

DIAZONIUM SALTS IN PHOTOCHEMISTRY II: SCAVENGING OF NORRISH TYPE II BIRADICALS

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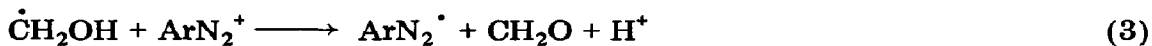
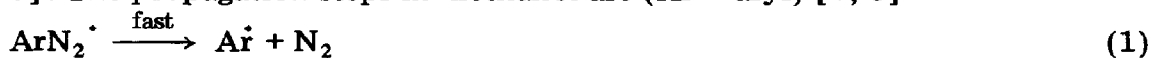
Summary

Diazonium salts are excellent scavengers of Norrish type II biradicals; the process triggers the free-radical loss of molecular nitrogen. For example, the biradical from γ -methylvalerophenone reacts with benzenediazonium tetrafluoroborate with a rate constant of $(3.3 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in methanol at 27 °C.

1. Introduction

The main reactions of diazonium salts frequently involve the loss of molecular nitrogen in a process usually called dediazonation [1, 2]. The reaction can occur by heterolytic or homolytic mechanisms; the products of the reaction are usually indicative of the predominant reaction path [2, 3].

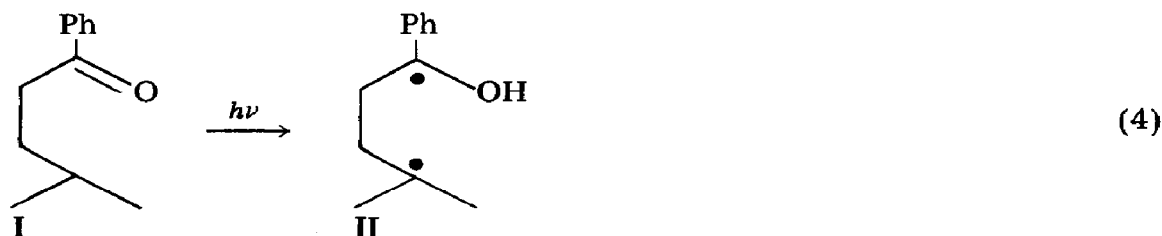
Homolytic processes can be driven by thermal or photochemical initiation, and in alcohol solvents frequently involve chain reactions [2, 4, 5]. The propagation steps in methanol are (Ar \equiv aryl) [4, 6]



While it is fair to say that the mechanism of reactions (1) - (3) is now well established, the kinetics of the key elementary step, *i.e.* reaction (3), have received only limited attention. In fact the only two studies of which we are aware [5, 7] were published while this paper was in preparation. One study reports the kinetics of the reactions of semiquinone radicals with diazonium salts [5], and the other [7] reports the reaction of some alcohol-derived radicals such as $\dot{\text{C}}\text{H}_2\text{OH}$ with *para*-substituted benzenediazonium salts, unfortunately excluding the parent unsubstituted substrate.

We have demonstrated in earlier studies that monoradical-like reactions of type II biradicals occur with essentially the same kinetics as free-radical reactions as long as the same substituent is present at the reactive site and the reagent is diamagnetic [8 - 10]. Thus biradical reactivities can be taken as representative of typical free-radical processes.

In this study we report the results of a laser flash photolysis examination of the reaction of the biradical produced in reactions with simple diazonium salts:



2. Experimental details

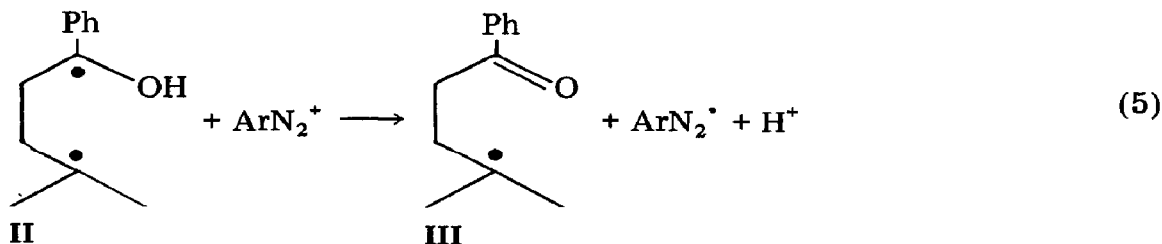
Diazonium tetrafluoroborates were prepared and purified by standard procedures. γ -methylvalerophenone was a Fluka product, and the methanol was obtained from Aldrich (Gold Label).

Laser flash photolysis experiments were carried out using pulses (337.1 nm, about 8 ns, up to 10 mJ) from a nitrogen laser for excitation. At this wavelength the diazonium salts used are essentially transparent. Further details of the instrument have been given elsewhere [11].

Steady state irradiation was carried out in Pyrex cells using a xenon-mercury lamp as the source. The samples were rotated in a conventional carousel apparatus and the progress of the reaction was monitored by gas chromatography (GC), gas chromatography-mass spectrometry (GC-MS) and UV-visible spectroscopy. The samples for GC analysis were usually trap-to-trap distilled under a vacuum.

3. Results and discussion

Biradical II has a lifetime τ of 97 ns in methanol at room temperature [12] and can be monitored using its characteristic absorption at about 415 nm [13]. When a biradical scavenger is added, the rate of decay, as measured by k_d ($k_d = \tau^{-1}$), increases and the slope of a plot of k_d versus the scavenger concentration yields the rate constant for the reaction



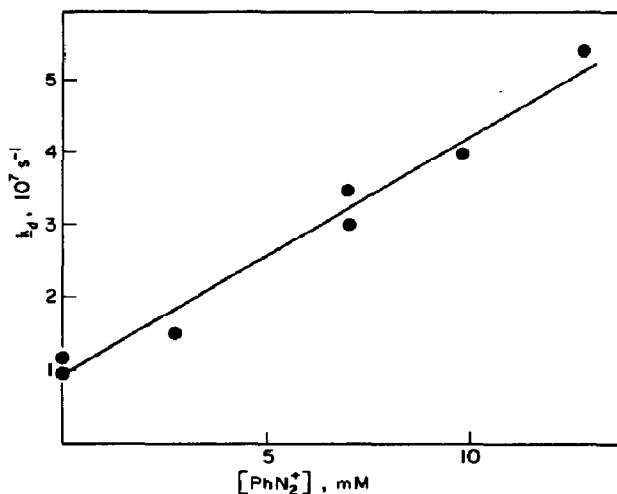


Fig. 1. Scavenging of II by benzenediazonium cations in methanol at 27 °C.

Figure 1 shows a typical plot for benzenediazonium tetrafluoroborate, leading to $k_5 = (3.3 \pm 0.5) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in methanol at 27 °C. Similar experiments with *p*-methoxybenzenediazonium tetrafluoroborate led to $k_5 = (5.5 \pm 1.8) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ under the same experimental conditions. In a substantially longer time scale (microseconds) we observed the formation of weak signals in the 350 - 400 nm region; these signals are almost certainly due to reactions of free radicals with the diazonium compounds. Similar processes have been characterized by Packer *et al.* [6].

The rate constants obtained clearly show that diazonium salts are excellent electron acceptors comparable with well-known oxidants such as methyl viologen dications [8, 12, 14].

It is also of interest to establish whether reaction (5) triggered a chain process, as expected. While our studies in this area are currently at a very preliminary level, the following points emerge clearly.

(a) The addition of diazonium salts leads to a decrease in acetophenone yields which results mainly from biradical scavenging with some contribution from quenching of the short-lived triplet state.

(b) Typical chain lengths, based on the diazonium salt consumed and the benzene formed, are in the 4 - 25 range; these naturally depend upon the experimental conditions and much longer chains may be achievable at low illumination intensities.

(c) The other product of chain propagation, formaldehyde, is transformed into methylal ($\text{H}_2\text{C}(\text{OCH}_3)_2$) during handling and analysis. Methylal was produced in good yields and was characterized by GC-MS.

Acknowledgment

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