

DIAZONIUM SALTS IN PHOTOCHEMISTRY V: PHOTSENSITIZED DECOMPOSITION OF BENZENEDIAZONIUM TETRAFLUOROBORATE IN SOLUTIONS OF CATIONIC DETERGENTS

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Summary

The photodecomposition of benzenediazonium tetrafluoroborate in solutions of cationic micelles was examined. While both direct and triplet-sensitized (employing a predominantly micelle-bound sensitizer) photolysis results in the formation of phenyl cations, the product mixtures indicate that the intermediate is formed, and subsequently reacts, in different micro-environments in the two cases. Thus phenol is formed as the almost exclusive product upon direct photolysis of the diazonium salt in dodecyltrimethylammonium bromide micellar solution, while phenanthrene-sensitized photolysis yields bromobenzene as the major product together with phenol and benzene. The formation of benzene is believed to result from short-chain processes involving phenyl radicals, perhaps formed by competing electron transfer by the sensitizer. This is substantiated by using anthracene, which is a good electron donor, as the sensitizer; this leads to the predominant formation of benzene. The addition of relatively large amounts of chloride ion to the mixtures does not affect significantly the product ratios, illustrating the known higher binding constant of bromide to cationic micelles.

1. Introduction

In a recent report Moss *et al.* [1] have shown that micellization can have a dramatic effect on the course of dediazonation reactions. For example, dediazonation of (*p*-diazoniobenzyl)-dimethyl-*n*-alkylammonium bromide led to a yield in excess of 95% of the corresponding phenol in non-micellar solution, while in micelles the products consisted of a yield in excess of 95% of the corresponding aryl bromide. The effect has been attributed to the favourable reaction of aryl cations with the high local concentration of bromide ions present as micellar counter-ions. Naturally, the possibility of steering a reaction to this extent can have important

synthetic implications. All the micellar examples examined by Moss *et al.* involve substrates that are themselves detergents, which places a considerable limitation on the use of these reactions for synthetic purposes. One obvious possibility is to use negatively charged surfactants with the diazonium salt as the counter-ion. This simply transfers the limitations from the diazonium salt to the counter-ion. Some binding constants for interactions of this type have been included in an earlier paper in this series [2].

If we wish to design a system where neither the diazonium salt nor its reaction partner are required to have detergent properties, we are limited to positively charged detergents. Here the negative counter-ion will be expected to act as an aryl cation trap [3, 4]. The problem is now reduced to generating the aryl cations in the vicinity of the micellar surface to benefit from the high local counter-ion concentration. Naturally, the approach of the diazonium cation to the positively charged micellar surface is unfavourable owing to coulombic repulsive interactions. In this paper we examine the possibility of using fully micellized photosensitizers to induce the decomposition of the diazonium salts in regions of high counter-ion concentration. Our experiments include fluorescence and laser flash photolysis investigations as well as product studies using gas chromatography-mass spectroscopy (GC-MS) and nuclear magnetic resonance (NMR) with normal and isotopically enriched samples.

2. Experimental details

Benzenediazonium tetrafluoroborate was prepared and purified following published procedures [5]. The sample of $^{13}\text{C}_6\text{H}_5\text{N}_2^+\text{BF}_4^-$ was prepared similarly on a 0.5 g scale from the corresponding aniline (Merck, Sharpe and Dohme; isotopic purity, 90%). Dodecyltrimethylammonium bromide (DTAB) (Eastman-Kodak) was purified by multiple recrystallizations from acetone-methanol. Dodecyltrimethylammonium chloride (DTAC) was prepared by reacting *N,N*-dimethyldodecylamine with chloromethane in anhydrous ether solution; it was purified by four recrystallizations from acetone.

The photosensitizers were all commercially available and were purified by recrystallization from alcohols. The micellar solutions of the sensitizers were prepared by sonication or by the addition of the sensitizer as a 0.1 M solution in methanol. A typical reaction solution for product study experiments contained sensitizer (0.9 - 2.5 mM) and benzenediazonium salt (about 9 mM) in 0.1 M surfactant. All experiments were carried out in deaerated solutions. Steady state irradiations were performed using a home-built carousel reactor with 12 RPR-3500 lamps for excitation in the case of phenanthrene sensitization. In the case of anthracene, the light used ($\lambda > 370$ nm) was obtained from a high pressure Hg-Xe lamp equipped with a suitable cut-off filter.

The GC-MS analyses were carried out using a Hewlett-Packard model 5995 system which also allowed simultaneous monitoring of the chromatogram with a flame ionization detector. A methyl silicone capillary column 12 m long of internal diameter 0.2 mm was used for all analyses. The samples for GC-MS analysis were treated with dilute perchloric acid and were then extracted with methylene chloride in order to recover the products (but not the excess diazonium salt) from the micellar solution. The extracts were dried over anhydrous sodium sulphate.

Proton-decoupled ^{13}C magnetic resonance (^{13}C MR) spectra were recorded at 28 °C on a Bruker WP80 Fourier transform NMR spectrometer within 2 h of completing the irradiations. Samples were contained in Pyrex NMR tubes of outside diameter 10 mm; detergent solutions were prepared using triply distilled deionized water for the GC-MS runs and D_2O (Merck, Sharpe and Dohme; isotopic purity, 99.7 at.% D) for the NMR runs. Methanol (1.72 M) was included in the NMR samples as an internal chemical shift reference ($\delta = 55.7$ ppm). The ^{13}C MR spectra of the (unlabelled) products were recorded using 0.1 M solutions in 0.1 M DTAB- D_2O containing methanol as the internal reference.

Laser flash photolysis experiments were performed using pulses (337.1 nm; about 8 ns; up to 10 mJ) from a Molectron UV24 nitrogen laser for excitation. Our experimental system employs a Tektronix R7912 transient digitizer to capture the signals which are then transferred to a PDP 11/23 computer that is used for experimental control, data gathering and data processing and also provides suitable storage and hard copy facilities. Further details have been reported elsewhere [6].

Fluorescence measurements were carried out using a Perkin-Elmer LS5 spectrofluorometer and a model 3600 data station. The solutions were contained in Suprasil quartz cuvettes of dimensions 1 cm \times 1 cm.

3. Results

3.1. Fluorescence quenching

Experiments with anthracene and phenanthrene in DTAB micelles showed that diazonium salt concentrations of up to 5.6 mM are completely inefficient as singlet quenchers. Quite clearly, the diazonium ions are unable to overcome the combination of electrostatic repulsion forces and short singlet lifetimes. In contrast, singlet quenching is known to be efficient in homogeneous solutions [2, 7].

3.2. Triplet quenching

Aromatic hydrocarbon triplets can have very long triplet lifetimes in micellar solution, frequently exceeding 100 μs in carefully deaerated samples. Triplet quenching is thus favoured relative to singlet quenching. For example, triplet phenanthrene, which has a strong triplet-triplet absorption band at 483 nm, is quenched by benzenediazonium tetrafluoroborate. The

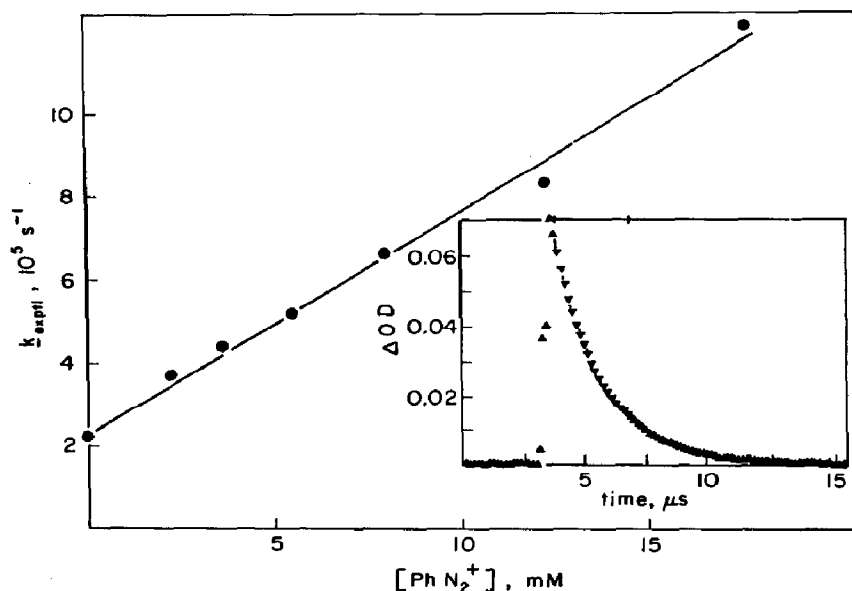


Fig. 1. Quenching of phenanthrene triplets by benzenediazonium tetrafluoroborate in 0.1 M DTAB at 300 K. The inset shows the triplet decay trace in the presence of 5.58 mM of the diazonium salt for $\lambda = 490$ nm.

corresponding quenching plot obtained in DTAB micelles (0.1 M surfactant) is illustrated in Fig. 1 and leads to a linear dependence of the experimental first-order rate constant for triplet decay k_{exptl} on quencher concentration. An apparent bimolecular rate constant k_q can be derived from the slope of this line, *i.e.*

$$k_{\text{exptl}} = k_0 + k_q[\text{quencher}]$$

where k_0 is the first-order rate constant for triplet decay in the absence of quencher. The value of k_q obtained was $(5.4 \pm 0.4) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at 300 K. For comparison, the rate constant in homogeneous solutions (acetonitrile) has been reported [8] to be $3.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The corresponding values for the anthracene triplet are $(6.3 \pm 1.2) \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ for micellar and homogeneous solutions respectively.

3.3. Product studies in unlabelled samples

The studies on unlabelled samples were performed on extracted samples (see Section 2) using GC-MS techniques.

In the absence of a photosensitizer direct photodecomposition of benzenediazonium tetrafluoroborate in DTAB micelles leads to a phenol yield in excess of 95%. No benzene and only a 3% yield of bromobenzene were detected. When anthracene (0.9 mM) was used as the triplet sensitizer, the only product of the reaction was benzene. In the presence of phenanthrene (2.2 mM) the products consisted of a mixture of benzene, bromobenzene and phenol in the ratio 1.58:1.0:1.14.

A general decrease in product yields was observed in phenanthrene-sensitized reactions in the presence of 0.08 M DTAB and 0.77 M added chloride (as NaCl). Despite the large excess of chloride the [chlorobenzene]/[bromobenzene] ratio was only 0.087. In order to test this dramatic preference for bromide we carried out several experiments in DTAC micelles to which we added various concentrations of bromide (as NaBr). These experiments confirmed the preference mentioned above.

The approach to product studies in this section required considerable handling of the samples before the actual data were obtained. The approach in the following section, while somewhat less quantitative, leaves no doubt that the products result from the photoreaction under study and not from further reactions of the primary photoproducts.

3.4. Nuclear magnetic resonance studies of ^{13}C -labelled samples

To assist in the chemical shift assignment for ^{13}C -labelled samples, spectra of the unlabelled products were recorded under identical conditions. Methanol ($\delta = 55.7$ ppm) was used as the internal standard. The spectrum of 0.1 M benzene in 0.1 M DTAB showed a singlet at 131.2 ppm, that of phenol showed prominent peaks at 118.2 and 132.5 ppm and less intense peaks at 122.7 and 159.0 ppm, and that of bromobenzene showed prominent peaks at 132.9 and 134.1 ppm and less intense peaks at 129.8 and 160.3 ppm.

The ^{13}C MR spectra of solutions of ^{13}C -labelled benzenediazonium tetrafluoroborate in 0.1 M DTAC or DTAB showed a predominant complex pattern of multiplets at 130 - 136 ppm and a weaker complex absorption at 114 - 123 ppm. In some cases the presence of small amounts of phenol in the preirradiated samples was indicated by weak absorption centred at 118.2 ppm.

The ^{13}C MR spectra of irradiated samples of benzenediazonium tetrafluoroborate in both DTAC and DTAB in the absence of a photosensitizer reveal that phenol is the major product, identifiable by the two intense triplets at 118 and 132.5 ppm. While the spectra in both cases reveal an additional unidentified absorption at 130.0 ppm, absorptions due to benzene, bromobenzene or chlorobenzene were absent.

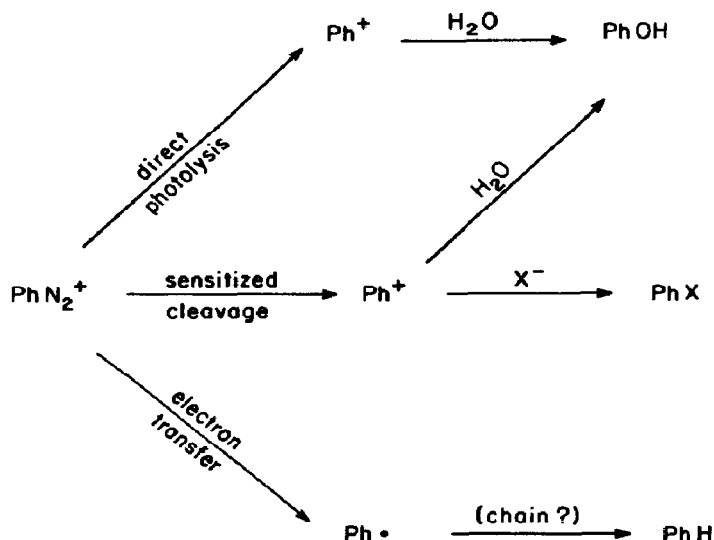
In the presence of phenanthrene the DTAB and DTAC solutions yielded different results. In both cases the presence of benzene in the irradiated samples was revealed by its overwhelming absorption at 131.2 ppm. In the case of DTAB peaks assignable to bromobenzene and phenol could be identified, and these had comparable intensities. A rough indication of the relative product yields could be obtained by assuming comparable enhancements induced by the nuclear Overhauser effect of the peaks at 131.2 ppm, 118 ppm and 134 ppm in the spectra of benzene- $^{13}\text{C}_6$, phenol- $^{13}\text{C}_6$ and bromobenzene- $^{13}\text{C}_6$ respectively; this yields a ratio of 1.3:1:1 for the relative yields of these three products, in satisfactory agreement with the GC-MS results. In the case of DTAC the ^{13}C MR spectrum of the irradiated sample showed it to consist predominantly of benzene. The spectrum also showed

an additional weak absorption centred at about 131 ppm (suggesting the presence of chlorobenzene), but phenol was not detectable. The peak at 130 ppm which was present in the unsensitized samples was not evident in the ^{13}C MR spectra of the phenanthrene-containing samples.

4. Discussion

In general the results obtained here are consistent with those recently reported by Moss *et al.* [1], as well as with those of related studies from other laboratories [9, 10].

The behaviour of aryldiazonium salts upon direct, triplet-photosensitized and electron-transfer-photosensitized excitation are summarized in the following scheme [3, 4]:



As the scheme reveals, the formal behaviour of the singlet and triplet states of aryldiazonium salts is identical, *i.e.* both undergo dissociation to yield the corresponding aryl cation. It is only a result of the fact that this intermediate is generated, and subsequently reacts, in different microenvironments in the two cases that the observed product distribution differs upon direct and triplet-sensitized excitation of the diazonium salt.

The fact that the direct photodecomposition of the diazonium salt yields phenol as the almost exclusive product in both aqueous homogeneous and micellar solutions provides a clear indication that the presence of micelles, the use of moderate concentrations of halide ion and the use of photochemical rather than thermal excitation are not by themselves sufficient to alter the course of the reaction substantially. The positively charged

diazonium salt resides in the aqueous pseudophase; as a result of simple electrostatic repulsion it tends to avoid the positively charged micelles and their associated halide counter-ions. Thus direct excitation is viewed as resulting in the generation of aryl cations in the presence of only a small local concentration of halide ion, with the subsequent predominant formation of phenol.

When a hydrophobic triplet sensitizer is added to the system under conditions such that only it absorbs the incident radiation, decomposition of the diazonium salt can only take place by triplet photosensitization. Since the sensitizers employed in this study are essentially exclusively micelle bound [11], sensitization can only occur when the diazonium salt approaches a sensitizer-containing micelle close enough for energy transfer to take place. This process is expected to be inefficient, as is borne out by the observation that the measured rate of quenching of phenanthrene triplets by benzenediazonium fluoroborate in DTAB micelles ($k_q = 5.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) is a factor of about 60 slower than that in homogeneous solution. However, when energy transfer does take place, the result is the formation of an aryl cation in the presence of a very high local concentration of bromide ion which leads to a dramatic increase in the yield of bromobenzene. However, the increase is not as pronounced as that reported by Moss *et al.* [1] for the thermal decomposition of micelle-incorporated diazonium salts. This may reflect the fact that some direct photodecomposition of the diazonium salt was unavoidable in the present case; this could presumably be minimized by a more exhaustive search for better photosensitizers.

The presence of benzene among the reaction products of the photosensitized decomposition is believed to be the result of phenyl radical formation. It is not clear at this point whether a limited free-radical chain process might also be taking place. Proof of the intermediacy of phenyl radicals in the formation of benzene has been obtained by using anthracene as the sensitizer; it has previously been shown that aryl diazonium salts quench anthracene via electron transfer and in micellar solution yield benzene as the exclusive product [8].

Reports from other laboratories have shown that the bromide ion binds to cationic micelles far more strongly than the chloride ion does [12]. This selective binding is also manifest in our results which show that bromobenzene is the favoured product even when the anion concentration ratio would be expected to favour the chloride by as much as an order of magnitude. Similar effects have been observed in the quenching of aromatic ketones by bromide ions in cationic micelles [13].

In conclusion, the present results provide a clear indication of the possibility of altering the behaviour of aryl cations through the use of detergent systems, employing reactants that do not have surfactant properties. Further development of the full potential of a process of this type, however, will require improvement in the sensitization process to avoid direct photodecomposition of the diazonium salt and to minimize the importance of free-radical processes.

Acknowledgments

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