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**Solvolyses of 4-methylbenzenediazonium ions in trifluoroethanol/water mixtures. Effects of [TFE], acidity and temperature on the kinetics and mechanism of the reaction.**

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**Abstract**

We studied the solvolyses of 4-methylbenzenediazonium, 4MBD, ions in 2,2,2-trifluoroethanol, TFE, – water mixtures by employing a combination of spectrometric (UV-VIS) and chromatographic (high performance liquid chromatography, HPLC) techniques. HPLC analyses of the reaction mixtures show that very small amounts (< 8%) of the reduction product toluene, ArH, are obtained, suggesting that the reaction occurs primarily through a heterolytic mechanism. Kinetic results show that  $k_{\text{obs}}$  values do not change significantly on changing solvent composition, which means that nucleophilic attack by solvent is not involved in the rate-limiting step of the reaction. On lowering the acidity, both  $k_{\text{obs}}$  values and product distributions remained basically unchanged, in contrast with the behaviour of dediazoniations in alcohols such as MeOH, EtOH or BuOH. In these reactions, the results support the formation of diazo ethers, Ar-N=N-O-R, suggesting that diazo ethers do not form in THE. To obtain additional evidence for the ionic mechanism, we determined the effect of temperature on  $k_{\text{obs}}$  at different acidities and calculated the corresponding activation parameters.  $\Delta H^\ddagger$  values are high compared to those of bimolecular and radical reactions, and  $\Delta S^\ddagger$  values are small, but positive. The results are consistent with the traditional heterolytic  $D_N + A_N$  dediazonation with a rate-determining formation of a highly reactive aryl cation that traps any nucleophile available in its solvation shell.

## Introduction.

Reactions of arenediazonium,  $\text{ArN}_2^+$ , ions are both synthetically useful and mechanistically interesting. They are exploited industrially in the manufacture of pharmaceuticals and dyestuffs among others. New applications are emerging: they are currently widely used as initiators to modify carbon surfaces, to probe the interfacial compositions of colloidal systems and their role in carcinogenic and mutagenic processes is being explored.<sup>[1-3]</sup> Reaction mechanism of arenediazonium ions have been studied by a wide variety of techniques for over a century. New applications continuous to be found in contemporary organic synthesis<sup>[4-11]</sup>, however, few kinetics studies accompany by product analyses. Consequently, mechanistic understanding of the relationships between molecular structure of reactant, solvent, and reaction conditions is less than complete.

Dediazoniations have been studied in a number of solvents,<sup>[4, 12, 13]</sup> and two main mechanisms are reported, heterolytic (1A) and homolytic (1B), Scheme 1. Literature reports<sup>[4]</sup> indicate that, in the absence of electron donors and depending on experimental conditions, both homolytic and heterolytic mechanisms occurs in a variety of solvents. Until recently, [3] the initiation step of the homolytic dediazonation pathway was hypothesized to be an electron transfer from the solvent, but the absence of evidence in for or against, this hypothesis means that the nature of the initiation step remains a matter of debate.<sup>[4]</sup>

Based on recent solvolytic studies in our laboratory,<sup>[14, 15]</sup> we concluded that the initiation step is the formation of *Z*-diazo ether adducts,  $\text{Ar-N=N-O-R}$  and not an electron transfer. These kinetically controlled products undergo isomerization to the stable *E* isomer or homolytic bond rupture initiating a radical process, Scheme 2, leading to the formation of

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3 reduction products. The evidence for this mechanism is based on the observed sigmoidal  
4 variation in both  $k_{\text{obs}}$  and product yields with acidity for a number of arenediazonium ions.  
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6 Product distribution analyses of the reaction mixtures indicate that at relatively high acidities (  
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8  $-\log([\text{HCl}] = 2)$ ) only heterolytic products are formed, but upon decreasing the acidity, the  
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10 reduction products become predominant at the expense of the heterolytic ones, suggesting a  
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12 change in the reaction mechanism. In addition, sigmoideal variations of  $k_{\text{obs}}$  with acidity are  
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14 usually observed in reactions of acid-base pairs where both forms are attainable and show  
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16 different reactivities.<sup>[16]</sup> But under our experimental conditions, the solvent ionization is  
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18 negligible and a potential reaction between  $\text{ArN}_2^+$  and  $\text{OH}^-$  ions is unlikely,<sup>[14, 15, 17]</sup> therefore  
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20 the formation of an O-adduct (the diazo ether) that initiates a radical process.  
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29 The results of our solvolytic studies<sup>[14, 15, 17]</sup> permit demonstration the identification of  
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31 the dual role of ROH molecules as nucleophiles that either (i) solvate the diazonium ions  
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33 (allowing them to undergo thermal heterolytic decomposition, i.e. decomposing through an  
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35 ionic mechanism), or (ii) react directly with arenediazonium ions to yield O-coupling adducts  
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37 in a highly unstable *Z* configuration, i.e. *Z*-diazo ethers. The *Z*-diazo-ethers then undergo  
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39 homolytic fragmentation initiating radical processes. The kinetics of methanolysis of 4-NO<sub>2</sub>-  
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41 and 4-Br-benzenediazonium ions under acidic conditions provides an excellent example of  
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43 the influence of solvent composition and temperature on the change from a heterolytic  
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45 mechanism to a homolytic one.<sup>[15, 17]</sup> For these compounds, the formation of the diazo ethers  
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47 is favored on increasing [ROH] by the mass action effect but is inhibited by the medium  
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49 effect on the equilibrium constant for the formation of the diazo ether, which decreases upon  
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51 increasing [ROH].<sup>[15, 17]</sup>  
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3 Here we expand our solvolytic studies with a kinetic study of the solvolysis of 4-  
4 methylbenzenediazonium, 4MBD, ions in 2,2,2-trifluoroethanol, TFE, – water mixtures. The  
5 purpose is obtain evidence for or against, the formation of diazo ethers in TFE, by measuring  
6 the effects of solvent composition, acidity and temperature on the observed rate constants,  
7  $k_{\text{obs}}$ , and on the product distributions.  
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## 20 Experimental Section

### 21 INSTRUMENTATION

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24 UV-VIS spectra and some kinetic experiments were followed on an Agilent 8453  
25 spectrophotometer equipped with a cell carrier thermostatted by Julabo F12-ED bath and  
26 attached to a computer for data storage. Product analysis was carried out on a WATERS  
27 HPLC system which included a model W600 pump, a W717 automatic injector, a W2487  
28 dual wavelength detector, and a computer for control and data storage. Products were  
29 analyzed on a Nova Pak (Waters) reverse phase column (150 mm length, 3.9 mm internal  
30 diameter, and 4  $\mu\text{m}$  particle size) using a mobile phase of 50/50 v/v MeOH/H<sub>2</sub>O containing  
31 10<sup>-4</sup> M HCl. The injection volume was 25  $\mu\text{L}$  in all runs and the UV detector was set at 220  
32 and 280 nm.  
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### 50 MATERIALS

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52 4-Methylbenzenediazonium (4MBD) tetrafluoroborate was prepared by an anhydrous  
53 method,<sup>[18]</sup> purified three times from CH<sub>3</sub>CN/cold ether, stored in the dark at low  
54 temperatures to minimize its decomposition, and recrystallized periodically. 4-Cresol (ArOH),  
55 4-chlorotoluene (ArCl) and toluene (ArH) were from Sigma-Aldrich and 2,2,2-  
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3 trifluoroethanol was from Acros Organics, they were used without further purification. Other  
4 reagents were of maximum available purity from Panreac or Riedel de H en. Solution  
5 composition was expressed as percent TFE by volume. Molar concentrations were calculated  
6 by ignoring the small excess volume of mixed solvents.<sup>[19]</sup> All aqueous solutions were  
7 prepared by using Milli-Q grade water.  
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## 20 METHODS

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22 Beer's law plots (not shown) of 4MBD aqueous solutions up to  $2.00 \times 10^{-4}$  M were linear (cc.  
23  $\geq 0.999$ ). Kinetic data were obtained spectrometrically by monitoring the disappearance of the  
24 absorbance of  $\text{ArN}_2^+$  at an appropriate wavelength. Observed rate constants,  $k_{\text{obs}}$ , were  
25 obtained by fitting the absorbance-time data to the integrated first-order equation (1) using a  
26 non-linear least squares method. All runs followed first-order kinetics for at least three half-  
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$$39 \ln\left(\frac{A_t - A_\infty}{A_0 - A_\infty}\right) = -k_{\text{obs}}t \quad (1)$$

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46 where  $A_t$ ,  $A_0$  and  $A_\infty$  are the absorbances at any time, at  $t = 0$  and when the reaction is  
47 finished (i.e., infinite time). Reactions were initiated by adding an aliquot ( $< 100 \mu\text{L}$ ) of the  
48  $\text{ArN}_2^+$  stock solution to the previously thermostated reaction mixture. Duplicate or triplicate  
49 experiments gave average deviations less than 10%.  
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58 Product yields were obtained by HPLC after dediazonation was complete.  
59 Preliminary HPLC experiments showed that up to four dediazonation products may be  
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3 formed, 4-cresol, ArOH, 4-fluorotoluene, ArF, aryl trifluoroethyl ether, ArOCH<sub>2</sub>CF<sub>3</sub>, and  
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5 toluene, ArH. Linear (cc. > 0.999) calibration curves for converting chromatographic peak  
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7 areas, A, into concentrations were obtained for ArOH, and ArH by employing commercial  
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9 samples dissolved in MeOH. ArOCH<sub>2</sub>CF<sub>3</sub> is not a commercial product, it was not synthesized,  
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11 and its yield was not determined. Yields of ArF were determined either because the product  
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13 was not available in our laboratory. The absence of these products yields produces a  
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15 systematic error in the total yields. However, this error does not affect the kinetic results  
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17 because dediazonation products are formed competitively. This variations in the yields of the  
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19 ArOH or ArH does not affect the main mechanistic conclusions, that is the reaction with  
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21 trifluoroethanol goes by a heterolytic pathway unlike aliphatic alcohols, that can be ruled out  
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23 from the experimental data.<sup>[15, 17, 20]</sup>  
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32 Yields of a dediazonation product, Y, were obtained from the product concentration,  
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34 [Analyte]<sub>∞</sub>, and the initial arenediazonium salt concentration, [ArN<sub>2</sub><sup>+</sup>]<sub>0</sub>, estimated by weight,  
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36 i.e.  $Y = 100[\text{Analyte}]_{\infty} / [\text{ArN}_2^+]_0$ , as described elsewhere.<sup>[4, 7, 21]</sup>  
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## 44 Results

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50 *1.- Effects of percent TFE on the observed rate constant,  $k_{\text{obs}}$ , and on the product distribution.*  
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54 The effects of solvent composition on  $k_{\text{obs}}$ , was determined by changing the percent  
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56 TFE in the reaction mixture at a fixed acidity (-log[HCl] = 2). In the absence of TFE,  $k_{\text{obs}} \sim 8$   
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58  $\times 10^{-4} \text{ s}^{-1}$  at T = 60 °C, consistent with literature values.<sup>[20, 22]</sup> Values of  $k_{\text{obs}}$  increase by a  
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3 factor of almost 3 as % TFE increases from 0 to 98%. At 98%TFE,  $k_{\text{obs}} = 16 \times 10^{-4} \text{ s}^{-1}$ , close  
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5 to a previously reported value.<sup>[23]</sup>  
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10 At this high acidity ( $-\log[\text{HCl}] = 2$ ), the size of the observed rate enhancement is  
11 similar to that obtained in solvents such as MeOH or EtOH,<sup>[20]</sup> but the linear increase in  $k_{\text{obs}}$   
12 with TFE contrasts with the non-linear variation found in those solvents where exponential  
13 variation of  $k_{\text{obs}}$  with  $[\text{ROH}]$  were found.  
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22 The effect of % TFE on the product distribution was determined by HPLC analysis of  
23 the reaction mixture at the end of the reaction, that is, at infinite time. Figure 2 shows that, in  
24 the absence of TFE, the major dediazonation product is ArOH, in keeping with previous  
25 results. As expected, ArOH yields decrease upon increasing the percentage of TFE in the  
26 reaction mixture and only small amounts of the reduction product ArH were detected in  
27 reaction mixtures with TFE content higher than 80% ( $\% \text{ArH} < 10\%$ ). The ArOH yields at  
28 58% and 85% TFE are very close to those reported in the literature, which have been reported  
29 as 65% and 34% ArOH, respectively.<sup>[5]</sup>  
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## 43 2.- Effects of acidity on $k_{\text{obs}}$ and on the product distribution.

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48 Solution acidity has a major effect on the formation and decomposition of diazo ethers  
49 intermediates in previous solvolytic studies in MeOH and EtOH.<sup>[17, 20]</sup> To investigate possible  
50 formation of diazo ethers in TFE solutions, we studied the effect of acid strength on  $k_{\text{obs}}$  and  
51 the product distributions at two TFE/H<sub>2</sub>O compositions (35% and 70% TFE). The results in  
52 Table 1 show that, at both percentages of TFE, the  $k_{\text{obs}}$  values increased gradually with  
53 increasing the acidity ( $0.1 < -\log[\text{HCl}] < 6$ ). The average  $k_{\text{obs}}$  values,  $k_{\text{obs}} = (11.9 \pm 0.9) \times 10^{-4} \text{ s}^{-1}$   
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<sup>1</sup> (35% TFE) and  $k_{\text{obs}} = (13.8 \pm 0.5) \times 10^{-4} \text{ s}^{-1}$  (70% TFE) are the same as the  $k_{\text{obs}}$  values at the same %TFE, Figure 1.

Figure 3 shows the variation of the product distribution with [HCl]. As shown, the percentage of both the heterolytic product ArOH and the reduced product ArH remain virtually constant from 1M to  $10^{-7}$  M HCl. The constant  $k_{\text{obs}}$  values and product distributions over a wide range of acidities suggests that diazo ether formation is not important and the reaction mechanism remains unchanged. By contrast in EtOH-H<sub>2</sub>O solutions, rate enhancements of 320 fold and stoichiometric amounts of the reduced product were found.

### 3.- Effect of temperature on $k_{\text{obs}}$ for dediazonation of 4MBD in TFE-H<sub>2</sub>O mixtures.

The temperature effect on  $k_{\text{obs}}$  was studied at different acidities in two binary mixtures (35 and 70% TFE) at 50°C and 60°C, Figure 4. Very similar variations in  $k_{\text{obs}}$  with acidity were obtained independently of the percentage of TFE in the reaction mixture.

The activation parameters of the reaction were estimated by using the Arrhenius equation and the theory of absolute rates, equation 2, where  $k_B$  and  $h$  stand for the Boltzmann and Plank constants respectively. The results are in Table 2.

$$\ln\left(\frac{hk_{\text{obs}}}{k_B T}\right) = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (2)$$

## DISCUSSION

All runs obeyed first order kinetics for more than three half-lives at any solvent composition. Upon increasing [TFE],  $k_{\text{obs}}$  increases modestly, Figure 1 and no significant changes in  $k_{\text{obs}}$

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3 with acidity were detected, in contrast with results of solvolytic dediazoniations in more  
4 nucleophilic solvents such as MeOH or EtOH, where S-shaped variations of  $k_{obs}$  with acidity  
5 were found,<sup>[14, 15, 17]</sup> indicating that formation of diazo ethers of the type Ar-N=N-O-CH<sub>2</sub>-CF<sub>3</sub>  
6 does not seem to be important. The low sensitivity of  $k_{obs}$  to changes in %TFE is related to its  
7 properties as solvent, which combines a lower nucleophilicity, basicity but a higher ionizing  
8 power compared to alcohols such as MeOH or EtOH, which makes TFE an excellent solvent  
9 to probe nucleophilic solvent assistance and, in general, for solvolytic dediazonation  
10 studies.<sup>[5-7, 24, 25]</sup>

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12 Further evidence supporting the hypothesis comes from the product analyses. Only  
13 heterolytic dediazonation products are obtained in significant yields with increasing %TFE,  
14 temperature and acidity, and reduction products like ArH are in low yield. To the contrary,  
15 large amounts of the reduction product ArH were obtained upon decreasing the acidity in  
16 solvolytic reactions carried out in MeOH or EtOH, for instance, stoichiometric amounts of  
17 ArH are found in the ethanolysis of 4MBD at  $-\log[\text{HCl}] = 5$ , meanwhile negligible amounts  
18 are found at  $-\log[\text{HCl}] = 2$ .<sup>[15, 26]</sup> Therefore, the absence of significant amounts of reduction  
19 products like ArH or biaryls, Ar-Ar indicates that dediazonation is heterolytic mechanism,  
20 Scheme 3.  
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41 Rate-limiting nucleophilic attack of TFE on 4MBD would lead to a strong dependence  
42 of  $k_{obs}$  on solvent composition, which is not observed, Figure 1. The results are consistent  
43 with rate determining formation of a highly reactive aryl cation that is trapped by available  
44 nucleophiles, Scheme 1. Aryl cations have not been isolated to date in aqueous systems  
45 because they are extremely short-lived intermediates ( $< 0.5 \text{ ns}$ <sup>[27]</sup>). However, Winkler *et al.*<sup>[28]</sup>  
46 isolated them in a solid argon matrix and other reports indicate that photolyzed  
47 arenediazonium ions generate aryl cations that can be observed as addition products with  
48 aromatic compounds.<sup>[29]</sup>  
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3 Pre-association stepwise mechanisms, Scheme 3, in which the aryl cation has a short  
4 but finite lifetime, have been used to describe product distribution in terms of ion-molecule or  
5 ion-nucleophile pairs.<sup>[22, 30]</sup> Nucleophilic attack may occur on “free” carbocations, contact  
6 ion-molecule pairs or contact ion-solvent pairs. Various research groups have proposed  
7 formation of ion-molecule pairs involving ground state arenediazonium ions. Zollinger et  
8 al.<sup>[31]</sup> suggested formation of ion molecule pairs with N<sub>2</sub> at high N<sub>2</sub> pressures. More recently,  
9 transient colored complexes between arenediazonium ions and aromatic hydrocarbons have  
10 been observed and characterized<sup>[32]</sup> and solid arenediazonium tetrachlorocuprate(II)  
11 complexes<sup>[33]</sup> have been isolated that decompose to give ArCl in high yields<sup>[34]</sup>.

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27 Rate constants for nucleophilic attack on carbocations have been reported to be close  
28 to the diffusion control limit,  $\sim 10^9\text{-}10^{13} \text{ M}^{-1} \text{ s}^{-1}$ .<sup>[29]</sup> Aryl cations have lifetimes on the order of  
29 nanoseconds and they do not have much time to diffuse away reorganizing their nearest  
30 neighbour ions and molecules, similar to the behaviour of than other extremely short lived  
31 carbocations.<sup>[35]</sup> Thus, at low concentration of other components, e.g. anions of salts,  
32 arenediazonium ions decompose primarily with solvent in the immediate vicinity of the aryl  
33 cation, that is, once the N<sub>2</sub> leaves, one nucleophile molecule in the first coordination shell will  
34 form its corresponding dediazonation product. In other words, to obtain a specific  
35 dediazonation product the precursor nucleophile must be in the solvation shell of the aryl  
36 cation prior to N<sub>2</sub> departing. Consistent with this interpretation, Scheme 1, the formation of  
37 the aryl cation does involves change transfer into the ring and only a small reorganization of  
38 the solvent shell is expected upon formation of the corresponding aryl cation.<sup>[36, 37]</sup>

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58 Previous solvolytic dediazoniations in TFE are line with the above conclusions.  
59 Maskill and coworkers<sup>[7]</sup> investigated the source of fluoride atoms in ArF, concluding that  
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3 ArF was formed by fluorine abstraction by the presumed aryl cation, in part from the solvent  
4 and in part from the tetrafluoroborate counterion within an undissociated ion-pair. They,  
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6 however, could not identify the nature of the species remaining after fluoride abstraction from  
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8 TFE or whether fluoride abstraction is concerted or stepwise.<sup>[6, 7]</sup>  
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15 Analysis of the activation parameters, Table 2, show that both  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$  values are  
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17 very similar to those found in water and in short chain alcohols such as MeOH or EtOH.<sup>[20]</sup>  
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19 Solvolytic unimolecular reactions can show positive or negative  $\Delta S^\ddagger$  values.<sup>[38, 39]</sup> The positive  
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21  $\Delta S^\ddagger$  values in Table 2 suggest that the transition state has a greater structural freedom than  
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23 reactants, in line with the reported positive volumes of activation,  $\Delta V^\ddagger$ , for a number on  
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25 dediazoniations in different solvents.<sup>[40-43]</sup> On view of Scheme 1, the parent arenediazonium  
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27 ion and the aryl cation polarize the surrounding solvent molecules to a similar extent, thus the  
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29 gain of entropy due to the increase in molecular vibrations is not compensated by the loss of  
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31 entropy due to the restricted motion of the solvating molecules. On the other hand,  $\Delta H^\ddagger$  values  
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33 are relatively high as in many unimolecular reactions,<sup>[44, 45]</sup> unlike  $\Delta H^\ddagger$  values usually found  
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35 for bimolecular reactions. In typical  $S_N2$  reactions,<sup>[45]</sup> activation enthalpies are substantially  
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37 lower because the bond breaking of old bonds, which requires energy, and bond making,  
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39 which releases energy, are highly concerted, usually synchronous and of similar energies.  
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41 Thus the relatively high  $\Delta H^\ddagger$  values for 4MBD in TFE/H<sub>2</sub>O solutions suggest a transition state  
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43 that has undergone substantial bond breaking with little compensating bond making. Positive  
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45  $\Delta S^\ddagger$  values, as those found in this work, compensate the large enthalpy term making  
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47 dediazoniations and  $\Delta G^\ddagger$  is relatively small. Thus dediazonation are often faster than other  
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49 unimolecular reactions, and consistent with results for a number of dediazoniations, that show  
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51 a much lower solvent dependence than typical unimolecular reactions.<sup>[4, 23, 43, 46]</sup>  
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3 Finally, it may be worth noting the change in the behaviour of 4MBD ions compared  
4 with that of arenediazonium ions bearing electro-withdrawing substituents such as 4-NO<sub>2</sub> or  
5 4-Br-benzenediazonium ions.<sup>[15, 17]</sup> Substituent effects on the aromatic ring have a significant  
6 effect on the stability and reactivity of arenediazonium ions, but their effects can not be  
7 accounted for in terms of the Hammett equation but a dual substituents parameter equation  
8 separating the resonance and inductive effects is needed.<sup>[4, 47, 48]</sup> It is well known that 4-alkyl  
9 substituents in the aromatic ring make ArN<sub>2</sub><sup>+</sup> ions less prone to decomposition through  
10 homolytic pathways than those bearing electronwithdrawing substituents<sup>[4]</sup> and this is  
11 reflected in the lower values of the equilibrium constant *K* for the formation of diazo ether of  
12 4MBD compared with those for 4-NO<sub>2</sub> and 4-Br-benzenediazonium ions.<sup>[15, 17]</sup>  
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29 In conclusion, the kinetic and product yield results are not consistent with the  
30 formation of diazo ethers with leads to reduction products in TFE. This is in keeping with  
31 previous solvolytic studies showing that heterolytic dediazoniations tend to occur in solvents  
32 of low nucleophilicity such as H<sub>2</sub>O or fluorinated alcohols such as TFE, but that both ionic  
33 and homolytic dediazoniations occur in non-fluorinated alcohols of higher nucleophilicity  
34 such as MeOH and EtOH or DMSO. Our results are completely consistent with the  
35 heterolytic D<sub>N</sub> + A<sub>N</sub> mechanism shown in Scheme 3, that is rate-limiting formation of an  
36 extremely reactive aryl cation that is trapped by any nucleophile available in its immediate  
37 vicinity.  
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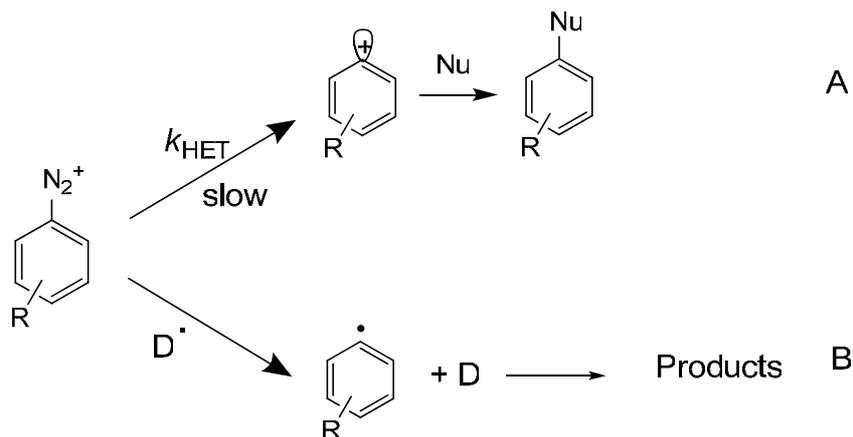
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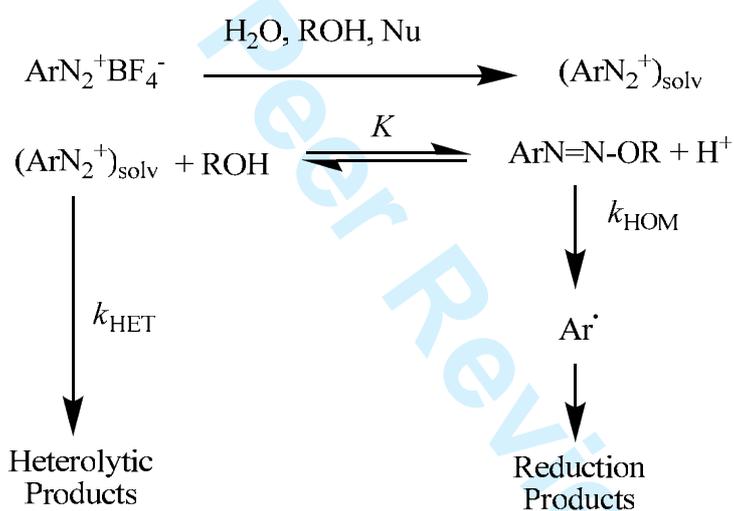
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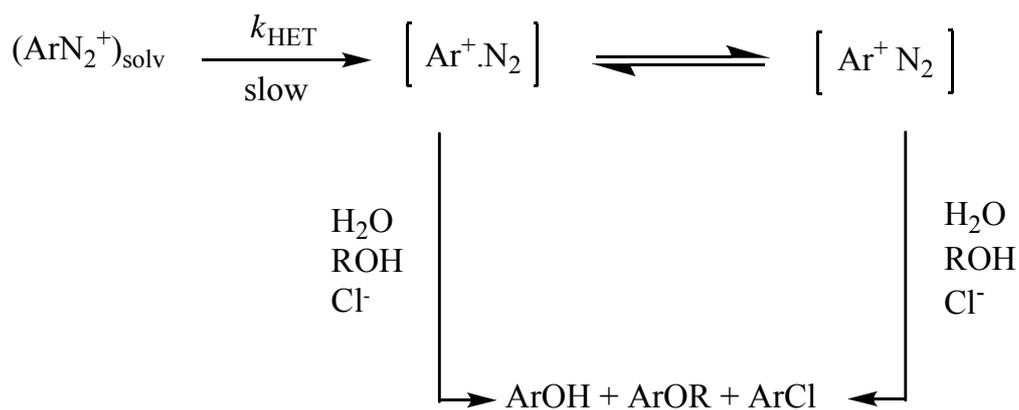
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18 Scheme 1. Simplified dediazonation mechanisms. (A) Heterolytic; (B) homolytic.



45 **Scheme 2.** Proposed competitive heterolytic (HET) and radical mechanisms (HOM) for the  
46 reaction of arenediazonium ions with alcohols under acidic conditions.  
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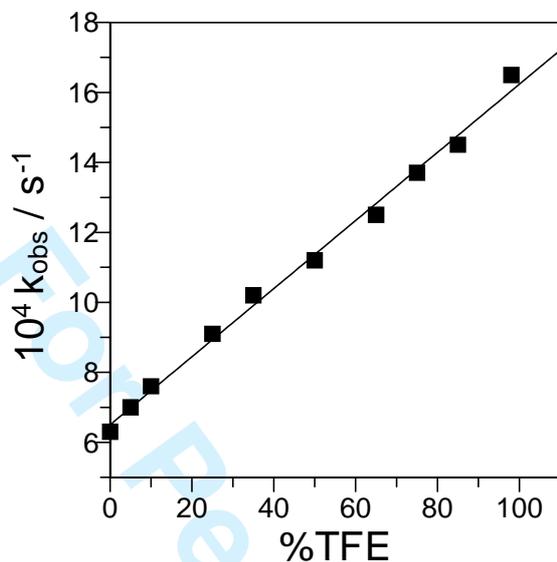
17 **Scheme 3.** Proposed heterolytic (HET)  $\text{D}_\text{N} + \text{A}_\text{N}$  dediazonation mechanism for solvolyses of  
 18 4MBD in TFE. Intimate  $[\text{Ar}^+ \cdot \text{N}_2]$  and solvent separated  $[\text{Ar}^+ \text{N}_2]$  ion-molecule pairs trap any  
 19 nucleophile available in their solvation shells.  
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$-\log[\text{HCl}]$	$10^4 k_{\text{obs}} / \text{s}^{-1}$ (35% TFE)	$10^4 k_{\text{obs}} / \text{s}^{-1}$ (70% TFE)
0.1	$11.2 \pm 0.2$	$12.8 \pm 0.2$
0.3	$11.5 \pm 0.2$	
0.5	$11.2 \pm 0.2$	$13.4 \pm 0.2$
0.7	$11.3 \pm 0.2$	$13.9 \pm 0.2$
0.9	$11.1 \pm 0.2$	$13.5 \pm 0.2$
1.3	$11.8 \pm 0.3$	$13.4 \pm 0.2$
1.7	$11.7 \pm 0.3$	$13.3 \pm 0.2$
2.0	$12.4 \pm 0.4$	$13.2 \pm 0.3$
2.7	$12.1 \pm 0.5$	$14.0 \pm 0.3$
3.3	$11.5 \pm 0.5$	$14.7 \pm 0.3$
4.2	$12.8 \pm 0.5$	$14.5 \pm 0.3$
5.1	$12.8 \pm 0.6$	$15.4 \pm 0.5$

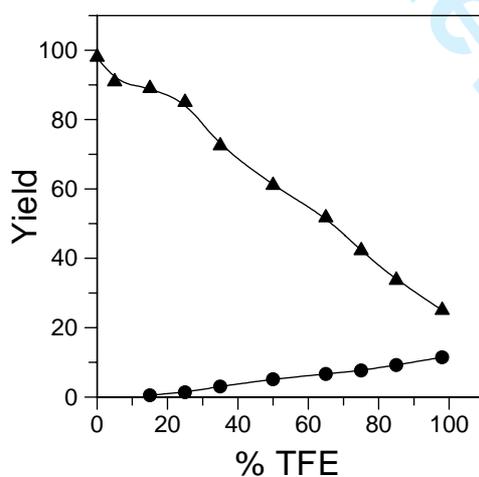
**Table 1.** Influence of  $[\text{HCl}]$  on  $k_{\text{obs}}$  for the decomposition of 4MBD in two selected TFE/ $\text{H}_2\text{O}$  reaction mixtures.  $[\text{4MBD}] = 1.2 \times 10^{-4} \text{ M}$ ,  $T = 50^\circ\text{C}$ .

Solvent	T (°C)	- log[HCl]	$10^4 k_{\text{obs}} / \text{s}^{-1}$ (T = 50)	$E_a$ kJ mol <sup>-1</sup>	$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ J mol <sup>-1</sup> K <sup>-1</sup>	$T\Delta S^\ddagger$ kJ mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>
35% TFE <sup>a</sup>	50 - 60	1	3.2	119 ± 3	114 ± 2	41 ± 7	14	100
70% TFE <sup>a</sup>	50 - 60	1	3.9					
H <sub>2</sub> O <sup>b</sup>	40 - 60	2	2.0	112.4	110	21.6	7	103
99.5% MeOH <sup>b</sup>	40 - 65	2	3.5	114	109	25.6	9	100
98% EtOH <sup>b</sup>	40 - 65	2	4.0	116	114	41	14	102

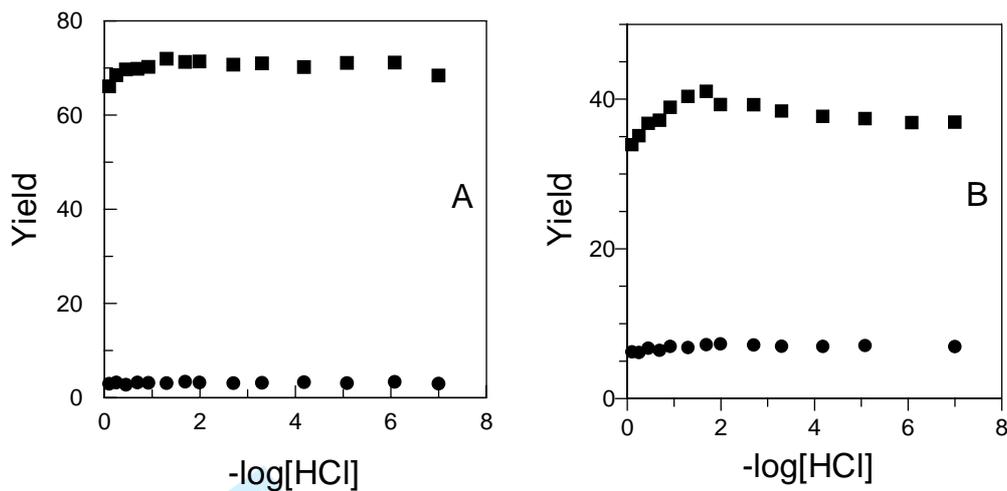
**Table 2.** Estimated activation parameters for the solvolyses of 4MBD in 35% and 70% TFE-H<sub>2</sub>O reaction mixtures. For comparison, literature values in other solvents are included.



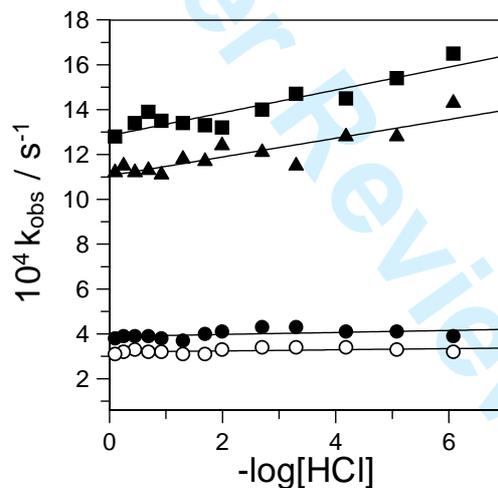
**Figure 1.** Influence of %TFE on  $k_{\text{obs}}$  for dediazonium decomposition of 4MBD. [4MBD] =  $1.2 \times 10^{-4}$  M, T = 50°C and  $-\log[\text{HCl}] = 2$ .



**Figure 2.** Influence of % TFE on the product distribution for the solvolyses of 4MBD in TFE-H<sub>2</sub>O binary mixtures. ▲ 4MBOH, ● 4MBH. [4MBD] =  $1.8 \times 10^{-4}$  M,  $-\log[\text{HCl}] = 2$ , T = 50°C.



**Figure 3.** Influence of [HCl] on the product distribution for the decomposition of 4MBD in A) 35% TFE-H<sub>2</sub>O, B) 70% TFE-H<sub>2</sub>O. ■ 4MBOH, ● 4MBH, [4MBD] =  $1.7 \times 10^{-4}$  M, T = 50°C.



**Figure 4.** Influence of acidity on  $k_{\text{obs}}$  at two selected temperatures for the solvolyses of 4MBD in TFE-H<sub>2</sub>O binary mixtures. ○ 35% TFE, T = 50°C, ● 70% TFE, T = 50°C, ▲ 35% TFE, T = 60°C, ■ 70% TFE, T = 60°C. [4MBD] =  $1.2 \times 10^{-4}$  M.