerations emerge from kinetic data obtained in acetonitrile. When the usual UV/Vis spectrophotometric concentration value ranges of arenediazonium salt (from 2×10^{-5} to $1 \times 10^{-4} \text{mol dm}^{-3}$) and of naphthol (from 2×10^{-4} to $2 \times 10^{-3} \text{mol dm}^{-3}$) are used, the reaction is too slow for reproducible data to be obtained. This kinetic feature parallels that observed for reactions carried out in methanol/water, negative catalysis by H^+ released during the reaction being involved.

When higher initial concentration values of **2** and **4** are used, $([\text{2}]_0, [\text{4}]_0 = 1.2 \times 10^{-3} \text{mol dm}^{-3}, [\text{5}]_0$ from 0.01 to $0.02 \text{mol dm}^{-3})$, there is a rapid increase in the absorbance value (corresponding to the absorbances of the reaction products) until an apparently constant value of the absorbance is reached. This value is much lower than the "infinite" absorbance (i.e., the absorbance value calculated by assuming complete conversion, see Exp. Sect.). The apparent final absorbance value, calculated as a percentage of conversion, is proportional to the initial concentration value of naphthol, as shown in the plot in Figure 1.

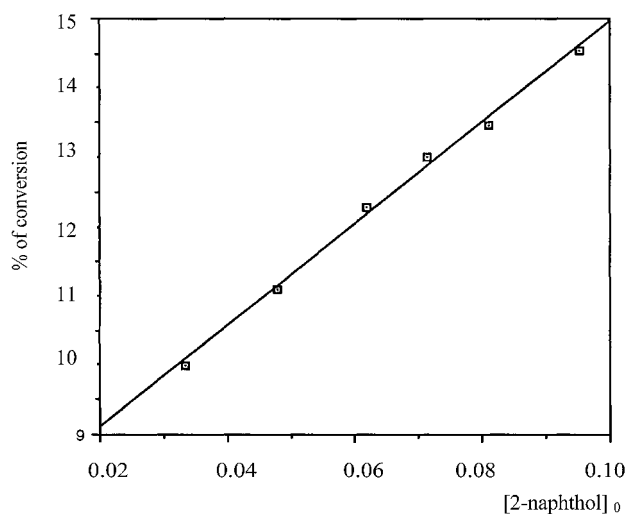


Figure 1. Percentages conversion in reactions between **2** and 2-naphthol in acetonitrile

The apparent stopping of the reaction probably corresponds to the end of the reaction of naphtholate ion, the reaction of the undissociated naphthol being too slow for the "true infinite" value of the absorbance to be reached. With reference to Scheme 1, this reaction corresponds to

Table 2. The reaction between **1** and **5** in methanol/water (2:1 by volume) at 20 °C; $[\text{1}]_0 = 1.8 \times 10^{-4} \text{mol dm}^{-3}$, $[\text{5}]_0 = 1.1 \times 10^{-3} \text{mol dm}^{-3}$; $k_{\text{obsd.}}$ in s^{-1}

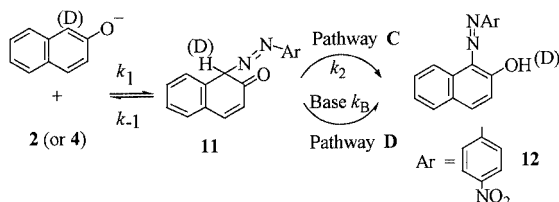
$10^{-3} t$ (s)	0.013	0.030	0.045	0.090	0.270	0.540	0.900	1.26	1.62	1.80
$10^3 k_{\text{obsd.}}$	76.9	33.3	22.2	11.1	3.70	1.85	1.11	0.794	0.617	0.555
$10^{-3} t$ (s)	2.25	2.70	3.150	3.60	4.05	4.50	4.95	5.40	5.85	6.30
$10^3 k_{\text{obsd.}}$	0.444	0.370	0.317	0.278	0.247	0.222	0.202	0.185	0.171	0.159

the reaction pathway B of the naphtholate ion arising from the equilibrium related to K_a . The acidity of 2-naphthol in acetonitrile is very low.^[14]

Apparent k' values (in s^{-1}), as the initial reaction rate, were calculated from the analytical data. From the k' values and from a pK_a value for **5** (27 in CH_3CN ^[14]) it is possible to calculate approximate k_O^- ($s^{-1}mol^{-1}dm^3$) values ($k_O^- = k'/[naphtholate]_0$). These k_O^- values are $1.62 \times 10^9 s^{-1}mol^{-1}dm^3$ and 1.40×10^9 for **2** and **4**, respectively. The azo coupling reactions with naphtholate ion in acetonitrile are slightly faster than those in MeOH reported in Table 1 (entries 6 and 7). The polarity of acetonitrile is lower than that of methanol, which is a better solvent than acetonitrile for charged starting reagents: acetonitrile favours the transition state towards **11**, because the starting charges in **11** are partially neutralised.^[16]

From the neutral intermediate **11**, the formation of the azo dye may occur by two main pathways: i) the spontaneous rearomatization of the naphthalene ring by proton expulsion, and ii) a base-catalysed proton departure pathway.

To check the importance of the proton abstraction from the intermediate **11** in Scheme 5, we examined the reactions of **2** and **4** with 1-deuterio-2-naphthol, and the k_O^- ($s^{-1}mol^{-1}dm^3$) values are 1.54×10^9 and 9.11×10^8 for **2** and **4**, respectively. The k_H^-/k_D^- ratios are 1.21 and 1.54 for **2** and **4**, respectively. When proton abstraction from **11**-like intermediates is rate-limiting, a strong hydrogen/deuterium isotopic effect is observed in aprotic solvents: k^H/k^D may be 6 or 7.^[7,17] In the present case, the moderate isotopic effect indicates that proton abstraction is a less important process: spontaneous proton elimination competes strongly with possible base catalysis (pathway D of Scheme 5), a process well known in the literature. In fact, Zollinger and co-workers^[18] reported that the reactivity of diazonium salts toward naphtholate ion is catalysed by the presence of bases. In the current system, base catalysis may be performed either by the same naphtholate ion (arising from the equilibrium shown in Scheme 1), or by the counter-ion of the diazonium salt. This second possibility is indicated by the fact that the isotopic effect is more evident for the less basic tetrafluoroborate ion than for the anion of the *o*-benzenedisulfonimide **10** (pK_a of HBF_4 is 0.5, pK_a of phenylsulfondiimide is 1.45^[19]).



Scheme 5

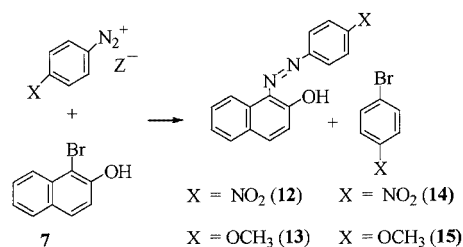
However, the behaviour of the two diazonium salts **2** and **4** in CH_3CN is also very similar: in this case as well, the reactivity of diazonium salt is not affected by the nature of the counter-ion.

In acetonitrile, the observed behaviour is similar to that reported in MeOH/ H_2O mixtures.

Obviously, the catalysis (both positive or negative) cannot be observed in buffered reaction mixtures.

Reactions between 1-Bromo-2-naphthol and Diazonium Salts

Some remarks on the reaction between 1-bromo-2-naphthol (**7**) and **2**, **3**, **4** and **5** are worthy of consideration (Scheme 6).



Scheme 6

In 1906, Hewitt and Mitchell reported^[20] that **7** reacts with arenediazonium salts to afford the usual azo dyes, through a debromination coupling reaction. Fischer and Zollinger studied^[21] the reaction of 1-bromo-2-naphthol, and reported catalysis of the debromination coupling reaction by sulfite ion, a bromonium ion being eliminated from the intermediate **16**, which is similar to **11**.

In our reaction mixtures, when **7** and **3** were mixed in equimolar amounts in the presence of an excess of base (NaOH) in CH_3CN (or in THF), the azo dyes were formed in 40–60% yields and 20–30% of bromo derivatives **14** and **15** were recovered from the reaction mixtures, as shown in Scheme 6. The formation of bromo derivatives **14** and **15** was unexpected. Several sets of experimental conditions and yields of the obtained reaction products are summarised in Table 6 in the Exp. Sect. The formation of 1-bromo-4-nitrobenzene is unaffected by the presence of water: the same amount of **14** is obtained both in anhydrous (freshly distilled) acetonitrile and in commercial acetonitrile with a few drops of added water.

The reaction of 2-naphthol **5**, carried out under the same experimental conditions as for **7**, is fast and affords **12** in almost quantitative yields (entry 16 in Table 6).

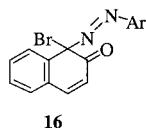
When naphthol **7** is used in large quantities, the azo dye **12** is obtained in almost quantitative yields, and no traces of bromo derivative are recovered from the reaction mixtures (entry 9 in Table 6). Substituted bromobenzenes are obtained both from tetrafluoroborate and from *o*-benzenedisulfonimide diazonium salts. In some case, small amounts of nitrobenzene (less than 1%) were recovered from the reaction mixtures of **7** and **2** (GC-MS analysis).

We checked the reactions between diazonium salts and bromide ion (tetraethylammonium bromide), which afforded bromo derivatives (entry 15 in Table 6). The reaction between *N*-bromosuccinimide and **1** slowly (24 h) produced **15** in low yields (about 15%). The reaction shown in

Scheme 5, carried out in the presence of bromide ion, showed the formation of large amounts of bromo derivative (80%, entry 10 of Table 6) and low amounts of azo dye (15%).

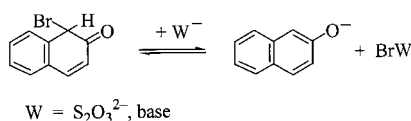
In deuterated methanol the mixing of **7** and **4** (or **2**) (in molar ratio 1:1) afforded 4-deuterio-1-nitrobenzene in 70% yields with small amounts of **12**.

Diazo-coupling reactions of **7**-like naphthols have been reported to be catalysed by thiosulfate ion, thiosulfate being believed to trap bromonium ion from the intermediate **16**. Under the current experimental conditions, the reactions in Scheme 6, when carried out in the presence of solid sodium thiosulfate, produced (entry 13 in Table 6) small amounts of 1-bromo-4-nitrobenzene and the expected azo dye **12**.



Clearly, the formation of bromo derivatives **14** and **15** is a parallel reaction to the azo-coupling reaction. The bromo-dediazoniation reaction becomes important when the azo-coupling reaction is slow, as in the case of **7** in 1:1 molar ratio with respect to the diazonium salt.

A possible reaction pathway for the formation of **14** or **15** may start from the spontaneous (or base-catalysed) debromination of 1-bromo-2-naphthol in the oxo tautomeric form, as represented in the equilibrium shown in Scheme 7.



Scheme 7

This is the same equilibrium as the bromination reaction of anionic species of 2-naphthol and it may be shifted toward the right by the presence of bromonium scavenger; it was invoked by us to explain the kinetic features of the dehalogenation of **7** by sodium thiophenoxide.^[22] Sulfur nucleophiles may produce a debromination reaction. The reaction between **7** and sodium thiosulfate produces **5** in high yield. The equilibrium shown in Scheme 7 affords the naphthol **5**, which is more reactive than **7** in the production of the azo dye.^[21] Scheme 7 offers an alternative explanation to the sulfite catalysis in the azocoupling reaction of **7** reported by Zollinger. In Scheme 7, the bromonium species must be converted into bromide to attack the diazonium salt. Obviously, other possible reaction pathways may involve radical species, as suggested by the reactivity of *N*-bromosuccinimide toward **2**. However, the initial presence of radical scavengers (2,2,6,6-tetramethyl-1-piperidinyloxy TEMPO) does not affect the yields of **14** (entry 6 in Table 6).

Another possible reaction pathway for the formation of bromobenzenes as in Scheme 6 may start from the interme-

diate **16**. The departure of the bromine atom from **16** should be as bromonium ion, which must be converted into bromide ion in order to attack the unchanged diazonium salt. This reaction pathway agrees with the fact that, in the absence of initial quantities of bromide ion, the bromobenzene derivatives are formed in lower amounts than the azo dye, with the exception of the reaction carried out in the absence of NaOH and in the presence of DABCO. The surprising data in entry 4 are the average (mean) of several determinations.

Up to now, it has been difficult to discriminate between the two reported reaction pathways. Even if both mechanisms may be in competition, we think that **16** may reasonably be considered into the intermediate to obtain bromo derivatives **14** and **15**.

Clearly, the equilibrium of Scheme 7 is a slow step, but the formation of **14** and **15** is also observed when the base is added to enhance the rate of azo coupling from the anionic naphtholate species.

Conclusion

In agreement with previous comparative studies between arenediazonium tetrafluoroborates, chlorides and sulfates,^[23] the behaviour of arenediazonium *o*-benzenedisulfonimides parallels that of tetrafluoroborates. For the reactions considered here, the reactivity of arenediazonium salts also does not depend on the nature of the counter-ion from a quantitative point of view. This makes it possible to use arenediazonium *o*-benzenedisulfonimides as alternatives to the less stable classical arenediazonium salts.

From the mechanistic point of view, our data agree with the general behaviour of the reactivity of diazonium salts. The reaction behaviour of 1-bromo-2-naphthol reveals an interesting bromo-dediazoniation reaction, which probably starts from the neutral intermediate **16**, a simple Wheland-like intermediate. The catalysis of this reaction performed by sulfite ion may be explained not only by the ability of sulfite ion to facilitate the departure of bromonium ion from **16**, but also (in an alternative reaction pathway) by the formation of 2-naphthol, which is more reactive than 1-bromo-2-naphthol. In any case, when the rate of diazo coupling is depressed, other reactions (dediazoniation or bromo-dediazoniation) become the main reactions.

Experimental Section

General Remarks: ¹H NMR measurements were recorded on a Varian Gemini 300 MHz instrument. The δ_H values are expressed in ppm from the solvent signal. Mass spectra were recorded at an ionisation voltage of 70 eV on a VG 7070 E spectrometer. GC-MS analyses were performed on a Agilent-6890 gas chromatograph equipped with a methyl silicone capillary column and an Agilent-5973 Network mass detector. UV/Vis spectrophotometric data were recorded with a Perkin–Elmer (model Lambda 12) spectrophotometer. Arenediazonium *o*-benzenedisulfonimides **1** and **2** were pre-

Table 3. Absorbance values extrapolated at zero reaction time for mixtures of **1** and **5** in MeOH/H₂O (2:1 by vol) at 20 °C

[5] ₀ × 10 ²	0.84	1.25	2.10	2.90	4.20	4.23	5.00	5.50	5.80	6.30	6.35	7.19	8.46
A	0.125	0.160	0.188	0.205	0.222	0.222	0.232	0.237	0.243	0.250	0.256	0.252	0.260

pared as previously described.^[2] All other reagents were commercially available.

Preparation of Compounds 8, 12 and 13. General Procedure: The diazonium salt was added to an appropriate, vigorously stirred solution of naphthol/NaOH. The reaction was monitored by TLC analysis on silica gel (eluent: dichloromethane/petroleum light, 7:3) until it appeared to be complete, and the mixture was then extracted with dichloromethane, washed with water and dried over sodium sulfate. The crude reaction product was purified on a silica gel column (eluent dichloromethane/light petroleum, 7:3). The chemical and physical data of compounds **8**, **12** and **13** are in agreement with those reported.^[2,11]

Determination of the Equilibrium Constant of the Molecular Complex Between 1 and 5: The appropriate solutions of **1** were added to a vigorously stirred solution of **5** (4.0×10^{-2} mol dm⁻³) in

Table 4. ¹H NMR spectroscopic data of arenediazonium salts **2** and **4**; [**2**], [**4**] = 0.3 mol dm⁻³

Compound	Solvent	δ 2-H	δ 3-H	J (Hz)
2	[D ₃]acetonitrile	8.65	8.80	9.3
2	[D ₄]methanol	8.94	9.10	9.6
4	[D ₃]acetonitrile	8.68	8.81	9.3
4	[D ₄]methanol	8.95	9.11	9.6
1	[D ₄]methanol	7.62	8.73	9.2
3	[D ₄]methanol	7.62	8.72	9.4
1 ^[a]	[D ₄]methanol	7.60	8.70	9.2

^[a] In the presence of 0.5 mol dm⁻³ of 2-naphthol.

MeOH/H₂O (2:1 by volume). Each reaction was quickly monitored by UV/Vis spectrophotometry and the absorbance values, reported in Table 3, were extrapolated at zero reaction time.^[24] From the analytical data the equilibrium constant of Scheme 3 was calculated by the usual equation^[24,25,26]

$$[1]_0 / A = 1/(K_c \epsilon) \times 1/[5]_0 + 1/\epsilon$$

where *A* is the experimental value of the absorbance and ϵ is the absorption coefficient of the molecular complex. At $\lambda = 420$ nm, $1/\epsilon = (1.41 \pm 0.01) \times 10^{-2}$, $1/K_c \epsilon = (1.49 \pm 0.03) \times 10^{-4}$; number of points: 13, *R* = 0.998; *K_c* = 92.

Kinetic Measures

All kinetic runs were performed by spectrophotometric analysis, by following the increase of the azo dye product with time.

The *A_∞* and ϵ values of compounds **8**, **12** and **13** (in each solvent used) were determined on pure authentic samples synthesised as

Table 5. Reactions between *p*-methoxybenzenediazonium *o*-benzenedisulfonimide (**1**) and sodium 1-naphthol-4-sulfonate in CH₃OH/H₂O (2:1); [**1**] = 1.23×10^{-4} (mol dm⁻³); [**6**] = 1.12×10^{-3} (mol dm⁻³)

10 ³ ×	1.01	1.08	1.15	1.23	1.29	1.37	1.44
[4-methylsulfonic acid] ₀ ^[a]							
10 ⁴ ×	9.10	8.61	8.17	7.70	7.62	6.96	6.64
<i>k</i> _{obsd.} (s ⁻¹ mol ⁻¹ dm ³)							

^[a] Mol·dm⁻³.

Table 6. Reactions between 1-bromo-2-naphthol (**7**) or 2-naphthol (**5**) and *p*-nitrobenzenediazonium salts **2** and **4** in the presence of other added substances in acetonitrile (unless otherwise indicated) at 20 °C and in the presence of 1 equivalent (with respect to **7** or **5**) of NaOH.

Entry	Naphthol	ArN ₂ ⁺	7/ArN ₂ ⁺ ^[a]	Others ^[b]	Time	12 ^[c]	14 ^[c]	Others ^[d]
1	7	2	1:1	—	12 h	65	26	<1% of A
2	7	4	1:1	—	14 h	61	22	<1% of A
3	7	4	1:1.2	—	12 h	51	20	
4	7	4	1:1	DABCO (1)	3 h	10	80	
5	7	4	1:1	— ^[e]	10 h	44	33	
6	7	4	1:1	TEMPO (0.5)	10 h	60	22	
7	7	2	1:2	—	12 h	38	28	
8	7	2	2:1	—	12 h	46	26	
9	7	2	10:1	—	5 min	97	—	
10	7	2	1:1	N ⁺ Br ⁻ (3) ^[f]	10 h	15	80	
11	7	4	1:1	N ⁺ Br ⁻ (3) ^[f]	10 h	10	73	<1% of B
12 ^[g]	7	4	1:1	—	24 h	10		70% of A
13	7	2	1:1	S ₂ O ₃ ²⁻ (1.5) ^[h]	5 h	72	11	<1% of A
14	7	3	1:1	—		50 ^[i]	20 ^[i]	
15	— ^[m]	4	— ^[m]	N ⁺ Br ⁻ (3) ^[f]			80	
16	5	4	1:1	—	5 min	97		
17	5	4	1:1	S ₂ O ₃ ²⁻ (1.6)	—	78		

^[a] Molar ratio. ^[b] Other added substances (the molar ratio with respect to the amount of 1-bromo-2-naphthol in brackets) in addition to 1 equivalent (with respect to **7**) of NaOH. The NaOH was absent in the case of the reaction in the presence of DABCO. ^[c] Yields (%), after separation by chromatographic column. ^[d] **A** = nitrobenzene, detected by GC-MS analysis of the crude reaction mixtures. **B** = 1,2-dihydroxynaphthalene, isolated by chromatographic column. ^[e] NaOH was added 2 hours after the mixing of **7** and **4**. Before the NaOH addition, the TLC analysis showed the presence of traces of **14** and small amounts of **12**. ^[f] Tetraethylammonium bromide. ^[g] Reaction (in CD₃OD) performed and monitored in the NMR tube. ^[h] As a solid, without addition of NaOH. ^[i] Azo-dye **13** ^[j] Bromo derivative **15**. ^[m] Reaction carried out in the absence of naphthol and of base.

described in the appropriate section. ϵ and $\lambda_{\max}$ values are as follows:

Compound 8: methanol/water (2:1), $\lambda_{\max} = 509$ nm ($\log \epsilon = 4.16$)

Compound 8: acetic acid/sodium acetate buffer, $\lambda_{\max} = 509$ nm ($\log \epsilon = 4.26$)

Compound 12: acetonitrile, $\lambda_{\max} = 480$ nm ($\log \epsilon = 4.46$)

Compound 12: methanol, $\lambda_{\max} = 480$ nm ($\log \epsilon = 4.45$)

Compound 13: methanol/water (2:1), $\lambda_{\max} = 420$ nm ($\log \epsilon = 4.13$)

Compound 13: methanol, $\lambda_{\max} = 420$ nm ($\log \epsilon = 4.23$)

Compound 13: acetonitrile, $\lambda_{\max} = 420$ nm ($\log \epsilon = 4.22$)

Usually, the experimental A_{∞} values, obtained from reaction mixtures after addition of appropriate amount of base (DABCO, NaOH), at the end of the reaction are very near to the 'theoretical' A_{∞} values obtained from ϵ values. In a few cases, though, the experimental A_{∞} values were lower than the theoretical A_{∞} values. In these cases, kinetic runs were not considered.

In particular, the reactions between *p*-methoxybenzenediazonium *o*-benzenedisulfonimide (**1**) or the related tetrafluoroborate **3** and sodium 1-naphthol-4-sulfonate (**6**) were performed in a buffered aqueous solution obtained by adding sodium acetate (4.10 g) to acetic acid (2.85 mL) in 100 mL of water and the pH value was checked by a pH meter with a glass electrode.

Under these experimental conditions, the formation of azo dye **8** takes place from the naphtholate ion.^[10,11] The rate for the naphtholate ion is usually about 10^7 – 10^9 times higher than the rate for the undissociated naphthol.

The equation $k_0^- = k_{\text{obsd.}} [\text{H}^+]/K_a$, where $k_{\text{obsd.}}$ is the experimental second order rate constant, K_a is the apparent dissociation constant of the considered naphthol ($K_a = 6.3 \times 10^{-9}$),^[11] $[\text{H}^+]$ is the concentration of the proton (pH = 4.66), allows to calculate k_0^- values.

$k_{\text{obsd.}} = 53.3$ ($\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$) mean of 4 determinations; [sodium 1-naphthol-4-sulfonate]₀ from 6.6×10^{-4} to 2.0×10^{-3} [**1**] = $1.13 \times 10^{-4} \text{ mol dm}^{-3}$.

$k_{\text{obsd.}} = 50.3$ ($\text{s}^{-1} \text{ mol}^{-1} \text{ dm}^3$) mean of 4 determinations; [sodium 1-naphthol-4-sulfonate]₀ from 6.6×10^{-4} to 2.2×10^{-3} [**3**] = $1.15 \times 10^{-4} \text{ mol dm}^{-3}$.

The pK_a of **5** in CH₃OH/H₂O (2:1 by vol.) was determined by the literature method.^[15]

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- [1] H. Zollinger, *Acc. Chem. Res.* **1973**, 6, 335–341. H. Zollinger in *The Chemistry of Functional groups. The Chemistry of amino, nitroso, nitro and related groups, Supplement F2s*. (Ed.: S. Patai), Part 2, John Wiley & Sons, New York, **1996**, chapter 13.
- [2] M. Barbero, I. Degani, R. Fochi, P. Perracino (National Research Council of Italy) PCT/EP98/01145, 1998; *Chem. Abstr.* **1998**, 129, 244942; M. Barbero, M. Crisma, I. Degani, R. Fochi, P. Perracino, *Synthesis* **1998**, 1171–1175.
- [3] C. Colas, M. Goeldner, *Eur. Org. Chem.* **1999**, 1357–1366.
- [4] M. Barbero, I. Degani, N. Diulgheroff, S. Dughera, R. Fochi, *Synthesis* **2001**, 585.
- [5] M. Barbero, I. Degani, N. Diulgheroff, S. Dughera, R. Fochi, M. Migliaccio, *J. Org. Chem.* **2001**, 65, 5600–5608.
- [6] M. Barbero, I. Degani, N. Diulgheroff, S. Dughera, R. Fochi, *Synthesis* **2001**, 2180–2190.
- [7] H. Zollinger, *Color Chemistry*, VCH Verlagsgesellschaft, Weinheim, **1991**.
- [8] H. Zollinger, *Diazo Chemistry I*, VCH Verlagsgesellschaft, Weinheim, **1994**.
- [9] R. Schank, in *The Chemistry of Functional groups. The Chemistry of Diazonium and Diazo groups*. (Ed.: S. Patai) Part 2, John Wiley & Sons, New York, **1978**, chapter 14.
- [10] A. F. Hegarty, *Kinetics and Mechanisms of Reactions Involving Diazonium and Diazo groups*. In *The Chemistry of Diazonium and Diazo Compounds*, (Ed.: S. Patai) John Wiley & Sons, New York, **1978**, chapter 12.
- [11] H. Kropacova, J. Panchartek, V. Sterba, K. Valter, *Coll. Czech. Chem. Commun.* **1970**, 35, 3287–3295.
- [12] S. Koller, H. Zollinger, *Helv. Chim. Acta* **1970**, 53, 78–89.
- [13] L. Forlani, *J. Phys. Org. Chem.* **1999**, 12, 417–424.
- [14] Y. Hashida, H. Ishida, S. Sekiguchi, K. Matsui, *Bull. Chem. Soc. Japan* **1974**, 47, 1224–1227.
- [15] M. S. Newman, J. Blum, *J. Am. Chem. Soc.* **1964**, 86, 503–507. K. Kalfus, V. Sterba, *Coll. Czech. Chem. Commun.* **1969**, 34, 3183–3186.
- [16] C. Reichardt, *Solvent Effects in Organic Chemistry*, Verlag Chemie, Weinheim, **1979**.
- [17] H. Zollinger, *Helv. Chim. Acta* **1955**, 38, 1597–1616, and 1617–1622.
- [18] H. Zollinger, *Helv. Chim. Acta* **1955**, 38, 1623–1631.
- [19] G. Dauphin, A. Kergomard, *Bull. Soc. Chim. France* **1961**, 486–492.
- [20] J. T. Hewitt, H. V. Mitchell, *J. Chem. Soc.* **1906**, 89, 1167–1173.
- [21] P. B. Fisher, H. Zollinger, *Helv. Chim. Acta* **1972**, 55, 2139–2146.
- [22] M. Bosco, L. Forlani, P. E. Todesco, *Gazz. Chim. Ital.* **1967**, 97, 1594–1603. M. Bosco, V. Calò, F. Ciminale, L. Forlani, L. Lopez, E. Nonnis, P. E. Todesco, *Gazz. Chim. Ital.* **1971**, 101, 685–693.
- [23] J. R. Penton, H. Zollinger, *Helv. Chim. Acta* **1971**, 543, 5573–5579.
- [24] L. Forlani, *Gazz. Chim. Ital.* **1982**, 112, 205–211.
- [25] R. Foster, *Organic Charge Transfer Complexes*, Academic Press, New York, **1962**.
- [26] S. D. Ross, I. Kuntz, *J. Am. Chem. Soc.* **1954**, 76, 3000–3005.

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