Journal of Molecular Liquids xxx (2015) xxx-xxx



Contents lists available at ScienceDirect

### Journal of Molecular Liquids



journal homepage: www.elsevier.com/locate/molliq

# Spectroscopic studies of arenediazonium ion stability in surfactant solutions

### Jolanta Narkiewicz-Michalek<sup>a,\*</sup>, Andrzej Sienkiewicz<sup>a</sup>, Marta Szymula<sup>a</sup>, Carlos Bravo-Diaz<sup>b</sup>

<sup>a</sup> Maria Curie-Sklodowska University, Faculty of Chemistry, 20-031 Lublin, Poland

<sup>b</sup> Departmento de Química-Física, Universidad de Vigo, 36-200 Vigo, Spain

#### ARTICLE INFO

Available online xxxx

*Keywords:* Benzenediazonium ions Surfactants Dediazoniation kinetics

### ABSTRACT

In the article a comparative study of dediazoniation of benzenediazonium, p-bromo- and pmethylbenzenediazonium ions in surfactant solutions is presented. The emphasis is put on the effects of temperature and surfactant type on decomposition. To monitor the kinetics of dediazoniation UV–VIS spectroscopy was employed. The observed rate constants,  $k_{obs}$ , were obtained by fitting the absorbance–time data to the integrated first-order kinetic equation and then the activation energies were obtained from the Arrhenius plot. It was found that temperature is the main factor determining the decomposition rate of arenediazonium ions in aqueous acidic solutions (pH = 1.81). The presence of –Br and –CH<sub>3</sub> groups in the benzene ring makes the ions more stable in comparison with the parent ion, increasing dramatically their half-life times. The effect of surfactant on the dediazoniation was rather small, indicating that in the investigated surfactant concentration range, the effects of surfactant aggregates (single molecules, premicelles and micelles) on the dediazoniation rate constant are small.

© 2015 Elsevier B.V. All rights reserved.

#### 1. Introduction

Arenediazonium salts,  $ArN_{2}^{+}X^{-}$ , constitute an important class of organic compounds because of a wide variety of chemical processes that they may undergo just by making slight changes in the reaction conditions. One of the current applications exploits the unique characteristics of the reactions between  $ArN_{2}^{+}$  ions and weakly basic nucleophiles (e.g., antioxidants) to probe their localization in the colloidal systems (foods, cosmetic and pharmaceutical formulations) [1–3]. One important limiting factor in the application of  $ArN_{2}^{+}$  for quantitative investigations of a variety of chemical processes is their stability.

Reactions of arenediazonium ions,  $ArN_2^+$ , were among the first to be studied mechanistically [4]. In 1940, Hammett [5] postulated a slow unimolecular heterolytic dissociation of arenediazonium ions into aryl cations and N<sub>2</sub>, and experimental support was provided [6]. The studies of these important reactions were continued by Zollinger [4,7,8] and other investigators [9–12].

Dediazoniations of aromatic diazonium ions can proceed through a number of mechanisms leading to a wide range of products [2,4]. They can take place via both spontaneous, (for example the Griess-Schiemann), and catalysed, (for example the Sandmeyer), reactions. They are believed to occur by either heterolytic (A), or, in the presence of an electron donor, homolytic (B) pathways.

http://dx.doi.org/10.1016/j.molliq.2015.04.002 0167-7322/© 2015 Elsevier B.V. All rights reserved. In the absence of catalysts, with weakly basic nucleophiles, in aqueous acid and in the dark, dediazoniations mostly proceed via rate determining loss of N<sub>2</sub>, generating a highly reactive phenyl cation that reacts rapidly, with very low selectivity with available nucleophiles [4,16]. In nonaqueous solvents, products associated with free radicals, for example, biphenyl derivatives and replacement of N<sub>2</sub><sup>+</sup> by H are often observed, especially when electron-withdrawing groups are present on the arenediazonium ion [4,17–21].

In this context heterolytic dediazoniation has been reported to occur with ortho-, meta- and para-methylbenzenediazonium (2MBD, 3MBD, 4MBD) and para-nitrobenzenediazonium (4NBD) ions in an aqueous medium [10,22], while other authors interpreted their results as showing evidence of heterolytic and homolytic processes during the thermal and photochemical dediazoniation of several arenediazonium ions in trifluoroethanol and ethanol [19–21]. However, in our latest article, we demonstrated that, at moderate pH, water can act as nucleophile giving rise to a diazohydroxide, which eventually can decompose to give radical products [23].

Therefore, it is obvious that reaction conditions need to be chosen carefully when trying to establish the mechanisms involved in the decomposition of such versatile compounds as arenediazonium ions. There are many factors influencing the arenediazonium ion decomposition. Besides its molecular structure, the most important are temperature, exposure to light, type and location of substituents in the benzene ring, the presence of catalysts and nucleophiles in the system. The character of microenvironment (its polarity, acidity, ionic strength,

<sup>\*</sup> Corresponding author. *E-mail address:* jolanta.narkiewicz-michałek@umcs.lublin.pl (J. Narkiewicz-Michałek).

J. Narkiewicz-Michalek et al. / Journal of Molecular Liquids xxx (2015) xxx-xxx



Scheme 1. Three types of reactions common for arenediazonium ions: A – heterolytic loss of dinitrogen in the presence of weakly basic nucleophiles, B – homolytic displacement of nitrogen by electron transfer from a donor molecule, C – addition to the terminal nitrogen by strongly basic nucleophiles [2].

etc.) as well as the presence of surfactant aggregates are also of some importance [13–15,24,25].

Determination of micellar interfacial layer composition is difficult because this layer cannot be physically isolated and analysed separately. Romsted et al. [26] have devised a novel method of determining concentrations of various nucleophiles (e.g., water, halide ions, alcohols, antioxidants) at the aggregate interface using arenediazonium ions.

Product yields from the reaction of weakly basic ions and molecules with arenediazonium ions – at least one of the reagents should be aggregate bound – are proportional to the concentrations of ions and molecules at the aggregate interface. In some cases the spontaneous loss of nitrogen by arenediazonium ions can make the application of the proposed method impossible. That is why the reaction conditions should be appropriately chosen and controlled.

Micelles are likely to affect dediazoniation reactions in two essential ways; first by governing their contact with other substrates incorporated in the micelle, with water or with ions present as counter ions in the micellar Stern layer; second by governing the polarity of their immediate environment which can be decisive for unimolecular decomposition reactions. Full understanding of the behaviour of  $ArN_2^+$  requires the knowledge of their location in the micelle since substrate reactivity depends largely on the microenvironment of the reaction and the extent of its penetration into the aggregate. Electrostatic considerations lead one to presume that the most hydrophilic arenediazonium ions will be mainly located in the bulk aqueous phase in cationic micellar systems; meanwhile they will be located close to the micellar aggregates in the anionic and nonionic systems. Hydrophobic arenediazonium ions are expected to be associated to the aggregate either in nonionic or ionic systems.

The purpose of our studies was to investigate the influence of temperature and surfactant type on the kinetics of three arenediazonium salts decomposition (benzenediazonium (BD), 4methylbenzenediazonium (4MBD) and 4-bromobenzenediazonium



Fig. 1. The decrease of absorbance of BD in time,  $\lambda_{max}=262$  nm, pH = 1.8, T = 60 °C. The dashed line denotes the absorption spectrum for phenol.

(4BRBD) tetrafluoroborates) in order to establish the best conditions of their use in the colloidal system structure investigations.

#### 2. Experimental

#### 2.1. Materials

Reagents were of maximum available purity and were used without further purification. HCl and NaOH, the materials employed in the preparation of the Britton–Robinson buffer and arenediazonium tetrafluoroborates,  $ArN_2^+$  BF<sub>4</sub><sup>-</sup>, were from Fluka or Aldrich. Benzenediazonium ions, BD, and the substituted 4-methyl-, 4MBD, and 4-bromo, 4BrBD, benzenediazonium ions were prepared from the corresponding anilines (Sigma, Fluka) following a standard non-aqueous procedure as described elsewhere [22]. Britton–Robison buffer of the desired pH was prepared by mixing solutions of 0.04 M acetic, boric and ortophosphoric acids with the appropriate amounts of 0.2 M NaOH to get the desired pH. Stock  $ArN_2^+$  BF<sub>4</sub><sup>-</sup> solutions were kept in the dark at low temperature to minimize its decomposition. The purity of  $ArN_2^+$  was checked periodically by employing UV–VIS spectroscopy.

The surfactants used were: sodium dodecyl sulphate, (SDS), hexadecyltrimethylammonium bromide (CTAB) and t-octyl phenoxy polyethoxyethanol (TRITON X-100) all Fluka Chemie Ag and RdH Laborchemicalien GmbH & Co. K production. All solutions were made with Milli-Q grade water. The CMC values in the Britton–Robinson buffer solution, pH = 1.81, determined by surface tension measurements were: 0.003 M for SDS, 0.0004 M for CTAB and 0.00013 M for TX-100.



Fig. 2. BD, 4MBD and 4BrBD decomposition in the buffered aqueous solution (pH = 1.81) at 60  $^\circ\text{C}.$ 

2

J. Narkiewicz-Michalek et al. / Journal of Molecular Liquids xxx (2015) xxx-xxx



Fig. 3. 4MBD decomposition in the buffered aqueous solution (pH = 1.81) in various temperatures.

#### 2.2. Method

The kinetics of arenediazonium ion decomposition was determined by ultraviolet spectroscopy using Specord 200, Analityk Jena, Germany, double-beam spectrophotometer. Stoppered quartz cells with an optical path length of 1.00 cm were used. In all experiments the ArN<sub>2</sub><sup>+</sup> concentration was  $1 \cdot 10^{-4}$  M. The initial absorbance value of solution was in the region of spectrometer linearity. All measurements were performed in thermostated and buffered (pH = 1.81) solutions. They were prepared just before the measurement by adding appropriate amount of arenediazonium salt to the equilibrated surfactant solution. The spectra were recorded at regular time intervals to monitor the decomposition kinetics of arenediazonium ions.

### 3. Results and discussion

Kinetic data were obtained spectrometrically by monitoring the disappearance of the absorbance of ArN<sup>+</sup><sub>2</sub> in an appropriate wavelength Table 1

Values of rate constants,  $k_{obs}$ , and half-life times,  $t_{1/2}$ , for BD, 4MBD and 4BrBD decomposition reaction.

T/°C	BD		4MBD		4BrBD	
	$k_{obs} \cdot 10^5 / \mathrm{s}^{-1}$	$t_{1/2}/h$	$k_{obs} \cdot 10^5 / s^{-1}$	$t_{1/2}/h$	$k_{obs} \cdot 10^5 / s^{-1}$	<i>t</i> <sub>1/2</sub> /h
22			0.38	50.23		
30			0.87	22.22		
40	58.00	0.33	4.17	4.62	0.22	88.87
50	201.00	0.10	19.00	1.01	1.00	19.25
60	739.00	0.03	68.00	0.28	4.50	4.28

range (240–400 nm). The exemplary spectra recorded for BD in a long time interval are shown in Fig. 1. The spectra for substituted ions (not shown) behaved similarly, i.e., they decreased in time to very low absorbance values. As shown in Fig. 1 the final spectrum for BD decomposition is almost the same as for phenol. It means that the reaction occurs according to the heterolytic mechanism and phenol is its sole product. It follows from literature [10,24,25] that the other two arenediazonium ions decompose according to the same heterolytic mechanism. The absorbances of decomposition products (p-cresol and p-bromophenol respectively) at the characteristic wavelength (278 nm for 4MBD and 292 nm for 4BrBD) are very low in comparison with those of parent arenediazonium ions.

Of the three investigated arenediazonium ions, BD appeared to be the least stable (Fig. 2). Decomposition of the other two ions 4MBD and 4BrBD was much slower, indicating the stabilizing effect of  $CH_3^-$  and  $Br^-$  substituents.

Electronic substituent effects [27] can be classified into those associated with their polarity (inductive field) and those associated with their ability to transfer charge (resonance). The methyl group has an electrodonating character and in 4MBD ion the aromatic ring, which separates the methyl group and the electron-deficient site, enables direct resonance interaction between these groups through the  $\pi$ -system (hyperconjugation). Such a direct resonance interaction is possible only when the groups are in the para position [10].

Contrary to the methyl group, the Br<sup>-</sup> group in the 4 position withdraws electrons by induction through the  $\sigma$  bonds but has an electron donating capability through the resonance. Such behaviour contrasts with other electron-withdrawing groups such for example 4-NO<sub>2</sub>, which has no electron donating capability. The electron-withdrawing Br<sup>-</sup> substituent in the 4-position destabilizes the aryl cation by induction more than it destabilizes the parent arenediazonium ion, and therefore its spontaneous decomposition reaction is much slower than that of



Fig. 4. A. Arrhenius plots (Eq. (2)) from which the activation energies E<sub>a</sub> for arenediazonium ion decomposition reaction were determined. B. Plots (Eq. (3)) from which the activation enthalpies and entropies of arenediazonium ion decomposition were estimated.

J. Narkiewicz-Michalek et al. / Journal of Molecular Liquids xxx (2015) xxx-xxx

**Table 2** The activation parameters of dediazoniations found from Eqs. (3) and (4).

$ArN_2^+$	lnA	E <sub>a</sub> (kJ/mol)	$\Delta S^{\#} \left(J  K^{-1}  mol^{-1}\right)$	$\Delta H^{\#}$ (kJ mol <sup>-1</sup> )		
BD	34.9	110.2	35.7	107.5		
4MBD	37.1	122.9	130.0	113.8		
4BrBD	37.4	131.4	57.3	128.7		

BD ion, or of arenediazonium ion bearing the electron-releasing  $CH_3^-$  group [11].

The next factor influencing the dediazoniation reaction, investigated by us is temperature. As follows from Fig. 3 4MBD decomposition becomes significantly faster when the temperature increases from 22 to 60 °C. The effect is similar for 4BrBD and BD ions.

Solid lines in Figs. 2 and 3 represent the first order kinetics plotted according to the equation:

$$C(t) = C_0 e^{-k_{obs}t} \tag{1}$$

where:  $C_0$  is the initial concentration of ArN<sub>2</sub><sup>+</sup>, *C* is its concentration after time *t* and  $k_{obs}$  is the temperature dependent rate constant.

Using Eq. (1) and the non-linear fitting procedure we determined the observed rate constants and half-life times at different temperatures. They are collected in Table 1.

One can see that the substituted ions decompose slowly in comparison with BD. For example the half-life times for 4MBD and 4BrBD are about ten and two hundred times higher than for BD, respectively. The obtained results are in accordance with literature data [6,10,17,19,22].

Knowing the rate constants at different temperatures, we were able to determine experimental activation parameters. Fig. 4A shows the corresponding Arrhenius plots:

$$\ln k_{obs} = \ln A - \frac{E_a}{R} \frac{1}{T}$$
<sup>(2)</sup>

where  $E_a$  is an activation energy, A is a pre-exponential factor and R is the gas constant.

The activation enthalpies and entropies were obtained according to the absolute rate theory by means of Eq. (3) (Fig. 4B):

$$\ln\left(\frac{hk_{obs}}{k_{B}T}\right) = \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{R}\frac{1}{T}$$
(3)

where k<sub>B</sub> and h are the Boltzmann and Planck constants, respectively.

Table 2 shows the obtained activation energies and activation parameters. The activation energies for the substituted  $ArN_2^+$  ions are higher than for BD, being in agreement with their greater stability. The pre-exponential factor for BD is smaller than the pre-exponential factors for 4MBD and 4BrBD which have approximately the same values.

The values of  $\Delta H^{\#}$  are positive and relatively high compared with those for bimolecular reactions, and the entropic terms are also meaningfully positive [27]. These values contrast with those usually found for bimolecular reactions, which are substantially lower because breaking of old bonds, which requires energy, and formation of new ones, which releases energy are usually synchronous [28]. Thus,  $\Delta H^{\#}$  values from Table 2 suggest a transition state that has undergone bond breaking which is partly compensated by bond formation.

Dediazoniation, as described in Scheme 1A, suggests that formation of the aryl cation does not involve separation of charge but its redistribution; thus, the parent arenediazonium ion and the aryl cation polarize the solvent to a similar extent; therefore, the gain of entropy is not compensated and dediazoniations show relatively high  $\Delta G^{\#}$  values, indicating slight solvent dependence [4]. Positive  $\Delta S^{\#}$  values, as we have found, suggest that the transition state has a greater structural freedom than the reactants. On the other hand, because  $\Delta S^{\#}$  values are positive, they compensate the large enthalpy term, making dediazoniations proceed at a considerable rate [4,29-31]. Substituents in the aromatic ring have a marked effect on the stability of arenediazonium ions [4]. As shown in Table 2, the methyl group in the para position is rate retarding compared with the value for the benzenediazonium ion. The same effect is observed for the Br<sup>-</sup> group.

The next part of our study concerns the investigation of inhibiting or promoting effects of surfactant micelles on the rate of decomposition of the investigated ArN<sub>2</sub><sup>+</sup> ions. Diazonium ions have proved to be very sensitive to their environment, [1,14,22,23] and thus proper understanding of their behaviour in the micellar systems is of great importance [14–16, 24,25]. Hydrophobicity of arenediazonium ion and charge of the micelle are believed to be the most important factors affecting the localization of ions in the micellar system. Positively charged hydrophilic arenediazonium ions do not associate with cationic micelles [32] whereas they are incorporated into negatively charged SDS micelles and their preferential location is very close to the micellar surface. At the same time no evidence of tight ion-pairs formation between diazonium ions and anionic micelles was found [24]. One could expect similar weak interactions of arenediazonium ions with nonionic micelles. According to the Pseudophase Model [33], the observed rate constant is given by Eq. (4).

$$k_{obs} = \frac{k_w + k_M \cdot K_S \cdot [M]}{1 + K_S \cdot [M]} \tag{4}$$

where:  $K_S$  is the association constant, [M] is the molar concentration of surfactant in the micelles, and the subscripts W and M refer to the aqueous and micellar pseudophases.

There are numerous methods of determining the association constant  $K_S$  [24,25]. Among them, the UV–VIS spectroscopy is very popular. By fitting Eq. (4) to the obtained pairs of data ( $k_{obs}$  and [M])  $K_S$  and  $k_M$ values can be estimated. However, in the case of our systems such an approach cannot be used. Firstly, because at low temperatures (20– 30 °C) kinetics is very slow (especially for 4MBD and 4BrBD) and thus the reliable estimation of  $k_{obs}$  from experimental kinetic data is difficult. Secondly, because at the highest temperature (60 °C) investigated by us, the shift in absorbance due to the presence of 0.01 M SDS is very small at least for BD and 4MBD ions (Figs. 5 and 6). The changes in absorbance due to the presence of SDS are evident only in the case of 4BrBD (Fig. 7). The SDS micelles have a stabilizing effect and the dediazoniation process becomes slower.



Fig. 5. BD decomposition in time for various SDS concentrations; pH = 1.81, T = 60 °C.

4

J. Narkiewicz-Michalek et al. / Journal of Molecular Liquids xxx (2015) xxx-xxx





Fig. 6. 4MBD decomposition in time for various SDS concentrations; pH = 1.81, T = 60 °C.

At room temperature (T = 22 °C), when the reaction is slow, the effect of surfactant is more distinct. In Fig. 8 the kinetic curves for 4MBD decomposition in the aqueous SDS solutions are shown. When small amounts of surfactant are added to the solution, the dediazoniation reaction becomes faster, then on further increasing surfactant concentration, the process slows down and at the concentrations exceeding the CMC it becomes even slower than in the absence of SDS. For CTAB and TX-100 the similar behaviour was observed but the effect of slowing down of the decomposition reaction near the CMC was less visible.

In Fig. 9 the plots of  $k_{obs}$  vs. surfactant concentration are presented for 4MBD in the TX-100, CTAB and SDS solutions at T = 22 °C and 60 °C. As can be expected the higher temperature the higher values of  $k_{obs}$ . At the lower temperature a maximum of rate constants is observed in the vicinity of CMC and than  $k_{obs}$  decreases to the value characteristic for the aqueous solution without surfactant or even lower in the case of

Fig. 8. 4MBD decomposition in time for various SDS concentrations; pH = 1.81, T = 22 °C.

SDS. The analogical effect of surfactant concentration we observed for ascorbic acid oxidation in the solutions of anionic, cationic and nonionic surfactants [34]. Irrespective of the surfactant head group charge, the effect was highest in the vicinity of CMC.

The observed effect of low surfactant concentration on the arenediazonium ions decomposition is unexpected and for the time being we cannot propose a simple explanation. In the case of cationic and nonionic surfactant molecules the interaction with positively charged arenediazonium ions is weak. In the case of negatively charged SDS one could expect electrostatic attraction but as follows from conductivity measurements [24], the arenediazonium ions employed in this work do not form ion pairs with SDS.

We are not aware of any literature report discussing the changes in the values of dediazoniation rate constants at low surfactant concentrations. In our opinion, the observation needs more attention and further studies are currently carried out and will be part of future reports.



Fig. 7. 4BrBD decomposition in time for various SDS concentrations; pH = 1.81, T = 60 °C.



**Fig. 9.** 4MBD decomposition in time for various TX-100, CTAB and SDS concentrations; pH = 1.81, (-) T = 22 °C and (- - -) T = 60 °C.

#### 6

# **ARTICLE IN PRESS**

#### J. Narkiewicz-Michalek et al. / Journal of Molecular Liquids xxx (2015) xxx-xxx

### 3.1. Conclusions

Analysis of the obtained results led us to the conclusion that dediazoniations in the acidic aqueous solutions (pH < 2) and in the acidic solutions containing surfactants proceed via heterolytic mechanism, i.e., the rate-determining formation of a very reactive aryl cation that traps weakly basic nucleophiles competitively. The final absorption spectra of the investigated ions corresponded to the products of heterolytic dediazoniation. This conclusion is in accordance with the earlier results showing that no products associated with radical pathways (like toluene or biphenyls) are formed under the aqueous acidic conditions. The substituted arenediazonium ions are more stable and at room temperature they have enough high half-life times to be safely used in the studies of O-coupling reactions in the colloidal systems.

Surfactants have rather weak influence on the dediazoniation kinetics. The noticeable effect is observed only at premicellar surfactant concentrations.

### References

- [1] L.S. Romsted, Langmuir 23 (2007) 414–424.
- [2] L.S. Romsted, in: J. Texter (Ed.), Reactions and Synthesis in Surfactant Systems, Marcel-Dekker, NY, 2001.
- [3] C. Bravo-Díaz, E. González-Romero, Current Topics in Colloid & Interface Science, vol. 4, 2001 ISSN 0972–4494, Trivandum, India.
- [4] H. Zollinger, Diazo Chemistry I, Aromatic and Heteroaromatic Compounds, VCH, Wein, 1994.
- [5] L.P. Hammett, Physical Organic Chemistry, McGraw Hill, New York, 1940. 295.
- [6] M.L. Crossley, R.H. Kienhle, C.H. Benbrook, J. Am. Chem. Soc. 62 (1940) 1400–1404.
- P. Burri, G.H. Wahl, H. Zollinger, Helv. Chim. Acta 57 (1974) 2099–2105;
   M.D. Ravenscroft, P. Skrabal, B. Weiss, H. Zollinger, Helv. Chim. Acta 71 (1988) 515–520.
- [8] H. Nakazumi, T. Kitao, H. Zollinger, J. Org. Chem. 52 (1987) 2825–2830;
   R. Glaser, C.J. Horan, M. Lewis, H. Zollinger, J. Org. Chem. 64 (1999) 902–913.
- [9] B.C. Gilbert, P. Hanson, J.R. Jones, A.C. Whitwood, A.W. Timms, J. Chem. Soc. Perkin Trans. 2 (1992) 629–636.

- [10] R. Pazo-Llorente, M.J. Sarabia-Rodriguez, C. Bravo-Díaz, E. Gonzalez-Romero, Int. J. Chem. Kinet. 31 (1999) 73–82.
- [11] C. Bravo-Díaz, L.S. Romsted, M. Harbowy, M.E. Romero-Nieto, E. Gonzalez-Romero, J. Phys. Org. Chem. 12 (1999) 130–140.
- [12] C. Bravo-Díaz, M.J. Sarabia-Rodriguez, P. Barreiro-Sio, E. Gonzalez-Romero, Langmuir 15 (1999) 2823–2828.
- [13] K.H. Saunders, R.L.M. Allen, Aromatic Diazo Compounds, 3rd ed. Edward Arnold, London, 1985.
- [14] A. Fernandez-Alonso, C. Bravo-Diaz, Helv. Chim. Acta 90 (2007) 1141–1151.
- [15] C. Bravo-Diaz, M. Pastoriza-Gallego, S. Losada-Barreiro, V. Sanchez-Paz, A. Fernandez-Alonso, Int. J. Chem. Kinet. 40 (2008) 301–309.
- [16] R. Pazo-Lorente, M.C. Rodriguez-Menacho, E. Gonzales-Romero, C. Bravo-Diaz, J. Colloid Interface Sci. 248 (2002) 169–175.
- [17] P.S.J. Canning, K. McCrudden, H. Maskill, B. Sexton, J. Chem. Soc. Perkin Trans. 2 (1999) 2735–2740.
- [18] A. Fernandez-Alonso, C. Bravo-Diaz, J. Phys. Org. Chem. 23 (2010) 938-943.
- [19] R. Pazo-Llorente, C. Bravo-Diaz, E. Gonzalez-Romero, Eur. J. Org. Chem. (2003) 3421–3428.
   [20] P. Berdelli, E. G. Dian, F. G. Dian, J. C. Barto, J. Barto, J. C. Barto, J. C. Barto, J. C. Barto, J. Barto, J. C. Barto, J. Barto, J
- [20] R. Pazo-Llorente, C. Bravo-Diaz, E. Gonzalez-Romero, Eur. J. Org. Chem. (2004) 3221–3226.
- [21] A. Fernandez-Alonso, C. Bravo-Diaz, Org. Biomol. Chem. 6 (2008) 4004–4011.
- [22] M.C. Garcia-Meijide, C. Bravo-Diaz, L.S. Romsted, Int. J. Chem. Kinet. 30 (1998) 31–39.
- [23] A. Sienkiewicz, M. Szymula, J. Narkiewicz-Michalek, C. Bravo-Diaz, J. Phys. Org. Chem. 27 (2014) 284–289.
- [24] C. Bravo-Diaz, M. Soengas-Fernandez, M. Jose Rodriguez-Sarabia, E. Gonzalez-Romero, Langmuir 14 (1998) 5098–5105.
- [25] E. Gonzalez-Romero, M.B. Fernandez-Calvar, C. Bravo-Diaz, Langmuir 18 (2002) 10311-10317.
- [26] L.S. Romsted, C. Bravo-Díaz, Curr. Opin. Colloid Interface Sci. 18 (2013) 3-14.
- 27] R. Glaser, C.J. Horan, H. Zollinger, Angew. Chem. Int. Ed. Engl. 36 (1997) 2210–2213.
- [28] H. Maskill, The Physical Basis of Organic Chemistry, Oxford University Press, Oxford, 1995.
- [29] K. Ishida, N. Kobori, M. Kobayashi, H. Minato, Bull. Chem. Soc. Jpn. 43 (1970) 285–286.
- [30] T. Kuokkanen, Finn. Chem. Lett. (1981) 52.
- [31] T. Kuokkanen, Finn. Chem. Lett. (1981) 81.
- [32] I.M. Cuccovia, M.A. da Silva, H.M.C. Ferraz, J.R. Pliego Jr., J.M. Riveros, H. Chaimovich, J. Chem. Soc. Perkin Trans. 2 (2000) 1896–1907.
- [33] C.A. Bunton, F. Nome, F.H. Quina, L.S. Romsted, Acc. Chem. Res. 24 (1991) 357–364.
- [34] M. Szymula, J. Narkiewicz-Michalek, Colloid Polym. Sci. 281 (2003) 1142–1148.