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Synthesis and photochemical properties of aromatic diazo-phosphonium salts

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Abstract

The phosphonium salts **I–VI** were synthesized which have potential applications in communication technologies, for example as photoresist materials. All these compounds show a broad absorption maximum in the range between 310 and 350 nm, depending on the nature of the substituent attached to the aromatic ring. The molar absorption coefficients were determined to be in the range from 10 000 to 15 500 $\mathrm{l\ mol^{-1}\ cm^{-1}}$. Their photochemical behaviour in solution was investigated by means of UV spectroscopy and compared with other photoreactive compounds containing the azo group. The quantum efficiency for the investigated compounds was found to be in the range from 0.009% to 0.026% at 308 nm, which is about two magnitudes smaller than that of pentazadienes or triazenes. Absorption difference (ΔA) plots of the experiments indicate basically a one-step decay with no significant amount of intermediate products on the observed time scale.
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1. Introduction

The photochemistry of aromatic azo compounds has been the subject of many reports [1,2] and is still under research [3–6] owing to a fascinating broad relationship between structure and properties. Generally these studies can be divided into two classes. The first deals with the photophysical interaction of an azo chromophore with radiation inducing no further chemical reactions, whereas the second focuses on photochemically induced reactions. A typical representative of the latter class is the fragmentation of the azo chromophore. In many cases azo compounds represent sensitive structures, changing their properties by a specific stimulus. This makes azo compounds potent candidates as basic chemical building blocks for applications in communication technology, such as printing, optical recording or microelectronics.

Certainly the diazo compounds are the best known reactive representatives; in recent years a series of investigations has been devoted to the class of compounds containing the R–N=N–X–R group (X = S, P, N, N_3, etc.).

Especially the class of triazenes (X: N) and pentazadienes (X: N–N=N) show very efficient photochemical decay when irradiated with excimer lasers and they have been tested successfully with respect to applications in photoablation [7–10].

Regarding the photochemistry, among the class of aromatic azo compounds the phosphorus-containing species Ar–N=N–P have only been studied in the highest oxidation state, i.e. P^{5+} [11,12]. Here we report new results concerning the photostability of selected aryldiazophosphonium Ar–N=N–P^{3+} salts.

2. Experimental details

2.1. Synthesis

All compounds were prepared by reacting tris(dimethylamino)phosphine with equimolar amounts of the corresponding aromatic diazonium tetrafluoroborate salt, as has been partially described in Ref. [13], by the following coupling procedure.

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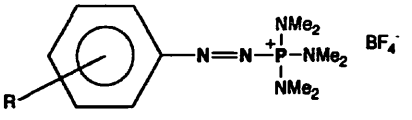

Symbol	Substituent R
I	4-Cl
II	2-Cl
III	2-CH_3,4-Cl
IV	4-$COOCH_2CH_3$
V	4-SO_2NH_2
VI	4-CN

Scheme 1. Structural formulae of compounds investigated in this study.

A concentrated solution of 10 mmol aromatic diazonium tetrafluoroborate salt in dry acetonitrile (approximately 50 ml) was stirred at 0 °C. Tris(dimethylamino)phosphine (10 mmol) was added carefully and quickly using a syringe. Immediately a change to a dark red colour of the solution takes place. The solution is allowed to stand at −20 °C for 12 h. The formed precipitates are isolated by filtration. Sufficient product stability to air allows simple handling without inert gas techniques. The yields for all syntheses were in the range 80%–95%.

Based on ^{31}P, ^{1}H-NMR analysis, the crystalline products were found to be very pure. All NMR data are in agreement with expected or reported data [13]. Therefore no additional purification steps were required.

The compounds shown in Scheme 1 were synthesized.

2.2. Photochemistry experiments

The substances were used without further purification and dissolved in chloroform p.a. Chloroform is not normally used for photochemical experiments because of its tendency to form radicals upon irradiation. However, a solvent with high transmission down to 250 nm was required, with the capability of dissolving sufficient quantities of the phosphonium salts to achieve optical densities high enough for absorption monitoring during the photochemical experiments (about OD 1/cm). This requirement was not fulfilled for many other solvents tested such as methanol, ethanol, and tetrahydrofuran.

The solutions were poured into standard quartz cuvettes (1 cm × 1 cm) with four polished windows. The concentration of the solutions was chosen such that the resulting optical densities where in the range of unity. This was necessary for performing the photolysis experiment in the optimum measurement range of our UV spectrometer. The cuvette was subsequently placed into a sample holder which provided for UV absorption measurements by fibre optics perpendicular to the direction of irradiation. For recording the UV spectra we used a Polytec diode array spectrometer equipped with fibre optics. The spectral resolution was set to 2.5 nm. This set-up allowed measurement of the spectra immediately after irradiation which was performed with an XeCl excimer laser (Lambda Physik, Compex 205) operating at 308 nm. Pulses with energies of about 40–150 mJ pulse^{-1} and 25 ns pulse length were delivered to a sample volume of 1.7 ml. All experiments were performed at room temperature. The repetition rate of the laser was limited to the range 1–10 Hz in order to avoid heating of the sample. From time to time the irradiation was interrupted to record the UV spectra. Typically we used an integration time of 5 times 0.8 s for each UV measurement.

3. Results and discussion

With the exception of compound V all substances could be dissolved in $CHCl_3$ and showed decay upon irradiation with 308 nm laser pulses.

In Figs. 1 and 2 the results of two typical irradiation experiments are shown. In all cases the absorption maximum above 300 nm decreases during the irradiation and reaches almost zero after several thousands of pulses. No significant shift of

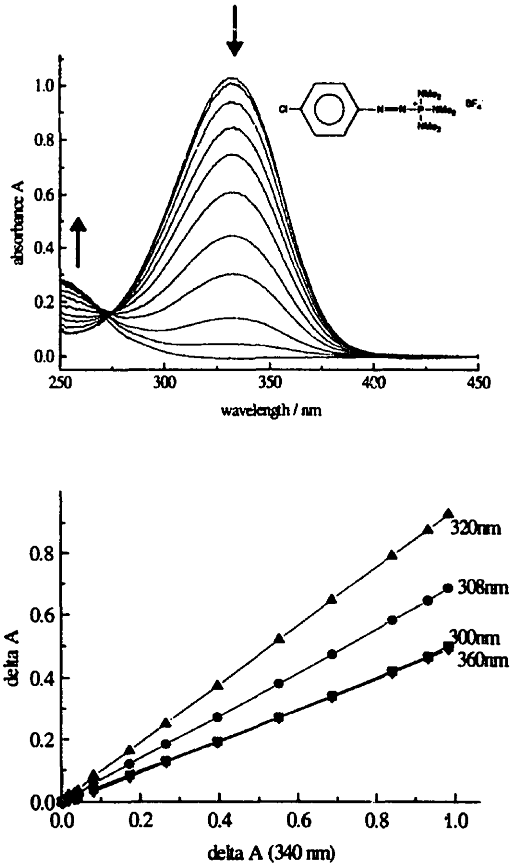

Fig. 1. Photolysis of **I** in $CHCl_3$. The upper part shows the UV absorption spectra recorded after irradiation by 0, 100, 300, 500, 700, 1000, 1300, 1600, 2000, 2500, 5000 excimer laser pulses (308 nm, 45 mJ pulse^{-1}). The lower part shows the corresponding absorption difference (ΔA) plot.

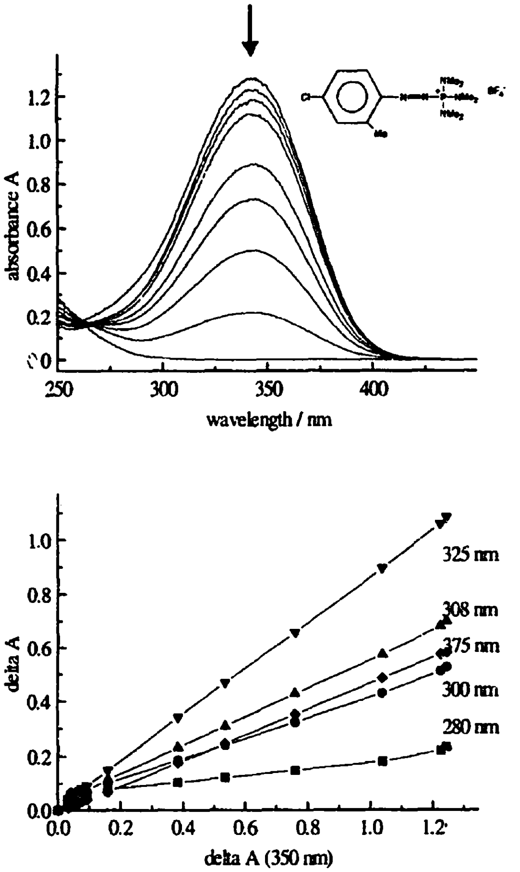

Fig. 2. Photolysis of II in $CHCl_3$. The upper part shows the UV absorption spectra recorded after irradiation by 0, 100, 1000, 2000, 5000, 7000, 10 000, 15 000, 25 000 excimer laser pulses (308 nm, 45 mJ pulse^{-1}). The lower part shows the corresponding absorption difference (ΔA) plot.

the maximum could be detected during the photolysis. When pulse numbers higher than about 1000 were applied to the sample, the generation of gas bubbles could be observed, which is a hint that nitrogen is released from the molecules during the decay.

In the case of compound **I** we observe an isosbestic point during the photolysis. The absorption difference (ΔA) diagram (Fig. 1, lower part) shows linear dependences which indicate a reaction of type A → B. (The theory of the interpretation of UV spectra from ΔA plots has been given by Mauser [14,15].)

The photolyses of the other compounds do not give rise to clear isosbestic points, and the ΔA diagrams show partial deviations from linearity (Fig. 2). This indicates that to a small extent side reactions are involved which may lead to intermediate products.

If there is a photolabile intermediate product with a lifetime on the order of 1 s or longer, the extent of the reaction after a certain number of pulses should depend on the pulse frequency. For this reason we prepared two portions of a solution of **VI** with the same concentration and applied 2000 pulses of the same energy to each sample. In one case, a laser repetition frequency of 1 Hz was chosen, while the other sample was irradiated with 5 Hz. At the end of the experiments both samples showed the same absorption, from which we can conclude that no long-living photosensitive intermediates are created.

A hint for the existence of intermediate products, however, resides in the following observation. In some cases the first pulses induced less changes in the absorption spectra than the subsequent pulses. This could indicate that, to a small extent, an intermediate with an absorption spectrum similar to that of the starting material is produced, e.g. an isomer, before the irreversible decay of the molecule.

Nevertheless, for an estimation of an overall quantum efficiency, the side reactions have been neglected. The first 1000 pulses of every photolysis experiment were taken into account, and the following assumptions were made.

1. Within the duration of a single laser pulse no significant change of the absorption is taking place.
2. Because of the low repetition rate of the laser no warming of the solution occurs.
3. The quantum efficiency is not dependent on the progress of the reaction.

In addition to these assumptions one has to take into account that, after each pulse, the absorption of the solution changes owing to the destruction of the phosphonium salt, and the formation of reaction products which have a lower absorption coefficient at the laser wavelength. To accommodate these changes when calculating the quantum efficiency, we developed a code that computes the changes in the absorption of the solution after each laser pulse. Quantities known from the experiment, such as pulse energy, volume of the solution, concentration, and coefficients of absorption are used as input parameters. The value of the quantum efficiency is then determined from a least squares fit to the series of spectra. The validity of the model may be verified by a comparison between calculated and observed absorption changes.

The relevant parameters of the investigated compounds and the resulting quantum yields are summarized in Table 1. It is found that the overall quantum efficiencies depend on the substituent attached to the phenyl ring. For example, compound **VI**, with the cyano group in 4-position, is almost three times as photosensitive as compound **II**, which has a chloro substituent in 2-position. Such behaviour is expected in view of effects observed for other classes of azo compounds with aromatic substituents, such as azosulphonates [16,17], triazenes [18], and pentazadienes [8,19] respectively. The comparison of compounds **I** and **II** shows that not only the nature of the substituent but also its position is of importance. Here, a shift of the chlorine atom from ortho- to para-position increases the efficiency of the photochemical cleavage by a factor of two. If, however, in addition to the para-chlorine substituent a methyl group is attached to the ortho-position, the quantum efficiency remains unaffected.

Table 1
Photophysical parameters and quantum yields of photolysis

Compound	Molecular mass (g mol^{-1})	$\lambda_{max,1}/\epsilon_1$	$\lambda_{max,2}/\epsilon_2$	ϵ (308 nm)	$\eta_{photochem}$ (%)
I	344.2	333/15400	470/375	10400	0.016
II	344.2	316/10150	518/119	9700	0.0094
III	358.2	345/15500	516/162	8400	0.015
IV	374.8	315/15400	514/117	15000	0.021
V		Not soluble in chloroform			
VI	334.8	311/13000	517/116	12800	0.026

4. Conclusions and outlook

Substituted aromatic diazo phosphonium salts are an interesting class of photoreactive compounds. They exhibit strong absorption maxima in the range of 308 nm, i.e. the wavelength of commercially available excimer lasers. They can be handled under atmospheric conditions in the laboratory without further precautions with rescept to oxidation, thermal decay and photochemical decomposition. When irradiated with excimer laser pulses of 308 nm these compounds decay under release of nitrogen, and the absorption in the near-UV decreases almost to zero. The quantum efficiencies are low compared with other azo compounds such as aromatic and aliphatic substituted triazenes and pentazadienes respectively, but are still high enough to envisage practical usage in communication technology, for example as photoresists.

Further avenues of research could include a more detailed look at the decay mechanism with respect to end products of the photochemical decay, as well as the existence and lifetime of short-living intermediates.

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