

## FLASH PHOTOLYSIS OF PHENYLAZOPYRAZOLONE DERIVATIVES IN SOLUTION

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### Summary

Flash photolysis investigations were performed on various derivatives of 3-methyl-1-phenyl-4-phenylazopyrazolone-5 in polar and non-polar media. The transients produced in alcohol-water mixtures at pH 7 possess two absorption bands in the range between 300 and 600 nm, which are different from those obtained at pH 12. These transients are assigned to substituted phenylhydrazyl radicals in their neutral and dissociated forms. They are not observed in dioxane and cyclohexane solutions. In these solvents an isomerization process is found. On addition of hydrogen donors, such as methanol, propanol-2 or *N*-allylthiourea, to dioxane hydrazyl radicals are also photogenerated. In all cases degradation and formation of stable products were also registered. The kinetic behaviour of the short-lived species is complex. Structures of the transients were discussed.

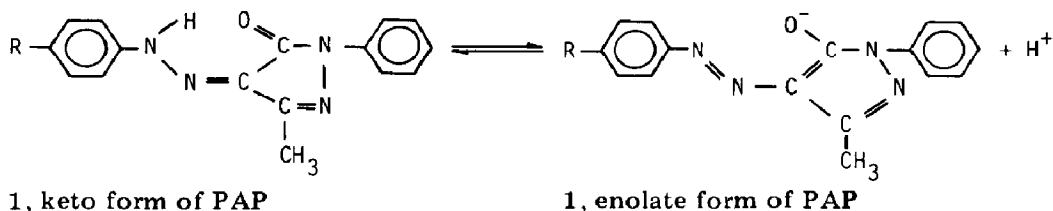
### 1. Introduction

The photostability of azo compounds is of major significance for their use as dyestuffs. Photoreduction is of particular interest in this respect as it is the only common photochemical reaction that ultimately results in the irreversible destruction of the azo linkage [1]. In addition to this process photochemical *cis-trans* isomerization [2 - 5], photocyclization in acidic media [6], photo-oxidation with singlet oxygen [7] and other processes [8] are known for these substances.

In spite of the possible significance of photoreduction processes for the irreversible fading of azo dyes under anaerobic conditions, relatively few systematic studies have been performed in this field. It has been shown that

photoreduction can proceed in two distinct ways: either via an excited state of the chromophore, that abstracts hydrogen from the solvent [5], or via excitation of a second species, resulting in the formation of a substance to reduce the azo compound [9 - 12].

The derivatives of 3-methyl-1-phenyl-4-phenylazopyrazolone-5 (PAP), which are the subject of this study, may exist in one of two possible tautomeric forms, as keto hydrazone or as azo enol:



As a rule in solution they are almost totally in the hydrazone (H) form. Only in strongly alkaline solution ( $\text{pH} > 11$ ) do they transform into the anion (A) form, which is common to both the hydrazone and the azo enol form [13 - 15]. It has been shown that fluorescence is exclusively due to the H form [16] as is the case with phenylazonaphtholes [17, 18].

The structural basis for the keto hydrazone form is the imine system. UV irradiation of this system may lead to a series of photoreactions such as isomerization [2, 19 - 21], hydrolysis [22], proton shift [23], photocyclization [24], oxidation [25] and photoreduction [12, 26 - 29]. Some of these possibilities are restricted to special cases. The photoreduction process, however, appears to be of general importance. Despite the variety of photoprocesses encountered with imine derivatives these compounds show remarkable photostability, most probably due to dissipation of electronic excitation energy via rotation around the  $\text{C}=\text{N}$  double bond in the excited state [19].

The purpose of the present work was to study the photochemical behaviour of the hydrazone and of the enolate form of PAP derivatives with particular respect to the photoreduction process. As strongly alkaline solutions were not studied in previous works on flash photolysis of azo compounds [9 - 12], experiments were also performed in this pH region.

## 2. Experimental details

The flash photolysis experiments were performed by means of modified Northern Precision equipment (flash duration,  $7 \mu\text{s}$  at an energy of 20 - 200 J) [30]. A photomultiplier (Hamamatsu R 955) or a photodiode (Siemens BPW 34) were used for detection. The transients were displayed on a storage oscilloscope (Tektronix 7623 A) and evaluated by means of a computer program. The absorption spectra of stable compounds were taken with a Perkin-Elmer Coleman 575 spectrophotometer.

The syntheses of compounds with  $\text{R} \equiv \text{N}(\text{CH}_3)_2$  (I),  $\text{R} \equiv \text{NH}_2$  (II),  $\text{R} \equiv \text{H}$  (III),  $\text{R} \equiv \text{CN}$  (IV) and  $\text{R} \equiv \text{Cl}$  (V) were performed by diazotization of the

corresponding substituted anilines and subsequent coupling in alkaline solution with 1-phenyl-3-methylpyrazolone-5 [31]. The purification and purity checks are described elsewhere [16].

Methanol, ethanol and propanol-2 (Merck) were purified by distillation over 2,4-dinitrophenylhydrazine and dioxane (Merck) was purified by distillation over KOH. Water was distilled four times. *N*-allylthiourea was recrystallized from ethanol. All other chemicals were of analytical grade.

Unless stated otherwise the solutions were purged with oxygen-free argon (Messer-Griesheim, Gumpoldskirchen).

### 3. Results

#### *3.1. 3-methyl-1-phenyl-4-phenylazopyrazolone-5 transients in neutral water-methanol solutions*

Within the single light pulse applied to the aqueous solutions of  $4 \times 10^{-6}$  -  $5 \times 10^{-5}$  mol dm<sup>-3</sup> substrate containing 5 - 10 mol dm<sup>-3</sup> methanol or ethanol degradation of the arylazopyrazolone under formation of at least one transient with absorption bands in the region of 300 - 355 nm and of 460 - 570 nm was observed. For some derivatives the degradation, which appeared as a "negative absorption" in the flash photolysis experiment, and the transient absorption overlapped in certain wavelength regions. In these cases the transient absorptions were corrected for the degradation by fitting the negative absorption by means of a microcomputer using the known shape of the absorption band of the dye.

As an example the spectrum obtained by flash photolysis of 4'-amino-phenylazopyrazolone in 10 mol dm<sup>-3</sup> methanol at neutral pH is displayed in Fig. 1. The transient maxima of the studied derivatives are compiled in Table 1.

The transients usually decay in second-order processes, with observable lifetimes ranging from 200 to 1000  $\mu$ s. A detailed kinetic analysis is in progress. The absorption of the starting compound is recovered within a few seconds to an extent of approximately 50%. This process shows a rather complex kinetic behaviour.

#### *3.2. 3-methyl-1-phenyl-4-phenylazopyrazolone-5 transients in alkaline water-methanol solutions*

Similar results were obtained in alkaline solutions (pH 12). An example is shown in Fig. 2; the transient absorption maxima are displayed in Table 1. The transient absorption maxima are different from those in neutral solutions. The transient spectra could only be registered in the long wavelength region. As well as the formation of a long-lived product with an absorption band at 200 - 300 nm the recovering of the initial absorption to about 70% within 1 ms, with complex kinetics, was observed. The measured transient lifetimes are in the range 200 - 700  $\mu$ s and also have complex kinetics.

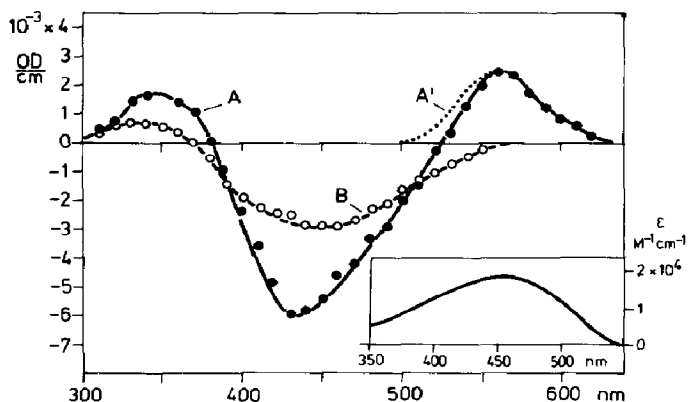


Fig. 1. Transient absorption spectra obtained by flash photolysis (discharge voltage, 15 kV) of deoxygenated solutions of  $4 \times 10^{-6} \text{ mol dm}^{-3}$  4'-aminophenylazopyrazolone in  $10 \text{ mol dm}^{-3}$  aqueous methanol (pH 7): spectrum A, 100  $\mu\text{s}$  after flash; spectrum A', corrected for absorption of the starting compound (see text); spectrum B, 3 s after flash. The inset shows the UV absorption spectrum of 4'-aminophenylazopyrazolone in  $10 \text{ mol dm}^{-3}$  aqueous methanol (pH 7).

TABLE 1

Absorption maxima of transients produced by flash photolysis of phenylazopyrazolone derivatives in deoxygenated aqueous  $10 \text{ mol dm}^{-3}$  methanol (discharge voltage, 15 kV)

Substance	Substituent R	Transient absorption maxima $\lambda$ (nm)	
		pH 7	pH 12
PAP 1	$-\text{N}(\text{CH}_3)_2$	355, 570	555
PAP 2	$-\text{NH}_2$	330, 560	550
PAP 3	$-\text{H}$	300, 470	475
PAP 4	$-\text{CN}$	300, 460	505
PAP 5	$-\text{Cl}$	460	485

### 3.3. Experiments in non-polar solvents

These transients are not observable in cyclohexane and dioxane solutions. The spectra obtained by flash photolysis of PAP 4 (H form) in dioxane are shown in Fig. 3. The light pulse generates a negative absorption in the range 350 - 450 nm owing to a pronounced degradation of the starting compound. This bleaching occurs during the flash and the initial absorption is restored according to a first-order reaction with  $k_1 \approx 2 \times 10^3 \text{ s}^{-1}$ . In addition, the formation of a stable product ( $\lambda \approx 300 \text{ nm}$ ) and a transient with an absorption band at about 300 nm is also observed ( $\tau/2 \approx 300 \mu\text{s}$ ). The transient formation and the degradation process of the starting compound are superimposed. Similar results were obtained for PAP 1 and PAP 4 in cyclohexane.

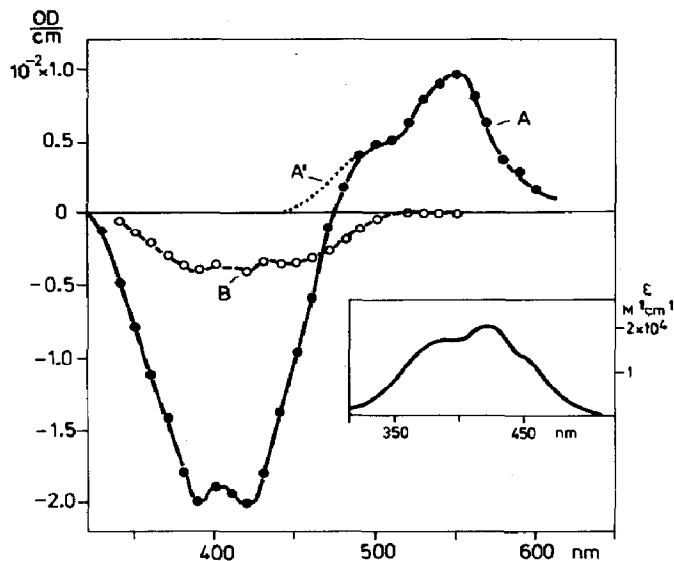


Fig. 2. Transient absorption spectra obtained by flash photolysis (discharge voltage, 15 kV) of deoxygenated solutions of  $2 \times 10^{-6} \text{ mol dm}^{-3}$  4'-aminophenylazopyrazolone in  $10 \text{ mol dm}^{-3}$  aqueous methanol (pH 12): spectrum A, 200  $\mu\text{s}$  after flash; spectrum A', corrected for absorption of the starting compound (see text); spectrum B, 3 s after flash. The inset shows the UV absorption spectrum of 4'-aminophenylazopyrazolone in  $10 \text{ mol dm}^{-3}$  aqueous methanol (pH 12).

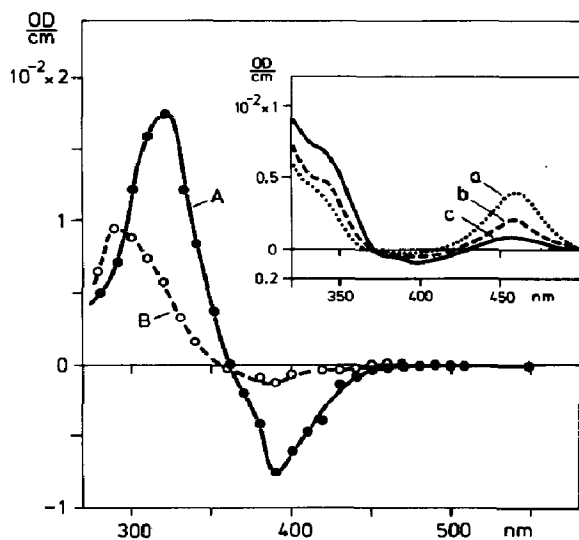


Fig. 3. Transient absorption spectra obtained by flash photolysis (discharge voltage, 15 kV) of deoxygenated solutions of  $10^{-5} \text{ mol dm}^{-3}$  4'-cyanophenylazopyrazolone in dioxane: spectrum A, 200  $\mu\text{s}$  after flash; spectrum B, 2 ms after flash. The inset shows spectra obtained 500  $\mu\text{s}$  after flash on addition of  $5 \text{ mol dm}^{-3}$  propanol-2 (spectrum a),  $5 \text{ mol dm}^{-3}$  methanol (spectrum b) and  $2 \times 10^{-4} \text{ mol dm}^{-3}$  *N*-allylthiourea (spectrum c). (The spectra are not corrected for the absorption of the starting compound.)

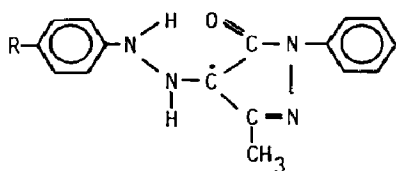
The transient absorption in the region 430 - 500 nm, as described for aqueous methanol solutions, was also observed in dioxane on addition of propanol-2, methanol or *N*-allylthiourea, as shown in Fig. 3, inset.

#### 4. Discussion

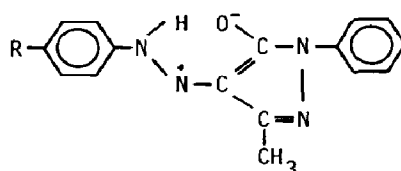
Flash photolysis of both the H and the A forms of PAP derivatives in alcoholic and in alcohol-water mixtures results in transients which are not observed in cyclohexane and dioxane solutions. In cyclohexane and dioxane, however, the formation of short-lived species, absorbing at shorter wavelengths, and the degradation of the substrate occur simultaneously. On the basis of similar findings for other hydrazo compounds [21] this observation is tentatively assigned to an isomerization process at the C=N bond. The isomerized form absorbs at shorter wavelengths (less than 300 nm for the CN derivative). Relaxation to the initial form takes place within about 1 ms in dioxane at room temperature. This isomerization process is subject to further studies.

Addition of alcohols, especially of propanol-2 or of *N*-allylthiourea [32], results in the formation of transients in flash photolysis, which are also formed in pure alcohols and in alcohol-water mixtures. Similar transients are found in alkaline solutions (pH 12) in the presence of aqueous 10 mol dm<sup>-3</sup> methanol.

Although other structures cannot be ruled out definitely, the transients are assigned to the following phenylhydrazyl radical structure:



2, transient in acid form



2, transient in basic form

This is supported by the following considerations.

(1) The transients are only formed in the presence of hydrogen-donating substances, such as aliphatic alcohols or *N*-allylthiourea. The formation of hydrazyl radicals in photoreduction processes has been previously shown by flash photolysis [9 - 12] and electron spin resonance [33] for other azo compounds.

(2) Steady state photolysis [34] results in the formation of substituted aniline and of pyrazole derivatives, as expected from the degradation of hydrazyl radicals [35, 36].

(3) The substituent effects on the transients also confirm the assignment as discussed below. Correlation diagrams were set up according to the Hammett equation

$$\Delta\nu_{\text{abs}} = \rho_{\text{abs}}\sigma_p + C$$

and are displayed in Fig. 4.

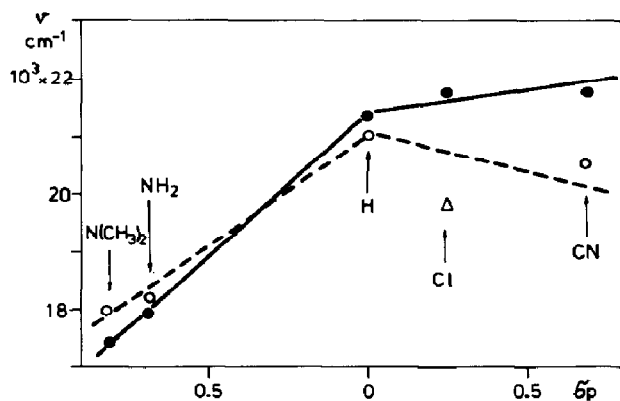


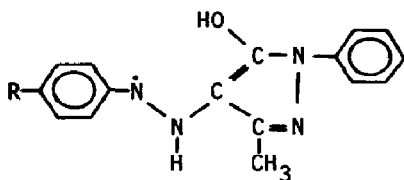
Fig. 4. Linear correlations of absorption maxima of radicals obtained by flash photolysis of substituted phenylazopyrazolones in deoxygenated aqueous  $10 \text{ mol dm}^{-3}$  methanol solutions (see text): —, pH 7; ---, pH 12.

The slopes are different for negative and positive  $\sigma_p$  values as is typical for many aromatic compounds [37] and free radicals [38]. The delocalization of the unpaired electron seems to have little influence on the acceptor properties of the C=O group and so the chromophore of the radical is to be regarded as a donor-acceptor system with the acceptor C=O, whereas the phenyl group can act as a donor or an acceptor according to the nature of the substituent R. Thus, free radicals stemming from compounds with electron donor substituents ( $R \equiv p\text{-N}(\text{CH}_3)_2$  or  $R \equiv p\text{-NH}_2$ ) show a strong bathochromic shift as expected (donor-acceptor system), whereas no significant shift is observed for the derivatives with electron acceptor substituents ( $R \equiv p\text{-Cl}$ ,  $p\text{-CN}$ ) as can be seen in Fig. 4.

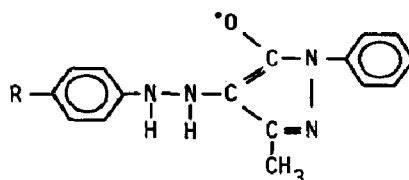
Reduction of the azo form results (possibly after a shift of a hydrogen atom) in a deprotonated form of the hydrazyl radical, which is characterized by an  $\text{O}^-$  group acting as donor. In contrast with the results in neutral solutions the donor substituents have a slightly smaller effect on the spectra of the radicals in alkaline solution, but a strong bathochromic effect is observed for the acceptor-donor system of anionic radicals with acceptor substituents.

For these reasons the observed transients are considered to be the non-ionized and the ionized forms of substituted hydrazyl radicals respectively.

For a related naphthylhydrazyl radical electron spin resonance investigations [33] support the above-presented structure 2, but the decision between 2 and alternative structures of PAP radicals, *e.g.*



3a



3b

still remains open for our particular case.

The occurrence of photoprocesses other than photoreduction makes it impossible to determine the extinction coefficients of the free radicals by comparison of their extinction with the negative absorption due to degradation of the starting compound.

For some aryl-*N*-alkylimines it has been found [27] that photoreduction does not proceed by hydrogen transfer from the alcoholic solvent to the excited state of the imine, but via a ground state reaction of the imine with ketyl radicals derived from carbonyl compound possibly present as an impurity in the starting material. Despite careful purification procedures this pathway cannot be ruled out completely at the moment. Further work in this respect is in progress.

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