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Spectroscopic studies of arenediazonium ion stability in surfactant solutions

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ABSTRACT

In the article a comparative study of dediazoniation of benzenediazonium, p-bromo- and p-methylbenzenediazonium 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 $–CH_3$ 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.

1. Introduction

Arenediazonium salts, $ArN^{+}{}_2X^{-}$, 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_2, 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.

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_2, 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_2^+ 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,

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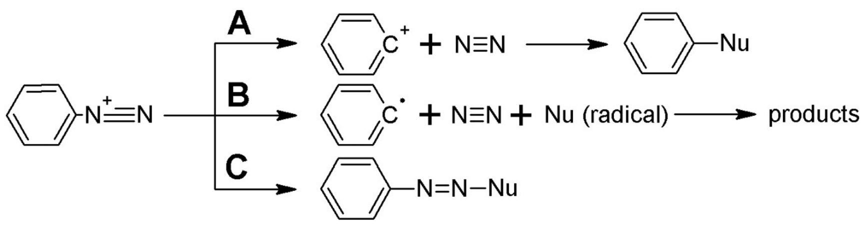

Scheme 1. Three types of reactions common for arenediazonium ions: A — heterolytic loss of dinitrogen in the presence of weakly basic nucleophiles, B — homolytic displacement of nitrogen by electron transfer from a donor molecule, C — addition to the terminal nitrogen by strongly basic nucleophiles [2].

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), 4-methylbenzenediazonium (4MBD) and 4-bromobenzenediazonium (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, $ArN_2^+\ BF_4^-$, 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 $ArN_2^+\ BF_4^-$ 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.

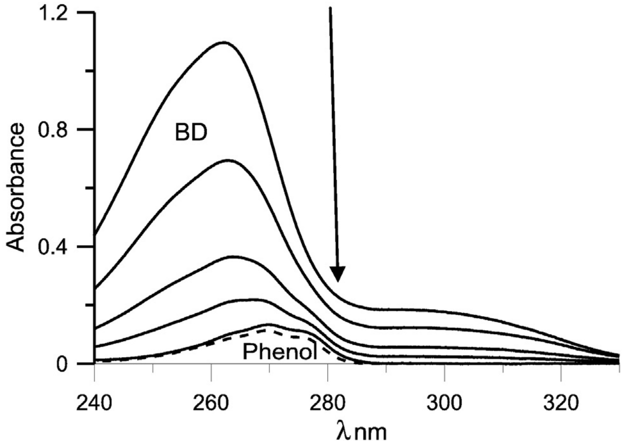

Fig. 1. The decrease of absorbance of BD in time, $\lambda_{max} = 262$ nm, pH = 1.8, T = 60 °C. The dashed line denotes the absorption spectrum for phenol.

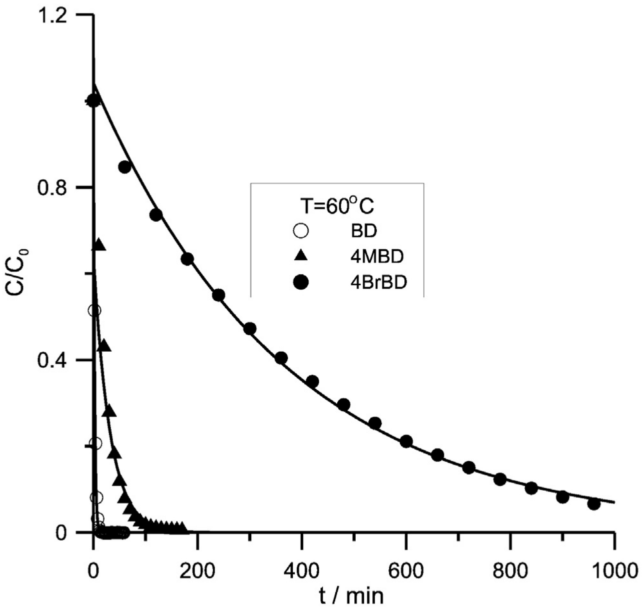

Fig. 2. BD, 4MBD and 4BrBD decomposition in the buffered aqueous solution (pH = 1.81) at 60 °C.

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