Formation and Decomposition of Diazo Ethers under Acidic Conditions. Effects of Ethanol Concentration, Acidity, and Temperature on the Ethanolysis of 4-Methylbenzenediazonium Ions

by **Alejandra Fernández-Alonso** and **Carlos Bravo-Díaz***

Universidad de Vigo, Facultad de Química, Dpt. Química Física, ES-36200 Vigo
(phone: +34-986-812303; fax: +34-986-812556; e-mail: cbravo@uvigo.es)

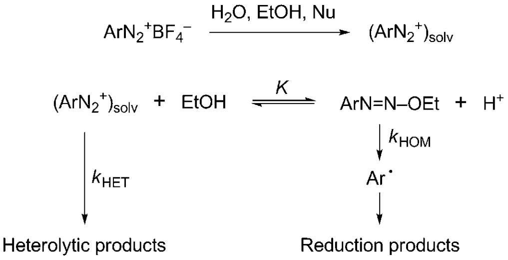
We investigated the effects of solvent composition, acidity, and temperature on the dediazoniation of 4-methylbenzenediazonium (4MBD) ions in EtOH/H_2O mixtures by employing a combination of spectrometric and chromatographic techniques. First-order behavior is found in all solvent composition ranges. HPLC Analyses of the reaction mixtures indicate that three main dediazoniation products are formed depending on the particular experimental conditions. These are 4-cresol (ArOH), 4-phenetole (ArOEt), and toluene (ArH). At acidities (defined as $-\log[\mathrm{HCl}]) < 2$, the main dediazoniation products are the substitution products ArOH and ArOEt but upon decreasing the acidity, the reduction product ArH becomes predominant at the expense of ArOH and ArOEt, indicating that a turnover in the reaction mechanism takes place under acidic conditions. At any given EtOH content, the plot of k_{obs} values against acidity is S-shaped, the inflexion point depending upon the EtOH concentration and the temperature. Similar S-shaped variations are found when plotting the dediazoniation–product distribution against the acidity. The acid dependence of the switch between the homolytic and heterolytic mechanisms suggests that the homolytic dediazoniation proceeds *via* transient diazo ethers, and this complex kinetic behavior can be rationalized by assuming two competitive mechanisms: *i*) the spontaneous heterolytic dediazoniation of 4MBD, and *ii*) an *O*-coupling mechanism in which the EtOH molecules capture ArN_2^+ to yield a highly unstable (*Z*)-adduct which undergoes homolytic fragmentation initiating a radical process (*Scheme*). Analyses of the effects of temperature on the equilibrium constant for the formation of the diazo ether and on the rate of splitting of the diazo ether allowed the estimation of relevant thermodynamic parameters for the formation of diazo ethers derived from methylbenzenediazonium ions under acidic conditions.

Introduction. – Many investigators have sought to determine the mechanisms by which the diazonium group is replaced by a H-atom in solvolytic dediazoniations to yield Ar–H derivatives. It is now accepted that heterolytic dediazoniations mainly take place in solvents of low nucleophilicity such as H_2O, MeOH, or CF_3CH_2OH, whereas homolytic dediazoniations are favored by an increase in the nucleophilicity of the solvent (hexamethylphosphoric triamide (HMPT), pyridine, *etc.*) [1–3]. For a given solvent, electron-withdrawing substituents at the aromatic ring favor homolytic dediazoniations; this is the case, *e.g.*, for the methanolyses of 4-nitro- and 4-bromobenzenediazonium ions under acidic conditions, where the addition of only small amounts of MeOH (10–20% in volume) leads to the almost quantitative formation of reduction products [4][5].

Bunnett and *Yijima* [6][7] concluded, on the basis of kinetic and product-distribution measurements, that in acidic MeOH, dediazoniations take place through competing ionic and radical mechanisms, a conclusion substantiated in subsequent investigations by other researchers [8–11], but they could not find convincing evidence for the nature of the initiation step and hypothesized a direct electron transfer from MeOH to the arenediazonium ion. However, in contrast to other dediazoniations, no obvious reductant is employed to initiate the radical mechanism, and hence the mechanism and nature of the initiation step remains a matter of debate [2][3][8][9] because what is lacking in these cases is a single yet convincing piece of evidence in favor, or against, the different mechanistic alternatives proposed.

In recent solvolytic dediazoniation work under acidic conditions [4][12], we proposed an initiation mechanism based on the formation of a transient diazo ether in a rapid pre-equilibrium step followed by a homolytic bond cleavage that initiates a radical mechanism (*Scheme*). The experimental basis for our proposal was the finding of S-shaped variations in both k_{obs} and product formation with acidity for 4-methylbenzenediazonium (4MBD) [4] and 4-nitrobenzenediazonium (4NBD) ions [4], and the results allowed identification of the dual role played by the ROH molecules as nucleophiles that *i*) simply solvate the diazonium ions (allowing them to undergo thermal heterolytic decomposition), and *ii*) react directly with the arenediazonium ions to yield *O*-coupling adducts in a highly unstable (*Z*)-configuration, *i.e.*, (*Z*)-diazo ethers. On the second route, the (*Z*)-diazo ethers then undergo homolytic fragmentation initiating radical processes [1][3][8][9][11–13]. Moreover, the kinetic investigation of the methanolysis of 4NBD and 4BrBD under acidic conditions provided an excellent example of the influence of solvent composition on the change from a heterolytic mechanism to a homolytic one [4][5].

Scheme. *Proposed Competitive Ionic and Radical Mechanisms for the Reaction of Arenediazonium Ions with Alcohols under Acidic Conditions*



Here, we report an extension of our solvolytic studies by investigating the ethanolysis of 4MBD ions over the whole $EtOH/H_2O$ composition range at different acidities and temperatures. Our aim was to confirm the proposed initiation mechanism and to gain insights into the energetics of diazo ether formation and decomposition. For this purpose, a combination of spectrometric and chromatographic techniques was employed.

Few comparative studies have been made of dediazoniations in MeOH and in EtOH under aqueous acidic conditions [3]. The 4MBD was chosen as a model arenediazonium ion because it is well recognized that substituents in the aromatic ring of diazonium ions have distinct mechanistic effects [8][9][14]. For instance, electron-releasing substituents in *para* position destabilize the parent arenediazonium ions by induction more than they destabilize the aryl cation, and therefore, its spontaneous decomposition is much faster than that of the parent, or of arenediazonium ions bearing electron-withdrawing groups such as NO_2 [10][15]. In addition, electron-releasing substituents in the aromatic ring make the arenediazonium ions less prone to decompose through homolytic pathways as opposed to NO_2. For example, transient diazo ether derivatives were detected in the dediazoniation of 4NBD ions in the presence of β-cyclodextrin [16][17] or antioxidants such as ascorbic acid [18] and methyl gallate [19]; for both nucleophiles, the adducts were detected experimentally and, in some instances, isolated [20].

As we will show, the results obtained for the ethanolysis of 4MBD provide further support for a radical-initiation mechanism *via* formation of a transient diazo ether, $Ar-N{=}N-OEt$, which undergoes homolytic fragmentation yielding an aryl radical ($Ar^{\bullet}$) and the ethoxy radical ($EtO^{\bullet}$). Formation of the *O*-adduct is dependent on the acidity and the ethanol concentration ([EtOH]), but it is independent of the temperature. At $-\log\,[HCl] > 2$, competitive homolytic and heterolytic mechanisms are observed, and the aryl radicals are able to abstract a H-atom from EtOH within the solvent cage leading to the formation of the reduction product $Ar-H$, *i.e.*, toluene. The formation of the *O*-coupling adduct is exothermic, but the large negative entropic term makes the *Gibbs* free energy for the equilibrium formation of the diazo ether to be small but positive at normal temperatures. An increase in the percentage of EtOH in the system increases the *Gibbs* free energy, stressing the opposing effects of [EtOH] as solvent molecules acting either as nucleophiles that simply solvate the diazonium ions (allowing them to undergo thermal heterolytic decomposition) or reacting directly with them to yield *O*-coupling products, as it was previously found in solvolytic dediazoniations. A change in the temperature does seem to have a significant effect on the diazo ether formation, even in reaction mixtures with a high EtOH content.

Results. – 1. *Effects of the Percentage of EtOH on the Rate of Decomposition of 4MBD and on the Product Distribution.* The effects of solvent composition on the observed rate constant, k_{obs}, was investigated by changing the percentage of EtOH in the reaction mixture at different acidities (HCl; $[H_3O^+]$ at least ten times greater than the initial concentrations of substrate). In the absence of EtOH, the thermal decomposition of 4MBD in aqueous acid solution is relatively slow, $k_{obs} = 8 \cdot 10^{-4}\ s^{-1}$ at T 60°, in keeping with literature values, and then increases steadily upon increasing the percentage of EtOH in the reaction mixture (*Fig. 1*), reaching a $k_{obs} \approx 16 \cdot 10^{-4}\ s^{-1}$ at 99% EtOH. HPLC Analyses of the product mixtures indicate (results not shown) that only the substitution products ArOH and ArOEt are formed in substantial amounts, in keeping with previous findings [12].

This remarkable thermal stability and the fact that a large change in [EtOH] has a negligible effect on k_{obs} is consistent with literature reports [3][8][9][11][21] and can be interpreted in terms of a mechanism involving a rate-determining formation of a highly unstable aryl cation which traps any nucleophile available in its solvation shell ($D_N + A_N$ mechanism).

2. *Effects of Acidity on* k_{obs} *and on the Product Distribution.* The effects of acidity on k_{obs} were investigated at two selected percentages of EtOH (*Fig. 2,a*). In both cases, S-shaped profiles were obtained. At 35% $EtOH/H_2O$, k_{obs} increases by a factor of *ca.* 10

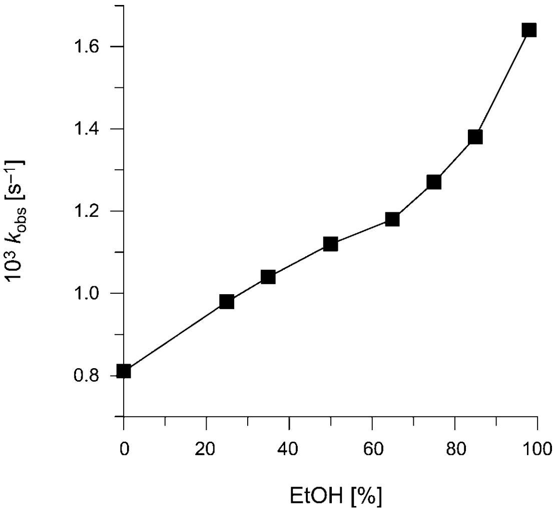


Fig. 1. *Effects of the concentration of EtOH on the observed rate constant for the thermal decomposition of 4MBD.* [4MBD] = 7.5 · 10^{-5} M; – log [HCl] = 1.94; *T* 60°.

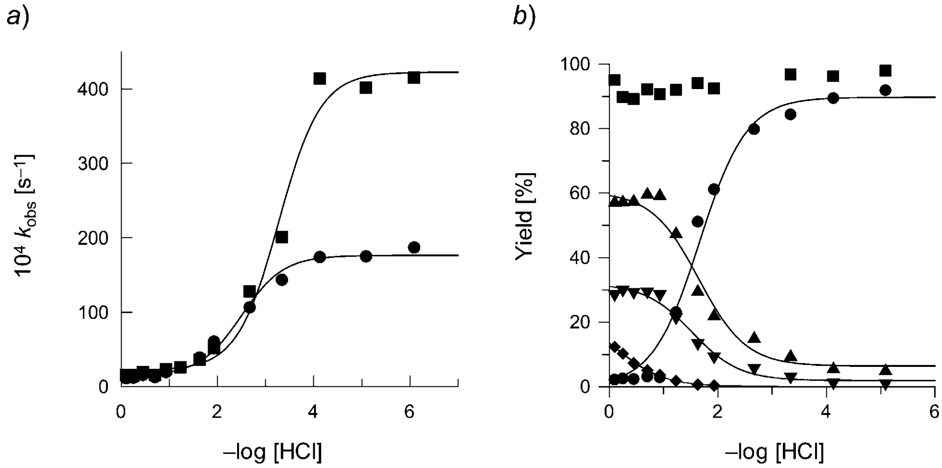


Fig. 2. a) *Effects of acidity on* k_{obs} *for the decomposition of 4MBD in 35%* $EtOH/H_2O$ (●) *and 70%* $EtOH/H_2O$ (■) *and* b) *effects of acidity on the dediazoniation product in 70%* $EtOH/H_2O$ (▲, ArOH; ▼, ArOEt; ◆, ArCl; ●, ArH; ■, total; [4MBD] *ca.* 1 · 10^{-4} M; *T* 60°.

on decreasing the acidity from – log [HCl] = 1–5, while at 70% $EtOH/H_2O$, rate enhancements of *ca.* 40 are obtained for the same changes in acidity. Note that the largest variations of k_{obs} are obtained in the – log [HCl] = 2–4 range compared to those in the 0–2 and 4–7 range, highlighting the crucial role of the acidity in the ethanolyses of 4MBD.

HPLC Analyses of the reaction mixtures indicate that three main dediazoniation products, ArH, ArOH, and ArOEt were formed. Minor amounts of ArCl (from reaction with Cl^- ions) were detected (at high acidities, yields were less than 12%) and total yields were close to 100% in all runs. *Fig. 2,b*, chosen as representative, displays the product distribution at 70% EtOH/H_2O showing S-shaped variations in the yield of a particular analyte with the acidity, illustrating the increase in the yield of the reduction product ArH at the expense of the substitution products ArOEt and ArOH. Note that, at $-\log[HCl] >$ *ca.* 4, the yield of ArH becomes almost constant and that the yields of ArOH and ArOEt are very similar.

The finding of S-shaped kinetic profiles is in keeping with previous findings showing parallel variations of k_{obs} or $t_{1/2}$ with the acidity in the course of solvolytic dediazoniations [4][5][12] and attributed to the formation of transient diazo ether intermediates from the arenediazonium ions which then lead on to the reduction product ArH (*Scheme*).

3. Effects of Temperature on k_{obs} *and on the Product Distribution. Fig. 3,a* and *b*, shows the effects of temperature on k_{obs} for the thermolysis of 4MBD at different acidities in two selected EtOH/H_2O mixtures. Again, S-shaped kinetics are obtained at any temperature and, at a given temperature, the largest variations in k_{obs} are obtained in the $-\log[HCl] = 2-4$ acidity range.

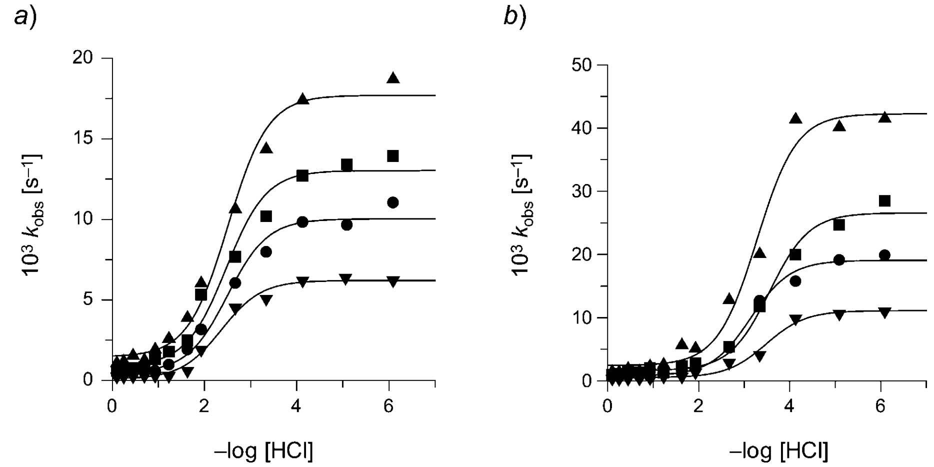


Fig. 3. *Effects of temperature and acidity on* k_{obs} a) *in 35% EtOH/H_2O and* b) *in 70% EtOH/H_2O.* *T* [°] 45 (▼), 50 (●), 55 (■), and 60 (▲); [4MBD] *ca.* $1 \cdot 10^{-4}$ M.

To determine the effect of the temperature on product distribution, the product mixtures obtained in two solvent systems at different acidities were chromatographed after the reaction was complete (*Fig. 4*). At a given temperature, S-shaped variations in the yields are observed on increasing the acidity, and, at a given acidity, temperature does not seem to have a major effect on the product distribution.

Discussion. – S-Shaped variations in k_{obs} with acidities such as those shown in *Figs. 2* and *3* are usually observed in reactions of acid–base pairs where both forms are attainable and show different reactivities [22]. Under our experimental conditions, only two specimens may undergo acid–base processes, the ArN_2^+ ions and EtOH. The pK_a

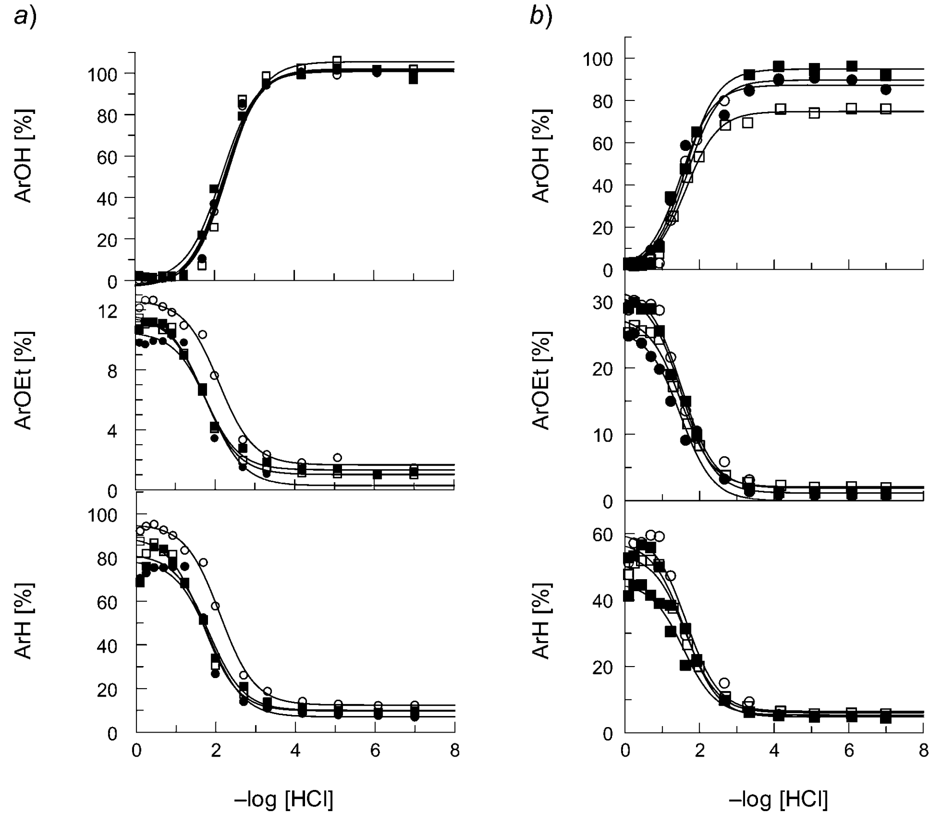


Fig. 4. *Effects of temperature and acidity on the product distribution for ethanolyses of 4MBD in* a) *35% EtOH/H$_2$O and* b) *70% EtOH/H$_2$O. T* [°] 45 (●), 50 (□), 55 (■), and 60 (○).

of EtOH is *ca.* 15, and the pK_a of 4MBD has been reported to be *ca.* 12 [23], so it appears unlikely that, under our experimental conditions, ArN_2^+ ions react with EtO^- or OH^- ions as in alkaline medium [6][7]. We thus propose the reaction mechanism shown in the *Scheme* which hypothesizes two competitive mechanisms: *i*) the thermal decomposition of the solvated ArN_2^+ ions through the heterolytic $D_N + A_N$ mechanism (not shown), and *ii*) the formation of an adduct between ArN_2^+ ions and EtOH in a rapid pre-equilibrium step followed by its rate-determining homolysis, initiating a radical process.

Similar mechanisms have been employed to interpret the reactivity of arenediazonium ions with a number of ascorbic acid derivatives where the formation of a diazo ether intermediate was detected experimentally by employing electrochemical methods [18][24] and for the ethanolysis of 4MBD ions [12] and methanolysis of 4NBD and 4BrBD ions [4]. The assumption of a rate-limiting decomposition of the diazo ether is also consistent with reported results for other *O*-coupling reactions [1][3][25][26], and was probed experimentally in reactions of arenediazonium ions where geometric restrictions apply [16][27].

From the *Scheme*, *Eqn. 1* can be derived where k_{HET} and k_{HOM} are the rate constants for the spontaneous thermal heterolytic decomposition of ArN_2^+ and the decomposition of the diazo ether, respectively, with K standing for the equilibrium constant for the diazo ether formation shown in the *Scheme.*

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{HET}}[\mathrm{H}^+] + k_{\mathrm{HOM}}K[\mathrm{EtOH}]}{K[\mathrm{EtOH}] + [\mathrm{H}^+]} \tag{1}$$

This equation is typical of processes where an S-shaped dependence of k_{obs} with $-\log\,[\mathrm{H}^+]$ is observed (where $[\mathrm{H}^+]$ represents the concentration of protonated solvent molecules). From *Eqn. 1*, and by considering limits, we find that when $[\mathrm{H}^+] \gg K[\mathrm{EtOH}]$, $k_{\mathrm{obs}} \approx k_{\mathrm{HET}}$, *i.e.*, the reaction proceeds wholly through the $D_{\mathrm{N}} + A_{\mathrm{N}}$ mechanism, and only products of heterolysis are obtained. On the other hand, when $[\mathrm{H}^+] \ll K[\mathrm{EtOH}]$, $k_{\mathrm{obs}} \approx k_{\mathrm{HOM}}$, *i.e.*, the reaction proceeds wholly through the diazo ether, and formation of reduction products is favored. The solid lines in *Figs. 2–4* were obtained by fitting the experimental data to *Eqn. 1* by means of a nonlinear least-squares method (provided by the GraFit 5.0.5 computer program), and the average K values obtained are listed in the *Table*. At a given temperature, K values at 70% EtOH/H_2O are lower than those at 35% EtOH/H_2O, in keeping with previous findings [4][5] and confirming that increasing concentrations of EtOH have opposing effects upon the formation of the diazo ether in this concentration range: it is favored modestly by higher concentrations of EtOH through the mass-action effect, but strongly opposed by the medium effect on the equilibrium constant.

Table 1. *Average Values for the Equilibrium Constant* K, *Determined by Fitting the Data in* Figs. 2–4 *to* Eqn. 1, *and Values for the Enthalpy and Entropy of the Formation of the Diazo Ether* (see *Scheme*) *Determined by Means of* Eqns. 2 *and* 3

		T [°]			
		45	50	55	60
35% EtOH/H_2O:	$10^3\,K$	1.0	1.1	1.1	0.9
	ΔH [kJ mol^{-1}]		-0.4		
	ΔS [J mol^{-1} K^{-1}]		-69		
70% EtOH/H_2O:	$10^4\,K$	3.0	3.2	2.7	3.0
	ΔH [kJ mol^{-1}]		-0.3		
	ΔS [J mol^{-1} K^{-1}]		-74		

An increase in the temperature does not seem to have a significant effect on K both at low and high percentages of EtOH, in contrast with the behavior found for arenediazonium ions with electron-withdrawing substituents such as 4BrBD [5]. The analysis of the variation of the K values with the temperature allows to gain some insight into the energetics of diazo ether formation (*Scheme*). *Fig. 5* shows a typical *van't Hoff* plot, according to *Eqn. 2*, illustrating the linear variation found between $-\log K$ and $1/T$ at the two EtOH percentages investigated and from which the enthalpy values shown in the *Table* were determined. Entropic terms, ΔS, determined by

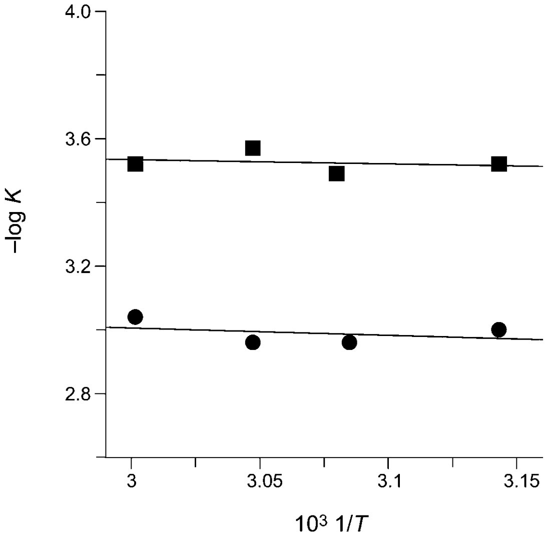


Fig. 5. van't Hoff *Plot according to* Eqn. 2 *for the equilibrium formation of the diazo ether* (*Scheme*). 35% EtOH/H_2O, ●; 70% EtOH/H_2O, ■; data from the *Table.*

employing *Eqn. 3*, are also displayed in the *Table*. Details on the assumptions and limitations on the use of *Eqns. 2* and *3* can be found elsewhere [28].

$$\Delta H = -2.3R\left[\frac{\partial(\log K)}{\partial(1/T)}\right]_P \qquad (2)$$

$$T\Delta S = \Delta H - \Delta G \qquad (3)$$

The data in the *Table* show that ΔH and ΔS are of the same sign, and so work in opposite directions. Formation of the diazo ether is exothermic yet has a positive standard free energy of formation at any of the temperatures investigated. The *Gibbs* free energy ΔG is higher for 70% EtOH/H_2O than for 35% EtOH/H_2O, highlighting the opposing effects of the concentration of EtOH, as it was previously found in solvolytic dediazoniations [4][5].

The analyses of the effects of temperature on k_{HET} (or $t_{1/2}$(HET)) and k_{HOM} (or $t_{1/2}$(HOM)) allowed us to estimate the values for the activation energy of the heterolytic and homolytic pathways (*Fig. 6*). The estimated value for the heterolytic process is in line with those reported in [29], $E_a \approx 100$ kJ mol^{-1}, and those for the decomposition of the diazo ether in 35% EtOH/H_2O ($E_a = 63 \pm 8$ kJ mol^{-1}) and 70% EtOH/H_2O ($E_a = 77 \pm 6$ kJ mol^{-1}) and are similar to each other but substantially lower than that for the heterolytic process [3].

Previous studies on the formation of diazo ethers under alkaline conditions suggest that diazo ethers are initially formed in a highly unstable, kinetically controlled (*Z*)-configuration which then may undergo subsequent isomerization to the thermodynamically stable (*E*)-form, which can be isolated in some instances [20], or, eventually, may

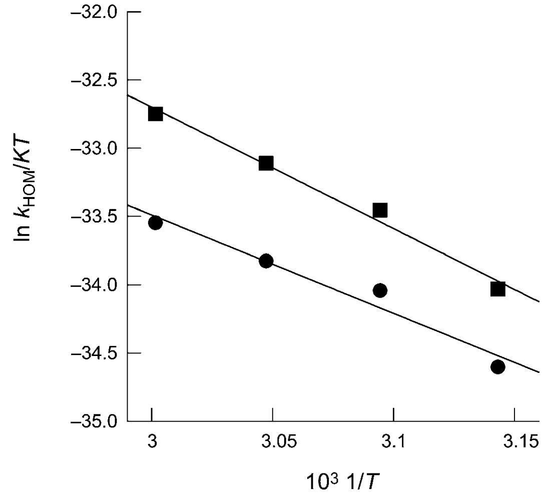


Fig. 6. *Variation of ln* k_{HOM}*, which refers to the fitted values at low acidities* (*see Eqn. 1*) *for the ethanolysis of 4MBD with the reciprocal of the temperature in 35% EtOH/H*$_2$*O* (●) *and 70% EtOH/H*$_2$*O* (■). [4MBD] *ca.* $1.40 \cdot 10^{-4}$ M, $-\log$ [HCl] = 6.0.

give rise to homolytic rupture of the bonds providing the initiation of a radical process [3][18][24][30]. This bond-rotating mechanism to transform the (*Z*)-isomers into the (*E*)-isomers has been recently described for *Sandmeyer* hydroxylations and chlorination reactions [30]. All kinetic and product-distribution evidence suggests, therefore, that, in the present case, there is no conversion of the unstable (*Z*)-diazo ether to the more stable (*E*)-form, which would eventually undergo acid-catalyzed fragmentation [1–3], as it was found for the methanolysis of 4NBD [4].

In conclusion, we have been able to show that the ethanolysis of 4MBD under acidic conditions takes place through two competitive mechanisms where an EtOH molecule may act as a nucleophile by simply solvating 4MBD (allowing it to undergo thermal heterolytic decomposition) or react directly with 4MBD to yield an *O*-coupling adduct which undergoes homolytic fragmentation. The formation of this adduct is favored by decreasing the acidity but suppressed by increasing [EtOH]. A change in the temperature does not have significant effects on the diazo ether formation.

Because large amounts of the reduction product ArH are formed under relatively mild conditions, the results obtained here also indicate a simple, effective, and quick practical method for replacing an aromatic amino group by a H-atom, representing an improved alternative to the method proposed by *Kornblum* and co-workers [31], which uses hypophosphorous acid as reducing agent, or those proposed by us, which use sodium dodecyl sulfate surfactants [32] or *β*-cyclodextrin [16].

Formation of diazo ethers with neutral and anionic nucleophiles in the course of dediazoniations has been described [16][18–20][24][33][34]. In most instances analyzed, the nucleophile must possess a charge, such as OH^-, CN^-, RO^-, or ascorbate ions, and experimental conditions are chosen so that substantial concentrations of the anionic form of the nucleophile are present [3][18][24][30]. However, our results suggest that the formation of (*Z*)-diazo ethers with neutral nucleophiles is much more common than expected, and further investigations to elucidate the role of the solvent, the effects of the substituents at the aromatic ring and those of the experimental conditions (acidity, temperature, electrolytes, *etc.*) on the formation and decomposition of diazo ethers are warranted.

We would like to thank Prof. *H. Maskill* for helpful discussions. Financial support from the following institutions is acknowledged: *Xunta de Galicia* (PGDIT06PXIB314249PR), *Ministerio de Educación y Ciencia* (CTQ2006-13969-BQU), *Fondo Europeo para el Desarrollo Regional* (FEDER), and Universidad de Vigo.

Experimental Part

Instrumentation. UV/VIS Spectra and some kinetics experiments: *Agilent-8453* spectrophotometer equipped with a *Julabo-F12-ED* thermostatted cell carrier and attached to a computer for data storage. HPLC for product analysis: *Waters* HPLC system, including a *W600* pump, a *W717* automatic injector, a *W2487* dual-wavelength detector, and a computer for control and data storage; *Nova Pak* (*Waters*) reversed-phase column (150 mm length, 3.9 mm internal diameter, and 4 μm particle size), mobile phase MeOH/H_2O 50 : 50 containing 10^{-4} M HCl; injection volume 25 μl in all runs, UV detection at 220 and 280 nm.

Material. The 4-methylbenzenediazonium (4MBD) tetrafluoroborate was prepared by employing an anh. method as indicated elsewhere [35], purified three times from MeCN/cold Et_2O, and stored in the dark at low temp. to minimize its decomposition. It was recrystallized periodically. The 4-cresol (=4-methylphenol; ArOH), 4-methylphenetole (=1-ethoxy-4-methylbenzene; ArOEt), 4-chlorotoluene (=1-chloro-4-methylbenzene; ArCl), and toluene (=methylbenzene; ArH) were from *Sigma–Aldrich* and were used without further purification. Other reagents were of maximum-available purity from *Panreac* or *Riedel de Haën*. Soln. composition is expressed as % EtOH by volume. Molar concentrations were calculated by ignoring the small excess volume of mixed solvents [36]. All aq. solns. were prepared with *Milli-Q* grade H_2O.

Methods. Kinetic data were obtained spectrophotometrically and by HPLC. Observed rate constants were obtained by fitting the absorbance–time data for at least three half-lives to the integrated first-order *Eqn. 4* with a nonlinear least-squares method.

$$\ln\left(\frac{M_t - M_\infty}{M_0 - M_\infty}\right) = -k_{\text{obs}}t \tag{4}$$

Duplicate or triplicate experiments gave average deviations less than 10%. Stock 4MBD salt solns. were prepared by dissolving 4MBD in the appropriate acidic (HCl) mixture to minimize diazotate formation [37]. Solns. of final concentrations of *ca.* $1 \cdot 10^{-3}$ M and [HCl] = $3.6 \cdot 10^{-3}$ M were used generally immediately or within 90 min with storage in an ice bath to minimize spontaneous decomposition. *Beer*'s-law plots (not shown) in aq. and EtOH solns. up to $2.00 \cdot 10^{-4}$ M were linear (*cc.* ≥ 0.999). Spectrophotometric kinetic data were obtained by following the disappearance of the absorbance of ArN_2^+ at an appropriate wavelength. Reactions were initiated by adding an aliquot (< 100 μl) of the ArN_2^+ stock soln. to the previously thermostated reaction mixture.

Product analysis of reaction mixtures was performed by HPLC after dediazoniation was complete. Preliminary HPLC experiments showed that three main products are formed, ArOH, ArH, and ArOEt. Linear (*cc.* > 0.999) calibration curves for converting HPLC-peak areas, *A*, into concentrations were obtained for these products by employing commercial samples. Percentage of formation, *Y*, of dediazoniation products were obtained from the dediazoniation-product concentration, $[\text{Analyte}]_\infty$, and the initial diazonium salt concentration, $[ArN_2^+]_o$, estimated by weight, *i.e.*, $Y = 100\,[\text{Analyte}]_\infty/[ArN_2^+]_o$, as described elsewhere [35].

REFERENCES

[1] A. F. Hegarty, 'Kinetics and Mechanisms of Reactions Involving Diazonium and Diazo Groups', in 'The Chemistry of Diazonium and Diazo Compounds', Ed. S. Patai, Wiley & Sons, NY, 1978, Vol. 1.
[2] C. Galli, *Chem. Rev.* **1988**, *88*, 765.
[3] H. Zollinger, 'Diazo Chemistry I, Aromatic and Heteroaromatic Compounds', Vol. 1, VCH, Weinheim, Germany, 1994.
[4] R. Pazo-Llorente, H. Maskill, C. Bravo-Díaz, E. González-Romero, *Eur. J. Org. Chem.* **2006**, 2201.
[5] A. Fernández-Alonso, C. Bravo-Díaz, *Org. Biomol. Chem.* **2008**, *6*, 4004.
[6] J. F. Bunnett, C. Yijima, *J. Org. Chem.* **1977**, *42*, 639.
[7] T. J. Broxton, J. F. Bunnet, C. H. Paik, *J. Org. Chem.* **1977**, *42*, 643.
[8] P. S. J. Canning, H. Maskill, K. McCrudden, B. Sexton, *Bull. Chem. Soc. Jpn.* **2002**, *75*, 789.
[9] P. S. J. Canning, K. McCrudden, H. Maskill, B. Sexton, *J. Chem. Soc., Perkin Trans. 2* **1999**, *12*, 2735.
[10] R. Pazo-Llorente, E. González-Romero, C. Bravo-Díaz, *Int. J. Chem. Kinet.* **2000**, *32*, 210.
[11] R. Pazo-Llorente, C. Bravo-Díaz, E. González-Romero, *Eur. J. Org. Chem.* **2003**, 3421.
[12] R. Pazo-Llorente, C. Bravo-Díaz, E. González-Romero, *Eur. J. Org. Chem.* **2004**, 3221.
[13] A. Chaudhuri, J. A. Loughlin, L. S. Romsted, J. Yao, *J. Am. Chem. Soc.* **1993**, *115*, 8351.
[14] S. J. Canning, K. McCruden, H. Maskill, B. Sexton, *Chem. Commun.* **1998**, 1971.
[15] C. Bravo-Díaz, L. S. Romsted, M. Harbowy, M. E. Romero-Nieto, E. González-Romero, *J. Phys. Org. Chem.* **1999**, *12*, 130.
[16] E. González-Romero, B. Malvido-Hermelo, C. Bravo-Díaz, *Langmuir* **2002**, *18*, 46.
[17] C. Bravo-Díaz, E. González-Romero, *Langmuir* **2005**, *21*, 4888.
[18] U. Costas-Costas, E. González-Romero, C. Bravo Díaz, *Helv. Chim. Acta* **2001**, *84*, 632.
[19] S. Losada-Barreiro, V. Sánchez-Paz, C. Bravo-Díaz, *Helv. Chim. Acta* **2007**, *90*, 1559.
[20] M. P. Doyle, C. L. Nesloney, M. S. Shanklin, C. A. Marsh, K. C. Brown, *J. Org. Chem.* **1989**, *54*, 3785.
[21] L. S. Romsted, 'Interfacial Compositions of Surfactant Assemblies by Chemical Trapping with Arenediazonium Ions: Method and Applications', in 'Reactions and Synthethis in Surfactant Systems', Ed. J. Texter, Marcel Dekker, NY, 2001.
[22] R. G. Wilkins, 'Kinetics and Mechanism of Reactions of Transition Metal Complexes', VCH, New York, 1991.
[23] K. H. Saunders, R. L. M. Allen, 'Aromatic Diazo Compounds', Ed. Edward Arnold, Baltimore, MD, 1985.
[24] U. Costas-Costas, C. Bravo-Díaz, E. González-Romero, *Langmuir* **2004**, *20*, 1631.
[25] W. J. Boyle, T. Broxton, J. F. Bunnett, *Chem. Commun.* **1971**, 1470.
[26] J. F. Bunnett, H. Takayama, *J. Org. Chem.* **1968**, *33*, 1924.
[27] E. González-Romero, B. Fernández-Calvar, C. Bravo-Díaz, *Prog. Colloid Polym. Sci.* **2004**, *123*, 131.
[28] H. Maskill, 'The Physical Basis of Organic Chemistry', V. Oxford University Press, Oxford, 1995.
[29] M. L. Crossley, R. H. Kienle, C. H. Benbrook, *J. Am. Chem. Soc.* **1940**, *62*, 1400.
[30] P. Hanson, J. R. Jones, A. B. Taylor, P. H. Walton, A. W. Timms, *J. Chem. Soc., Perkin Trans. 2* **2002**, 1135.
[31] N. A. Kornblum, G. D. Cooper, J. E. Taylor, *J. Am. Chem. Soc.* **1950**, *72*, 3013.
[32] C. Bravo-Díaz, M. E. Romero-Nieto, E. González-Romero, *Langmuir* **2000**, *16*, 42.
[33] U. Costas-Costas, C. Bravo-Díaz, E. González-Romero, *Langmuir* **2005**, *21*, 10983.
[34] U. Costas-Costas, C. Bravo-Díaz, E. González-Romero, *Langmuir* **2003**, *19*, 5197
[35] M. C. Garcia-Meijide, C. Bravo-Díaz, L. S. Romsted, *Int. J. Chem. Kinet.* **1998**, *30*, 31.
[36] H. Yamamoto, K. Ichikawa, J. Tokunaga, *J. Chem. Eng. Data* **1994**, *39*, 155.
[37] H. Zollinger, C. Wittwer, *Helv. Chim. Acta* **1952**, *35*, 1209.

Received September 7, 2009