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The photochemistry of phenyl azide

M F Budyka, M M Kantor, M V Alfimov
Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka

ABSTRACT. **The literature data on the photochemical reactions of phenyl azide under different conditions are reviewed. Its photoinitiated autocatalytic chain decomposition reaction is examined in detail. Questions relating to the structure and properties of intermediates formed during photolysis of aryl azides and the mechanism of formation of azo compounds are discussed. The existing information on photoinitiated chain reactions of alkyl and aryl azides is briefly considered.**

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I. Introduction

In the present review the photochemical reactions of phenyl azide (PhA)—the simplest compound from amongst the fairly extensive class of aromatic azides—are discussed. The photochemistry of aromatic azides has been widely studied in connection with the use of these compounds in photoresists and vesicular light-sensitive materials and as photoaffinity labels in biology.

By analysing the photochemical reactions of PhA it is possible to derive some idea of the typical properties of this whole class of aromatic azides. Moreover, Waddell, et al. recently published a series of articles[1–8] in which photoinitiated autocatalytic chain decomposition (PACD) was described. As a result of detailed studies the mechanism of reaction and structure of the intermediate products were proposed, and the maximum apparent quantum yield of photodissociation of PhA (Φ_{-PhA}) was 15 300.[7]

The high quantum yield of dissociation and also their kinetic analysis led the authors to claim "a molecular explosion observed for the first time in solution".[7] Information about the PACD reaction is given in a number of reviews[9,10] but so far it has not been possible to confirm that this reaction takes place, despite the fact that direct attempts have been made to do this.

Processes with a quantum yield $\Phi > 1$ are of interest both for the theoretical and practical points of view; so information about the PACD reaction of aromatic azides is examined in this review. Since the basis of this reaction is assumed to be the interaction of triplet phenylnitrene (PhN) with PhA and the final product is azobenzene, it is logical to start this review with the findings on the properties of PhN in the mechanism for formation of azobenzene. The synthetic and applied aspects of the chemistry of azides have been discussed in a recent review.[11]

II. Triplet nitrene and the formation of azo compounds

Triplet PhN was first detected by Wasserman, et al.[12] in 1962 during the photolysis of vitrified solutions of PhA and other azides in poly(chlorotrifluoroethylene) at 77 K using EPR. The parameter D which was calculated from the spectrum and which characterises the magnitude of the interaction between the unpaired spins was determined as 0.99 cm^{-1}, less than $D = 1.625$ cm^{-1} for t-butylnitrene, which suggested that there is considerable delocalisation of one unpaired electron around the aromatic ring of PhN.[13] The parameter E, which characterises the difference in the distribution of spins about the molecular axes, was close to zero for both nitrenes ($E < 0.002$ cm^{-1}).

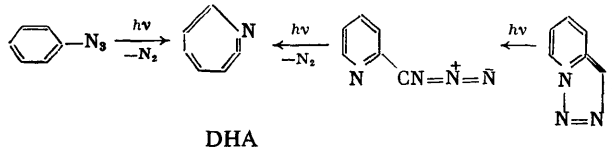
The hyperfine structure of the spectra of nitrenes generated in crystals of the corresponding azides,[14] the effect of substituents in PhN on the spectrum, and quantum-chemical calculations[15] confirmed the structure proposed for triplet PhN. A pair of electrons is situated in an *sp* orbital along the C–N axis, one unpaired electron occupies a molecular orbital enveloping the aromatic π-system, and the second electron is localised on an orthogonal *p* orbital of the nitrogen atom.

On the basis of EPR data Reiser, et al.[16] attributed the electronic absorption spectra obtained in 1965 under similar conditions of photolysis (77 K, organic matrix) to triplet nitrenes. Confirmation of this assignment was obtained from the following evidence:[17] the spectrum did not depend on the type of matrix (vitreous hydrocarbons, ether, ethanol, and their mixtures); the spectrum belonged to a single compound, since an isobestic point occurred on the spectrosocpic curves; quantum yields of photodissociation of about 0.5 were obtained for all the azides studied; the spectrum disappeared on heating the matrix to its softening point (90 K); the spectra had characteristic features relating to the occurrence of an "aromatic system with an open shell", for example, the spectrum of phenylnitrene (λ_{max} 314 and 402 nm) was similar to the spectrum of the aniline radical (λ_{max} 309 and 400 nm).

Subsequently similar spectra were obtained at 77 K by other authors,[18,19] and in all cases they were attributed to triplet PhN. Quantum-chemical calculations of the transition energies and oscillator strength corresponded satisfactorily to the experimental spectra of PhN.[18]

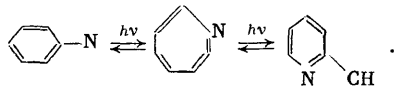
However, in 1978 Chapman, et al.[20] in studying the photolysis of phenyl azide in an argon matrix or in thin films at 8 K using IR spectroscopy demonstrated that the photolysis product under these conditions is dehydroazepine (DHA), which was detected from the

characteristic intense absorption due to the heterocumulated bonds in the IR region at 1895 cm^{-1} (close to the absorption of the spectroscopic model $-C_6H_5-\overline{C}=\overset{+}{N}=CH_2$ with ν_{CNC} = 1930 cm^{-1}). Its spectrum was also demonstrated by counter-synthesis from triazolopyridine:



DHA

At the same time an analysis of the photolysis products of PhA obtained under similar conditions (12 K) using EPR showed that triplet PhN was also present in the mixture,[21] and on subsequent irradiation it was converted to triplet 2-pyridylcarbene. Photolysis in the direction triazolopyridine→pyridylcarbene→phenylnitrene suggested that the nitrene and carbene were interconverted via dehydroazepine:[22]



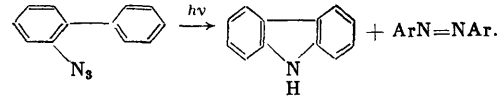
Hence the electronic absorption spectrum that was recorded in four studies[16–19] may belong not only to triplet PhN but also to a mixture of products. However, this assertion is contradicted by studies on the T_1-T_0 luminescence of PhN and its derivatives,[19,23] in which it was shown that the luminescence spectrum of triplet PhN is a mirror reflection of the absorption spectrum of the photolysis products of PhA and the latter coincides with the spectrum of luminescence excitation. Hence it was concluded that the absorption spectrum belongs to a single compound, namely, triplet PhN.

Thus, low-temperature studies have provided an ambiguous answer to the question as to what are the primary photodissociation products of PhA. It would appear that the inconsistency in the results may be due in part to the different conditions of the studies: 4–8 K in an argon matrix[20–22] or 77 K in an organic matrix.[16–19,23] Moreover, taking into account the revealed ability of PhN and DHA to undergo photochemical interconversion, the final result may depend to a significant extent on the intensity, duration, and spectroscopic range of incident light (see below).

The possibility that a number of intermediates are formed was also suggested by the results from a preparative study of the photochemical reactions of PhA and other azides and from flash photolysis of azides at room temperature.

In 1966 Doering and Odum[24] established that the final photolysis product of PhA in the presence of amines was a substituted 2-amino-3*H*-azepine. Subsequently Splitter and Calvin[25] concluded that the azepine was formed from singlet PhN on the basis of the evidence that in triplet sensitisation with *p*-dimethylaminobenzaldehyde the yield of 2-diethylamino-3*H*-azepine, for example, decreased from 34 to 2% while the yield of aniline increased from 70–80%.

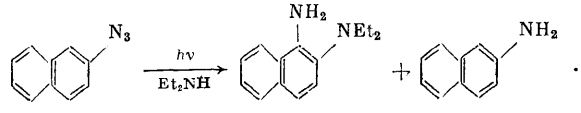
For singlet 2-biphenylnitrene the main reaction is cyclisation to carbazole, the yield of which amounted to 74% in the direct photolysis of azide, while at the same time about 12% azo compound was isolated:[26]



Quenchers of triplet excitation increased the yield of carbazole, reducing the yield of azo compound at the same time, while triplet sensitisers had the reverse effect. It followed from this that triplet nitrene is formed from triplet azide rather than singlet nitrene.

A study of the photolysis of 10^{-2} M solutions of PhA in alcoholic and hydrocarbon solvents showed that a polymer and product derived from insertion of solvent into the molecule are formed from singlet PhN, while aniline and azobenzene are formed from triplet PhN.[27] From the effect of the chemical nature of the solvent, the composition of the solvent mixture, and the added amounts of triplet sensitisers on the molar ratio of the reaction products it was estimated that in the photolysis of PhA only 12–13% PhN is directly generated in the ground triplet state.

A further type of reaction of singlet nitrene—formation of aromatic diamines with migration of the nitrogen atom of the azide group to the neighbouring position of the aromatic ring—occurred during photolysis of 2-azidonaphthalene in diethylamine. 2-Aminonaphthalene, which is probably formed in parallel from triplet nitrene, is also isolated:[28]



The method of flash photolysis at room temperature was first applied in 1966 to studies on the reactions of aromatic azides.[29] In the irradiation of a 5 × 10^{-4} M solution of 1-azidoanthracene in ethanol, 4 μs after the flash a spectrum was recorded that had a characteristic absorption at 342 nm, similar to that found previously at 77 K and attributed to triplet nitrene. The lifetime of nitrene was about 5 μs.

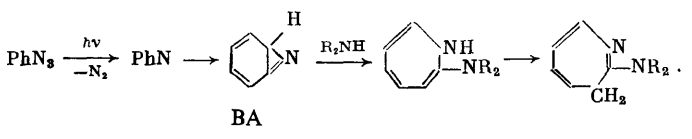
Other aromatic azides have been investigated in detail and the kinetics of certain reactions of nitrenes have been studied.[30] Reiser, et al.[30] maintained that for substituted phenyl azides, 1-azidonaphthalene, and also 1-azidoanthracene, the electronic absorption spectra of the intermediates that were recorded using flash photolysis matched the spectra of the corresponding triplet nitrenes obtained by irradiation of rigid matrices at 77 K, but the actual spectra were not depicted. Unsubstituted PhA was not studied and information on singlet intermediates was also absent.

This information was obtained subsequently by Sundberg, et al.[31] In the flash photolysis of a 10^{-4} M solution of PhA in hexane, an intermediate with an absorption spectrum in the region up to 300 nm was formed. The main reaction product was an unidentified polymeric compound, but the possibility that trace quantities of aniline and azobenzene were formed was not excluded. The presence of oxygen had no effect on the monomolecular kinetics of the increase in the unidentified absorption at a wavelength of 366 nm,

and $\tau_{1/2} \sim 5$ μs (22 °C) was found. It was suggested that the intermediate with this lifetime and spectroscopic properties ($\lambda < 300$ nm) has the stucture of a bicyclic azirine (benzazirine, BA), which is an isomer of singlet PhN.

The structure of BA as an intermediate in the formation of azepines was first proposed for thermal reactions of PhA and then extended to photochemical reactions.[32]

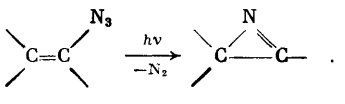
It was shown by Sundberg, et al.[31] that in the flash photolysis of PhA in the presence of dibutylamine, BA reacts with the amine with a rate constant of $k = 9.7 \times 10^5$ M^{-1} s^{-1} (hexane) and 3.5×10^7 M^{-1} s^{-1} (acetonitrile), and the primary product of this reaction—2-dibutylamino-1*H*-azepine—was detected, which then rearranged to the final 3*H*-isomer:



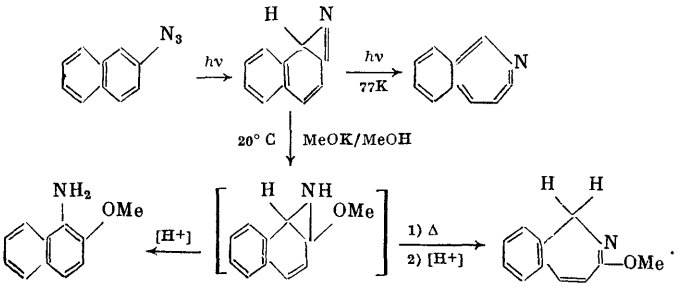
The yield of azepine by flash photolysis (from the increase in absorption) was 85%, and the recorded quantum yield for its formation during stationary photolysis $\Phi = 0.42$. The latter figure is in good agreement with the value of the quantum yield of photodissociation of PhA ($\Phi_{-PhA} = 0.53$),[33] if it is assumed that both flash and stationary photolysis give the same percentage (85%) conversion of azide to azepine. Moreover, this is in agreement with the estimate of Reiser and Leyshon[27] that 12–13% of phenylnitrene is generated in the triplet state, which does not give an azepine.

After dehydroazepine was detected amongst the photolysis products of PhA at 8 K, the reaction scheme involving bicyclic azirine became a subject of criticism.[20] DHA instead of BA was proposed as the isomer of singlet PhN and intermediate in the reactions of PhA. Chapman and Le Roux[20] related the prejudice against DHA to the results of quantum-chemical calculations[34] which showed that the structure of DHA must be less stable than that of BA or even singlet nitrene. However, the low-temperature studies of photolysis of Ph and the isomeric pyridyl diazomethanes provided clear evidence for the existence of such structures.[22]

On the other hand, supporters of the benzazirine structure doubted the validity of making direct use of the results of low-temperature studies to interpret the data obtained at a normal temperature. Moreover, evidence in favour of the BA structure was provided, for example, by the preparative isolation of azirines in the photolysis of vinyl azides:[35]



For naphthyl azides the formation of azirines was demonstrated in photolysis in argon matrices (12 K) from the appearance of bands in the region of 1708–1738 cm^{-1} in the IR spectra, and on further photolysis the azirines were converted to dehydroazepines (bands at 1910–1930 cm^{-1}).[36] At 20 °C photolysis of 2-naphthyl azide (and 2-anthryl azide) in methanol in the presence of potassium methoxide gave different final products depending on the subsequent conditions of treatment. On neutralisation directly after irradiation, 1-amino-2-methoxynaphthalene was formed, while on boiling the irradiated mixture or keeping it at 20 °C for several hours, methoxybenzazepine was isolated.[37] Rigaudy, et al.[37] suggested that a fairly stable intermediate with an aziridine structure is formed by photolysis, since the strongly alkaline medium inhibits its rapid isomerisation. These latter two studies are combined in the following scheme:



Thus, in contrast to phenyl azide, for condensed aryl azides the formation of aziridine structures during photodissociation has been demonstrated experimentally.

Without going further into the experimental details, it may be concluded that, despite the possible variants of the isomeric intermediates and the assertion that the same intermediates are formed at both 77 K and 20 °C,[30] at least for phenyl azide the majority of the results suggest that direct photolysis at room temperature mainly gives singlet PhN while low-temperature photolysis yields mainly triplet PhN.

We shall now turn to an examination of the data on the mechanism of formation of azo compounds in the decomposition of aromatic azides. Frequently the authors have confined themselves solely to an assertion that triplet nitrene takes part in this reaction without specifying the scheme in any detail. Nevertheless, three main reaction routes can be distinguished:[38–40]

dimerisation of nitrene in the triplet state:

$$2Ar-\dot{N}^{\cdot} \rightarrow Ar-N=N-Ar\ ,$$

reaction of triplet nitrene with the initial azide:

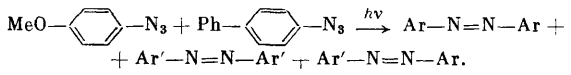
$$Ar-\dot{N}^{\cdot} + ArN_3 \xrightarrow[-N_2]{} Ar-N=N-Ar\ ,$$

dimerisation of aminyl radicals followed by oxidation of diarylhydrazine by nitrene:

$$Ar-\dot{N}^{\cdot} \xrightarrow{[H]} ArNH^{\cdot} \longrightarrow Ar-NH-NH-Ar \xrightarrow{2ArN} \rightarrow\ Ar-N=N-Ar + 2ArNH\ .$$

In terms of the PACD reaction under consideration, it is definitely the second scheme, in which the formation of an intermediate that decomposes to two nitrenes, namely, propagation (branching) of the chain (see below) is assumed, that is the specific reaction route of the greatest interest (in the first and third schemes chain termination occurs). There are a number of ambiguous results obtained by different authors which can either be used in support of a reaction between triplet nitrene and azide, to refute such a reaction, or included in an explanation of experimental results for a scheme that does not involve nitrenes.

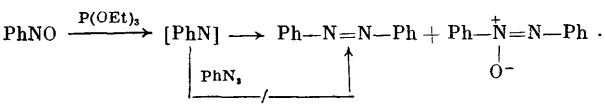
Thus, in the photolysis of a mixture of two azides—azidoanisole and azidodiphenyl—in benzene at 20 °C, almost equal quantities (about 30%) of all three possible azo compounds were formed:[41]



The formation of an asymmetric azo compound in this case may be due to the dimerisation of two different nitrenes that are formed simultaneously during photolysis, but the reaction of a single nitrene with another azide cannot be excluded.

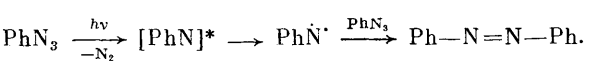
However, later findings on the thermolysis of a mixture of azides—the same *p*-azidoanisole and 1-methyl-3,5-diphenyl-4-azidopyrazole—at 80 °C testify against a reaction between nitrene and azide.[42] The temperature was selected in such a manner that the first azide was stable and only the second azide decomposed. These are the most favourable conditions for proving that a crossed reaction occurs between one nitrene and another azide. Despite the fact that *p*-azidoanisole was present in fivefold excess, the authors did not manage to detect any appreciable quantities of the product of this reaction.

Attempts were made to detect the reaction of nitrene with a suitable azide by generating the nitrene through reaction of a nitroso compound with triethyl phosphite.[43] It was found in this case that when PhA was added to the reaction mixture with nitrosobenzene, PhA did not undergo reaction and the main reaction products were azoxybenzene and tar, azobenzene being formed in trace amounts:

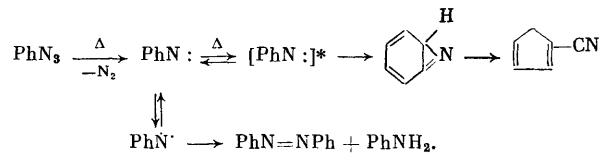


Although it was shown for a number of nitroso compounds that deoxygenation occurs via a nitrene intermediate,[44] in general it may not take place in this manner.[45] Therefore the possibility that it may nevertheless occur for other azides and/or other reaction conditions with nitrene giving an azo compound should not be completely ruled out.

The feasibility of this reaction occurring in the gas phase was demonstrated by Lehman and Berry.[46] The spectrum of PhN was recorded in the region of 340–370 nm on flash photolysis of PhA vapour in the presence of an inert gas—a quencher of excess excitation (rapid isomerisation occurred when the gas was not added). Azobenzene was formed (yield 6%) with a pseudo-monomolecular rate constant of 5×10^4 s^{-1}, from which the rate constant of the bimolecular reaction between PhN and PhA was determined as $k_{II} = 1.3 \times 10^{-12}$ cm^3 s^{-1}. The authors[46] note that because of the very high rate of reaction between PhN and PhA it was not possible to determine the rate of dimerisation of PhN, since higher concentrations of the latter were needed for this.



On the other hand, in an earlier study[47] of the pyrolysis of PhA in the gas phase (300–670 °C) it had been concluded from the dependence of the yield of azobenzene and aniline (and cyanocyclopentadiene) on the rate of admission of PhA into the hot zone (a decrease in yield of the first two with an increase in rate, namely, concentration, of reactant) that azobenzene was formed by the dimerisation of triplet PhN rather than as a result of a reaction with PhA:



It would appear that thermal generation achieved considerably higher concentrations of PhN than by photolysis.

On irradiaiton of a degassed 10^{-4} M solutions of 1-azidonaphthalene in hexane with low-intensity light, a mixture of amines was formed and the azo compound was not detected.[30] However, the latter was obtained as the main product by slow thawing of matrices irradiated at 77 K and by flash photolysis of solutions of this azide in organic solvents. The kinetics of the increase in absorption of azonaphthalene at a wavelength of 400 nm corresponded to second-order, and the rate constant for recombination of triplet nitrene was determined as $k = 5.5 \times 10^8$ M^{-1} s^{-1}. It was shown in the same study that on flash photolysis of a solution of 1-azidoanthracene in ethanol with light of reduced intensity, when only about 5% of the azide was converted to nitrene, the kinetics of the disappearance of nitrene corresponded to first-order with $\tau_{1/2}$ of 5 μs, from which the bimolecular constant for reaction between nitrene and azide was obtained ($k = 5 \times 10^8$ M^{-1} s^{-1}).[30]

At the same time, as was mentioned above, in studying the reactions of PhA using flash photolysis, Sundberg, et al.[31] did not observe the spectrum of triplet PhN at normal temperatures. The primary reaction product (not more than 30 μs after the flash) was benzazirine[31]—an isomer of singlet PhN—or dehydroazepine, as Chapman, et al. maintain.[20]

Thus, an azo compound may be formed by reaction of an azide and nitrene (which does not have to be in the triplet state),[48] but if an alternative exists for the formation of the azo compound, the nitrene reacts in a different manner.

With regard to the labile compound formed as an intermediate in the reaction between nitrene and azide, its structure was first suggested as a tetraazadiene derivative[41] ("tetrazene"), and it was assumed that it decomposes to an azo compound and nitrogen.

Subsequently, in a review Smith[38] extended this idea by the introduction of 1,2- and 1,4-isomers of substituted tetraazadiene, where the possibility of the latter decomposing to two nitrene molecules had already been admitted. Smith[38] noted that at a given ratio of the rate constants of the intermediate reactions dissociation of aryl azide will occur with first-order kinetics and it will not be possible to distinguish the formation of the azo compound by dimerisation of nitrene or by reaction of nitrene with azide. The data published by that time on the thermolysis of aryl azides suggested that the kinetics of the disappearance of azide are always first-order regardless of whether the final product is an azo compound or another product.[38]

III. Photoinitiated autocatalytic chain decomposition of aromatic azides

Let us examine the literature data of Waddell, et al. on the PACD reaction of aryl azides.

The first report on the PACD reaction of phenyl azide appeared in 1982.[1] For the photodissociation of PhA at 77 K in 3-methylpentane a value of $\Phi_{-PhA} = 0.49$ was determined (in good agreement with the results of Reiser and Marley).[33] It transpired, however, that the values of Φ_{-PhA} in solution were markedly dependent on the concentration of PhA, the solvent, and the presence of oxygen. A value of $\Phi_{-PhA} = 300$ was obtained for a 0.03 M solution of PhA in acetonitrile, and the yield decreased sharply on dilution, in the presence of oxygen, or by the addition of 2,3-dimethylbutene or tetracyanoethylene. The quantum yield of considerably greater than unity was also obtained for substituted PhA in degassed solutions: $\Phi = 210$ for *o*-tolyl azide (0.069 M), while $\Phi = 60$ for *p*-tolyl azide (0.066 M).

The authors reported that at the initial stage of photolysis in the spectroscopic curves an isobestic point was maintained at 261 nm, the absorption due to PhN at 250 nm decreased, and the absorption due to azobenzene in the region 270–360 nm increased. The latter was the sole reaction product with short irradiation times and a low conversion of PhA, on further irradiation there was considerable tar formation. It was shown by Reiser and Leyshon[27] that under similar conditions—photolysis of hydrocarbon solutions of PhA to 2% conversion—the main products are azobenzene and tar in equal ratio.

In order to explain the experimental phenomena, the authors took as a basis the possibility suggested by Horner, et al.[41] that nitrene reacts with azide to form an intermediate tetrazene. However, it was assumed that in accordance with Smith,[38] only the 1,2-isomer of the latter decomposes to azobenzene and nitrogen, while 1,4-diphenyltetraazadiene (DPTA) yields a molecule of nitrogen and two PhNs, thus propagating the chain reaction:

$$\mathrm{PhN + PhN_3 \longrightarrow Ph{-}\overset{+}{N}{=}N{-}Ph + Ph{-}N{=}N{-}N{=}N{-}Ph,}$$
$$\mathrm{\underset{N=\bar{N}}{|}}$$

$$\mathrm{Ph{-}\overset{+}{N}{=}N{-}Ph \longrightarrow Ph{-}N{=}N{-}Ph + N_2,}$$
$$\mathrm{\underset{N=\bar{N}}{|}}$$

$$\mathrm{Ph{-}N{=}N{-}N{=}N{-}Ph \rightarrow 2PhN + N_2.}$$

The formation of two PhNs directly by reaction of PhN with PhA without intermediates was also assumed:

$$\mathrm{PhN + PhN_3 \rightarrow 2PhN + N_2.}$$

The authors cited the formation of stable complexes between 1,4-diaryltetraazadiene and transition metal ions[49] as well the mass spectrometric reaction of the PhN anion with PhA to form the DPTA anion[50] as confirmation of the existence of the tetraazadiene structure.

An attempt was made[2] to demonstrate the involvement of DPTA as an intermediate in the decomposition of PhA by nanosecond laser photolysis (excitation wavelength 266 nm, pulse 10 ns) in a continuous-flow cuvette. It transpired that the spectroscopic properties of the intermediate were virtually the same for dilute and concentrated solutions. The spectrum was preserved with virtually no changes throughout the whole of the timescale studied—from 15 ns to 5.45 μs—whether oxygen was present or not.

Feilchenfeld and Waddell[2] conclude on the basis of the lifetimes that were determined that the spectrum observed in the region of 330–500 nm belongs to a single compound, and citing studies already reviewed on the photolysis of azides at 77 K[17] and 20 °C[30] and their own results at 77 K[3] they attribute the spectrum to triplet PhN. We should note that only the spectroscopic region and not the spectrum itself matches the results of Reiser, et al.,[17] while PhA was not investigated at all in the other study.[30] The reasons for the absence of a reaction between PhN and oxygen are not discussed, although reactions of this type usually takes place at a considerable rate.

A parallel study was made of the spectrum of the intermediate derived from phenyl isocyanate, which loses a CO molecule on photolysis and also yields phenyl nitrene:

$$\mathrm{PhNCO \xrightarrow{h\nu} PhN + CO.}$$

The spectra of the intermediates from both compounds as well as the lack of dependence of the shape of the spectrum on the concentration of PhA while the quantum yield of photodissociation of PhA changed by a factor of 10 made it possible for Feilchenfeld and Waddell[2] to conclude that there was no spectroscopic evidence for the formation of diphenyltetraazadiene as an intermediate (the spectroscopic region of 250–550 nm and a period of time up to 6 μs after a flash).

This conclusion was supported[3] by a study of the PACD reaction of phenyl isocyanate. A quantum yield of greater than unity was observed for this compound also, but formation of a tetraazadiene-type of structure from it is impossible. An estimate was made of the number of branches (length of chain n) of the autocatalytic chain on the basis of the ratio $2^n = \Phi/\Phi_0$, where Φ_0 is the quantum yield of dissociation at infinite dilution. For phenyl isocyanate $\Phi_0 = 0.057$, which is an order less than the corresponding value for PhA; but similar values of n were obtained at similar concentrations for both compounds.[3] When $[PhN_3] = 0.03$ M, $n = 9.2$; while when [PhNCO] = 0.015 M, $n = 7.35$. Unfortunately, a "crossed" experiment was not carried out. The spectra of PhA and phenyl isocyanate differ sufficiently for a particular reactant to be excited selectively: for PhA $\lambda_{max} = 250$ nm ($\varepsilon = 1 \times 10^4$ M^{-1} cm^{-1}) with a long-wavelength limit of the spectrum at about 292 nm, for phenyl isocyanate $\lambda_{max} = 227$ nm ($\varepsilon = 1 \times 10^4$ M^{-1} cm^{-1}) with a long-wavelength limit at about 280 nm (both spectra in acetonitrile).[2] Involvement of one reactant in the reaction when the other is excited while retaining high quantum yields and the formation of azobenzene would act as a significant argument in support of the reactions detected by Waddell, et al.[1–8] However, there is no information about this in these studies.

Despite the conclusion[3] that the chain reaction occurs through the phenyl nitrene-sensitised decomposition of PhA or phenyl isocyanate to give two PhNs:

$$\mathrm{PhN + PhN_3 \rightarrow 2PhN + N_2,}$$
$$\mathrm{PhN + PhNCO \rightarrow 2PhN + CO,}$$

intermediates such as diphenyltetraazadiene and its isomeric compounds were subsequently introduced again to explain the PACD reaction.[4,5]

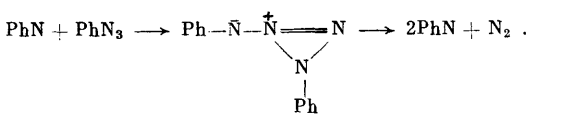
In one of these studies[4] the main focus of attention is a detailed analysis of the reaction products of PhA under different conditions. It is verified that the primary photoproduct in the irradiation of PhA in an inert atmosphere is (*E*)-azobenzene, which is then converted to the (*Z*)-isomer with a quantum yield of $\Phi = 0.14$. The data on the quantum yield of photodissociation of PhA differ somewhat from those reported previously,[1] when $\Phi_{-PhA} = 3$ at [PhA] = 3×10^{-5} M (acetonitrile, atmosphere of N_2) was recorded. In the later study[4] $\Phi_{-PhA} = 0.72$ when [PhA] = $10^{-5}-10^{-4}$ M; the latter figure is in closer agreement with the results of Reiser and Marley,[33] who found $\Phi = 0.53$.

In the presence of oxygen the primary product of the photolysis of PhA was established as nitrobenzene, which on further irradiation is converted to nitrobenzene and azobenzene. Since the value of Φ_{-PhA} in dilute solution did not depend on the presence of oxygen, it was concluded that azobenzene is formed under these conditions, probably by dimerisation of phenylnitrene. In concentrated solution oxygen significantly reduced the quantum yield of photodissociation of PhA, but when [PhA] > 3×10^{-3} M, $\Phi_{-PhA} > 1$ even in a solution saturated with oxygen.

In a later study[5] the range of concentrations of PhA studied was extended from 10^{-5} M to 0.218 M. Spectroscopic studies indicated that an isobestic point was maintained at 271 nm, i.e. in the opinion of Lee Go and Waddell,[5] the two-component nature of the system remained up to 40% conversion of PhA. High-performance liquid chromatography confirmed that the content of azobenzene increased linearly as the concentration of PhA decreased.

The quantum yield was determined up to a conversion of 3%; when [PhA] = 2.3×10^{-5} M, $\Phi_{-PhA} = 0.5$ was reported, while the maximum value of $\Phi_{-PhA} = 4330$ was obtained when [PhA] = 0.137 M. It was shown that the dependence of Φ_{-PhA} on the logarithm of the concentration of PhA is not linear but in fact has an exponential form, whereas the length of the chain n increases linearly with log [PhA].

In order to explain the autocatalytic chain reaction, the schemes already considered were supplemented with the possible intermediate formation of a triaza compound that decomposes to two phenylnitrenes and nitrogen:



The authors carried out an analogous process to this reaction with chain branching reactions during explosions in the gas phase and solid state, such as for metal azides. They note, however, that such reactions have not been recorded in solution. Since it was assumed in calculations of the chain length that the efficiency of the chain propagation stages is equal to unity (i.e., at the intermediate stages PhN is not lost through side reactions), the actual values of n could be even higher.

On repeated study of concentrated solutions of phenyl azide and phenyl isocyanate using pulsed laser photolysis, Feilchenfeld and Waddell[6] recorded a nonexponential decrease and oscillation of the induced optical density over the wavelength range 450–550 nm with a period of about 10 μs. For example, with a PhA concentration of 0.5 M, an increase in D_{450} occurred over a period of about 20 μs after a flash, then on the declining section of the curve there were six cycles of increase and decrease in optical density that were unaffected by the presence of oxygen. With a decrease in [PhA] the time for reaching a maximum value of D_{450} and the number of cycles decreased, and when [PhA] was 5×10^{-4} M the maximum of D was reached after 2–3 μs followed by a monoexponential decrease with a lifetime of 2.8 μs. A similar monoexponential decrease occurred for concentrated solutions in the presence of tetracyanoethylene.

Feilchenfeld and Waddell[6] concluded from these results and also the symbatic relationship between the decrease in the number of cycles on the oscillograms and the length of chain n and the decrease in concentration of PhA that they were detecting an oscillation in the content of triplet PhN in the reaction mixture.

The maximum value obtained—$\Phi_{-PhA} = 15300$ when [PhA] = 0.722 M in degassed acetonitrile and $\Phi_{-PhA} = 2280$ when [PhA] = 0.793 M in a solution saturated with oxygen—was subsequently reported.[7] An attempt was made to represent the PACD reaction of phenyl azide quantitatively. Four reactions form the basis of the kinetic scheme:

$$PhN_3 \xrightarrow{h\nu} PhN + N_2, \quad (1)$$

$$PhN + PhN_3 \xrightarrow{k_2} [Z] \longrightarrow 2PhN + N_2, \quad (2)$$

$$PhN + PhN_3 \xrightarrow{k_3} Ph{-}N{=}N{-}Ph + N_2, \quad (3)$$

$$2PhN \xrightarrow{k_4} Ph{-}N{=}N{-}Ph. \quad (4)$$

The scheme does not distinguish between the direct formation of two phenylnitrenes by reaction of PhN with PhA and the formation of an intermediate Z. On the basis of a quasi-steady-state condition for the PhN concentration with a fixed intensity of incident light I_0 and low conversions of PhA the following ratio was obtained:

$$\alpha = \beta + \lg\left[(k_2+k_3)^2\Phi_1 N_0/2k_4\right],$$

where: $\alpha = \lg\left[(\Phi-\Phi_1)^2/(1+2Q(\Phi-\Phi_1))\right]$,

$$Q = (k_2-k_3)/\left[2\Phi_1(k_2+k_3)\right],$$

$$\beta = \lg\left[[PhN_3]^2 V_0/(I_0(1-10^{-A}))\right],$$

Φ_1 is the quantum yield of reaction (1), $\Phi = \Phi_{-PhA}$, N_0 is the Avogadro number, V_0 is the volume of irradiated solution, and A is the optical density at the wavelength of incident light at an initial moment in time. All of the parameters in α and β were determined experimentally, with the exception of Q, whose value was found by trial and error. For degassed solutions a linear correlation between α and β was obtained with a gradient of unity when $Q = 0.0019$. For the complete series of 56 values of Φ_{-PhA} ranging from 0.3 to 15000 in solutions that were degassed or saturated with air and oxygen over a concentration range of 1.4×10^{-5} to 0.793 M, a linear correlation was also obtained, but with $Q = 0.0004$.

Costantino, et al.[7] consider that the excessively low values of Q indicate that the constants k_2 and k_3 are of virtually the same magnitude, which is not unexpected. The derived equation also accounts for the observed decrease in Φ_{-PhA} as the light intensity increases.

In the last of the series of publications by Waddell, et al.[8] on the PACD reaction, tetraazadiene is again rejected as an intermediate, and the species with the composition PhN is assumed to be the chain

carrier. In order to choose between four possibilities — singlet PhN, triplet PhN, benzazirine, or dehydroazepine — the authors studied the reactions of substituted phenyl azides and investigated triplet sensitisation†.

For all of the azides studied, the values of the quantum yields of photodissociation Φ were greater than 1. For example, at concentrations of 0.1 M, Φ = 81 for 4-bromo-PhA, Φ = 143 for 2,4,6-tribromo-PhA, and Φ = 434 for 4-nitro-PhA (for PhA itself, Φ = 1800 was found under similar conditions).[8] The quantum yields increased exponentially with the concentrations of the azides and at small degrees of conversion the corresponding azo compounds were established as photoproducts.

The following evidence illustrates that triplet nitrene is the intermediate that drives the chain:

for bromo-substituted PhAs, $\Phi \gg 1$, and it has been experimentally demonstrated for these compounds that because of accelerated intersystem crossing (heavy atom effect) they rapidly reach a triplet state;[51]

for nitro-PhA, $\Phi \gg 1$ also, and the formation of triplet nitrene has been demonstrated experimentally for this compound as well;[52]

in triplet-sensitised photodissociation of 4-nitro-PhA, $\Phi \gg 1$ also occurred regardless of the presence of n-butylamine in the mixture, whereas in direct photolysis the quantum yield decreased sharply on addition of the amine (a "singlet trap").

In summarising our review of the series of publications of Waddell, et al. on the photoinitiated autocatalytic chain decomposition (PACD) reaction of phenyl azide, it may be concluded that, despite the ambiguity of certain assumptions such as that concerning the spectrum of the intermediate in the photolysis of PhA at 20 °C, the actual existence of a chain reaction is not doubted by these authors.[1–8]

However, this cannot be said of other research workers, and we shall now turn to a discussion of their results.

IV. Different routes in the photochemical reactions of aryl azides

The first evidence for a lack of dependence of the quantum yield of photodissociation of aryl azides on their concentration was actually obtained much earlier than the first study on the PACD reaction. In 1968 Reiser and Marley[33] reported that over a concentration range from $10^{-5}-10^{-2}$ M the quantum yield of dissociation of 1-naphthyl azide was constant and equal to 1.00 ± 0.02.

The first studies in which the disagreement with the results of Waddell, et al. is directly indicated were published in 1984. On irradiation of 1-azido-4-naphthylsulphonic acid with light at 310 nm the quantum yield of dissociation (0.66) did not depend on the concentration of azide, the presence of oxygen, or the presence of a second azide — *p*-azidobenzenesulphonic acid, which hardly absorbs at all at 310 nm and whose concentration exceeded that of the naphthyl azide by a factor of up to 100.[53]

We should note again that selective generation of one nitrene, let us say ArN, in the presence of another azide—Ar′N_3—and isolation of an asymmetric ("crossed") azo compound—ArN=NAr′—is a powerful argument in favour of a reaction between nitrene and azide. Geiger, et al.[53] give no information about the photolysis products, but they concluded that the second azide is not involved in a reaction with the nitrene obtained from the first azide.

The absence of a chain reaction could be due to the structural changes in the azides, but these changes should in fact have resulted in an intensification of the expected effect. Thus, acceptor substituents in PhA are known to increase the activity of the nitrene[54] and assist its formation in the triplet state at room temperature.[51,52] Replacement of the benzene ring by a naphthalene ring effects it in the same way.[30,37]

In the same year Shrock and Schuster[55] published the results of a detailed examination of the photochemical properties of PhA using flash photolysis with identification of the reaction products. In contrast to the results of Waddell, the yield of azobenzene depended only slightly on the degree of conversion of PhA and, what is more significant, decreased as the concentration of PhA increased — when [PhA] > 10^{-3} M virtually all of the PhA was converted to polymer. Changing from a stationary source of radiation to a laser also led to a marked reduction in yield, despite the fact that intermediates with concentrations 20 000 times higher were generated at the same time. The spectrum of the intermediate with λ_{max} at about 340 nm (hexane) which was formed less than 20 ns after a flash and with a lifetime of about 100 μs was attributed by the authors, also in contrast to Waddell, to a single intermediate, namely dehydroazepine, since this intermediate was not formed by triplet sensitisation, did not react with oxygen, and did not react with the standard singlet "trap" — diethylamine.

The somewhat contradictory nature of this study[55] should be noted. Shrock and Schuster report that PhA effectively quenched the triplet state of benzophenone with a rate constant of $k = 2 \times 10^9$ M^{-1} s^{-1} (acetonitrile) and considerable quantities of azobenzene were formed at the same time, but subsequently the low efficiency of photodissociation of PhA by triplet sensitisation is indicated — about 20% of the Φ_{-PhA} during direct photolysis — as well as low yields of azobenzene in the sensitised reaction. However, it was found previously[56,57] for concentrated solutions that the quenching constants had values that were lower by a factor of 10^3 and that every second sensitised molecule of PhA dissociates. In order to explain this discrepancy in their results, Shrock and Schuster[55] mention the values of $\Phi_{-PhA} \gg 1$ obtained by Waddell for concentrated solutions, but in calculations $\Phi = 0.5$ is used and the results of their own measurements of the quantum yield are not given. In interpreting the results the authors[55] believe that a reaction of triplet PhN (PhN^3) or its precursor occurs with PhA, and they refer to the studies of Waddell, but in contrast to the latter, they indicate that a polymer is formed as the final product rather than azobenzene:

$$PhN^3 + PhN_3 \xrightarrow[-N_2]{} [\dot{P}hN]_2 \xrightarrow[-nN_2]{nPhN_3} [PhN]_{n+2} .$$

† Raising the question in this way seems strange since the evidence cited by Waddell, et al.[1–7] that it is indeed triplet nitrene which is the chain carrier has already been examined above. It may be assumed that the article[8] was published in response to the criticism of Leyva, et al.[51] of the studies on the PACD reaction. Jenkins, et al.[8] refer to the formation, as demonstrated in two studies,[51,52] of triplet nitrenes in the photolysis of tribromo-PhA and 4-nitro-PhA at room temperature, but nothing is said about the lack of confirmation that triplet PhN is formed under similar conditions and hence the impossibility of it fulfilling the intended function. Moreover, it is shown by Liang and Schuster[52] that the azo compound is formed as a result of the dimerisation of 4-nitro-PhN rather than by a reaction with the azide (for further details, see below).

In fact the only point of agreement between Shrock and Schuster[55] and Waddell, et al.[1-4] is that azobenzene is formed from triplet PhN.

The other study by Shrock and Schuster published at that time[58] on the photochemical properties of polynuclear azides did not shed light on this question. Certain arguments were put forward in favour of both the possibility of triplet nitrene reacting with azide and the formation at the same time of an intermediate that subsequently decomposes to the azo compound.

On irradiation of a mixture of two azides—PhA and 1- or 2-naphthyl azide (NA)—with low-intensity light of wavelength 350 nm, both azonaphthalene and the "crossed" asymmetric product, but not azobenzene, were obtained.

$$C_{10}H_7N_3 \xrightarrow[-N_2]{h\nu} C_{10}H_7N \xrightarrow[-N_2]{PhN_3} C_{10}H_7N{=}NC_{10}H_7 + C_{10}H_7N{=}NPh.$$

In contrast to the study of Horner, et al.[41] considered above, in which an asymmetric azo compound was also isolated, Shrock and Schuster[58] had a clearer result since light was absorbed by only one azide (NA). On laser photolysis (337 nm) the same mixture yielded only azonaphthalene, from which it was concluded that the rate of reaction of nitrene with azide is much lower than the rate of dimerisation of nitrene, the rate constant of which was determined as $k = 1 \times 10^9$ M^{-1} s^{-1} for 1-NA (but compare with the reaction of anthrylnitrene with anthryl azide:[30] $k = 5 \times 10^8$ M^{-1} s^{-1} and the reaction of PhN with PhA in the gas phase: $k = 1.3 \times 10^{-12}$ cm^3 s^{-1}).[46]

Interesting observations were made in analysing the products of stationary photolysis after standing in the dark. It transpired that the yields of azo compounds determined directly after photolysis gradually increased over a period of several hours, and in experiments with two azides this applied to both reaction products. Since the content of azides on standing in the dark did not change and the yield of azo compounds from laser photolysis remained constant and equal to that measured directly after irradiation, it was concluded that an additional quantity of azo compound is formed by decomposition of a fairly stable intermediate obtained by reaction between nitrene and azide. Shrock and Schuster,[58] with reference to the study of Waddell, et al.,[1] assumed that the intermediate had the structure of a tetraazadiene (tetraazine)[58] and defined the scheme for formation of the crossed azo compound as

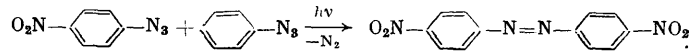
$$ArN + Ar'N_3 \longrightarrow$$

$$\longrightarrow [Ar{-}N{=}N{-}N{=}N{-}Ar'] \xrightarrow[-N_2]{} Ar{-}N{=}N{-}Ar'.$$

There is no spectroscopic or any other form of evidence for a tetraazadiene. Unfortunately, data on the quantum yields for formation of the azo compounds and photodissociation of the azides are also absent. On photolysis of solutions of pure PhA it was noted that the yield of azobenzene did not vary on standing in the dark.[55]

A direct refutation of the results of Waddell on the PACD reaction of aryl azides was made in subsequent studies of Schuster, et al.[59-61]

An investigation of the photochemical properties of 4-nitrophenyl azide showed that on irradiation of degassed acetonitrile or benzene solutions with low-intensity light the main reaction products were the azo compound (75%) and polymer, while the azo compound (>96%) was exclusively formed on laser photolysis[59] (a result that is in direct contradiction to that obtained by the same authors for PhA itself).[55] It followed from this that the azo compound was obtained by dimerisation of nitrophenyl azide; the experimental rate constant of dimerisation was $k = 1 \times 10^9$ M^{-1} s^{-1}. This conclusion was supported by an experiment with two azides. On irradiation of a mixture of PhA and 4-nitro-PhA under conditions where light was absorbed solely by the latter (313 nm), in contrast to the mixture of PhA and naphthyl azide,[58] neither a "crossed" azo compound nor azobenzene were formed, and only dinitroazobenzene—the dimerisation product of nitro-PhN—was isolated:



A quantum yield of $\Phi = 434$ was reported by Waddell, et al.[8] for concentrated (0.1 M) solutions of 4-nitro-PhA. Liang and Schuster[59] undertook a detailed examination of the dependence of Φ_{-N_2} on the concentration of azide. It transpired that over the concentration range 0.001–0.1 M azide, the quantum yield remained constant and equal to 0.7. A similar result was obtained for 3-nitro-PhA. It was therefore concluded[59] that there was no evidence to support the postulated PACD reaction of 4-nitro-PhA.

Another substituted PhA—4-dimethylaminocarbonylphenyl azide—was studied[60] by means of flash photolysis with the IR and electronic absorption spectra being recorded. Like PhA itself, irradiation of this azide in the presence of diethylamine resulted in the formation of a substituted 3*H*-azepine. On laser photolysis an intermediate was detected that was formed 20 ns after a pulse, and the kinetic curve for disappearance of this intermediate had an exponential form with a half-life of 1 μs, the rate of decay increasing in direct proportion to the content of amine. The spectroscopic properties—absorption in the UV region at 350–370 nm and in particular a band at 1887 cm^{-1} in the IR spectrum—provided clear evidence for the dehydroazepine structure of the intermediate. The characteristic band due to an azirine at 1730 cm^{-1} was absent. Since the kinetic and spectroscopic data and the reaction product accorded for dimethylaminocarbonyl-PhA and PhA,[55] Schuster, et al.,[60] by drawing a parallel between the properties of these two azides, concluded that the spectrum of DHA had been incorrectly attributed by Waddell, et al.[2] to triplet PhN and that the data on the "hypothetical molecular explosion in solution" should be carefully checked.

In order to explain the formation of 70% azo compound during stationary photolysis of dimethylaminocarbonyl-PhA in cyclohexane in the absence of an amine (and oxygen), it was suggested[60] that DHA may isomerise "with moderate efficiency" to triplet nitrene, probably via the singlet state.

The method of time-resolved IR spectroscopy was applied to PhA by Li, et al.[61] On laser photolysis of degassed heptane solutions of PhA, an intense band at 1887 cm^{-1} due to the cumulated double bonds of DHA was recorded, which shifted, in accordance with theory, to 1877 cm^{-1} when PhA enriched with ^{15}N isotope on the N(1) atom (joined into the ring) was used. The kinetics of the decrease in absorption of DHA had an exponential character, and the rate of decrease proved to be directly proportional to the concentration of PhA, from which the rate constant for reaction between PhA and DHA was obtained ($k = 7.5 \times 10^4$ M^{-1} s^{-1}). In the opinion of Li, et al.,[61] the reaction of DHA with PhA may, at least partly, account for the formation of tar (polymer) and the quantum yields of $\Phi_{-PhA} > 1$ in the photolysis of concentrated solutions of PhA. The lifetime of DHA (4.8 μs) was obtained by

extrapolation to zero concentration; this characterises the rate of irreversible conversion of DHA to triplet PhN‡.

In addition to PhA, 13 of its derivatives were also studied by Li, et al.[61] The formation of DHA was detected during photolysis at room temperature for all of them, with the exception of 4-dimethylamino-PhA. It had been demonstrated previously for the latter that singlet nitrene which is formed less than 25 ps after absorption of a quantum of light is completely converted to the triplet state over a period of 120 ps.[62] Relatively small quantities of DHA occurred for nitro- and iodo-substituted PhA because of the increase in the rate of intersystem crossing of singlet nitrene to the triplet state.

The possible occurrence of a chain reaction involving triplet PhN was examined.[61] The principal argument in favour of such a reaction was the increase in quantum yield of photodissociation to values of $\Phi \gg 1$ on increasing the concentration of PhA.[1-8] But Li, et al.[61] believed that at a high concentration it was doubtful whether any molecules of PhA would reach the triplet state PhN^3 after elimination of nitrogen. For example, they estimated that even when [PhA] = 0.05 M, less than one in twenty dissociated PhA molecules would be converted to PhN^3. This is also supported by the fact that with an increase in the concentration of PhA, the yield of azobenzene formed from PhN^3 decreases sharply. It was concluded[61] that the results obtained did not completely rule out the feasibility of a possible chain reaction but they limited its potential significance.

Thus, repeated studies of the properties of the intermediate formed during photolysis of PhA at room temperature clearly indicated a dehydroazepine structure rather than triplet phenylnitrene. However, the latter, according to the EPR data, is undoubtedly present in the photolysis products of PhA in rigid matrices at low temperatures. Leyva, et al.[51] proposed that competition between the two routes for conversion of singlet PhN—thermally activated isomerisation to DHA and temperature-independent intersystem crossing to PhN^3—leads to an almost complete change in reaction route on lowering the temperature from 20 °C to 77 K.

A study of the effect of temperature on the ratio of the final products of photolysis as well as the joint application of EPR, absorption and emission spectrosocpy supported this theory. It transpired that both intermediates—DHA obtained by laser photolysis of PhA in acetonitrile solution at 20 °C and PhN^3 obtained by photolysis in an EPA matrix (diethyl ether : isopentane : ethanol = 5 : 5 : 2) at 77 K—absorb in the region of 330–450 nm, which explains the certain amount of confusion in assigning the spectra. Nevertheless, the spectra are sufficiently clear for both intermediates to be distinguished: the spectrum of PhN^3 has distinct maxima at 490, 382, and 303 nm, which are absent in the spectrum of DHA (λ_{max} = 345 nm).

Leyva, et al.[51] demonstrated once again that the spectrum obtained at 77 K is actually that of PhN^3 rather than a mixture of products (in contrast to the previous findings of Reiser, et al.,[17] in which the spectrum of PhN^3 proved to be contaminated with DHA). Firstly, the EPR, absorption, and fluorescence spectra appeared and disappeared (on further photolysis) in the same way; secondly, the O–O bands in the latter two spectra were the same; and thirdly, the fluorescence excitation spectrum corresponded satisfactorily to the absorption spectrum (see the study of Smirnov and Brichkin).[23] The spectrum of DHA at 20 °C was unaffected by a change of solvent (benzene, hexane, acetonitrile), concentration of azide and wavelength of excitation (248 nm at 1×10^{-4} M and 308 nm at 1×10^{-3} M PhA), presence of oxygen.

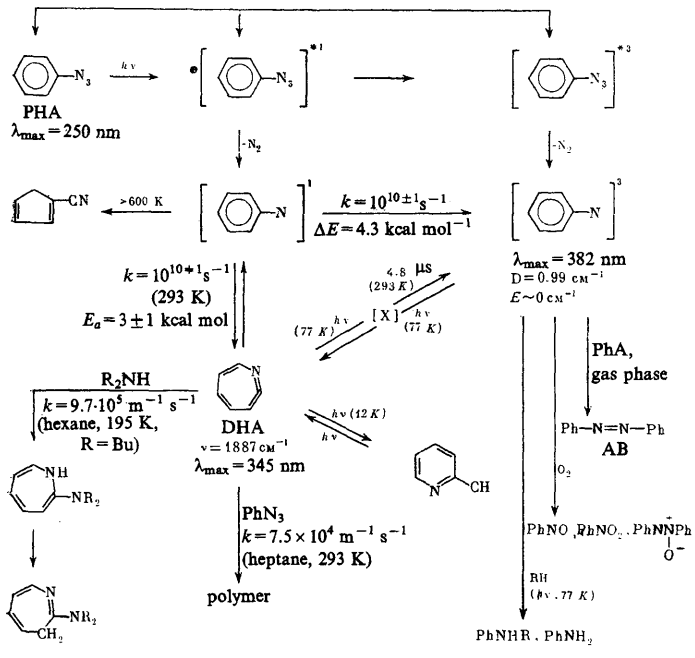
An attempt was made to generate PhN^3 by triplet sensitisation. At 77 K photolysis proved ineffective, while at 20 °C, despite the fact that the triplet states of sensitisers (benzophenone, 2,3-dimethylnaphthoquinone) were quenched by phenyl azide at a diffusion-controlled rate, the presence of PhN^3 could not be deduced from the spectra of the intermediates. This finding is in agreement with the study of Shrock and Schuster,[55] in which it was found that the quantum yield of photodissociation of PhA on triplet sensitisation was $\Phi < 0.1$, and with the study of Reiser, et al.,[30] in which the rate constant of reaction between 1-anthrylnitrene and the initial azide was determined as $k = 5 \times 10^8$ M^{-1} s^{-1}. Consequently, at the high concentrations of PhA necessary for flash photolysis experiments, even when small quantities of PhN^3 are formed the latter may rapidly disappear, so that it cannot be observed. Leyva, et al.[51] stated that these results did not support the mechanism of autocatalytic decomposition of PhA with triplet PhN as an initiator as proposed by Waddell, et al., and that they did not agree with the spectrum obtained by the latter authors[2] at 20 °C being attributed to triplet PhN. No data were given[51] on the quantum yields of dissociation of PhA.

The energy of activation of the isomerisation $PhN^1 \rightarrow$ DHA (E_a = 3 ± 1 kcal mol^{-1}), the rate constant of isomerisation at 20 °C ($k = 1 \times 10^{11\pm1}$ s^{-1}), and the temperature-independent rate constant of intersystem crossing ($k = 1 \times 10^{10\pm1}$ s^{-1}) were estimated[51] from the effect of temperature of the ratio of the photolysis products. The latter value is in good agreement with the recorded time of the singlet–triplet conversion of 4-dimethylamino-PhN ($\tau = 1.2 \times 10^{-10}$ s);[62] for the much more stable 1-pyrenylnitrene this value is substantially higher ($\tau \sim 3 \times 10^{-8}$ s).[63]

The results of the recent most exhaustive studies[51,61] supplemented with the data of earlier studies are combined in Scheme 1, which indicates the possible routes for (inter)conversion of intermediates in the photolysis of phenyl azide under different conditions.

‡ Processes with first-order kinetics in the photolysis of solutions of pure PhA had already been observed previously. It would appear that the increase in absorption at a wavelength of 366 nm in the flash photolysis of a solution of PhA in hexane[31] characterises the formation of the product derived by reaction between DHA and PhA. In that case, starting with an apparent constant of about 1.4×10^2 s^{-1} and a PhA concentration of 1×10^{-4} M, the rate constant of the reaction between DHA and PhA can be determined as $k = 1.4 \times 10^6$ M^{-1} s^{-1}, which is somewhat higher than in heptane.[61] If the spectrum observed by Waddell, et al.[6] is that of DHA rather than triplet PhN, from the lifetime of the intermediate of $\tau = 2.8$ μs and a PhA concentration of 5×10^{-4} M, we obtain the rate constant of the reaction between DHA and PhA in acetonitrile ($k = 7 \times 10^8$ M^{-1} s^{-1}). The considerable increase in the rate of reaction between DHA and PhA on changing from hexane to acetonitrile is comparable to the increase in the rate of reaction of DHA with dibutylamine: $k = 9.7 \times 10^5$ M^{-1} s^{-1} (hexane) and 3.5×10^7 M^{-1} s^{-1} (acetonitrile).[31]

Scheme 1



Excitation of PhA leads to excited singlet PhA^{*1} and then to excited triplet PhA^{*3}. Both of the latter can dissociate to a nitrogen molecule and nitrene, and more will be said later about the relative proportion of these two reaction routes at different temperatures. Quantum-chemical calculations showed that in both of the excited states of PhA dissociation starts with movement of the terminal N(3) nitrogen atom out of the plane of the molecule, resulting in a decrease in the N—N—N angle, followed by cleavage of the N(1)—N(2) bond.[64] Since the quantum yield of dissociation $\Phi < 1$, there exists a route for the deactivation of excited singlet and/or excited triplet PhA.

Depending on the reaction conditions, singlet phenylnitrene PhN^1 is converted to the triplet state or isomerises to dehydroazepine DHA, and at high temperatures its isomerisation to cyanocyclopentadiene has been recorded[47,65] (one of the possible isomers is shown in Scheme 1). Singlet PhN (the protonated form) is also likely to be responsible for the formation of substituted aminophenols during photolysis in acetic acid,[24] similar products being formed in the protolytic decomposition of PhA.[66] Moreover, certain substituted phenylnitrenes ArN^1 are capable of reacting with amines R_2NH to give hydrazines $ArNHNR_2$.[59,67]

In the presence of amines DHA can be converted to a susbtituted 3*H*-azepine, form a polymer on reacting with azide[61] or by self-polymerisation,[68] and isomerise photochemically or by a slow thermal process to PhN^3 (for the possible intermediate "X" in this process, see below).

Triplet phenylnitrene PhN^3 on reacting with hydrogen donors can be converted to aniline and/or a substituted aniline or dimerise to azobenzene (AB). In the gas phase AB is also formed by the reaction of PhN^3 with PhA;[46] in solution this process occurs for anthrylnitrene,[30] but it has been demonstrated for substituted phenyl azides that an azo compound is formed by dimerisation of triplet nitrene.[59] In the presence of O_2, PhN^3 gives oxygen-containing photolysis products.[4,11,59]

The structure of diphenyltetraazadiene DPTA as an intermediate is not shown in Scheme 1 since there is no indisputable evidence for its participation in the formation of AB. Two questions should evidently be singled out—is the formation of a diphenyltetraazadiene structure generally feasible; and, if it formed during the photolysis of PhA, is its decomposition to a nitrogen molecule and two phenylnitrenes possible?

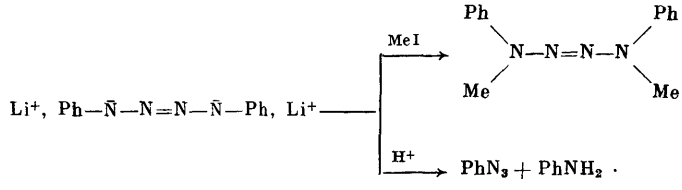
There is a positive answer to the first question. As has already been mentioned, the formation of DPTA and AB radical anions have been detected by mass spectrometry in the reaction between the PhN radical anion and PhA:[50]

$$PhN^{\cdot-} + PhN_3 \longrightarrow [Ph{-}N{=}N{-}N{=}N{-}Ph]^{\cdot-} + [Ph{-}N{=}N{-}Ph]^{\cdot+},$$

and the rate constant of this process ($k = 1 \times 10^{-12}$ cm^3 s^{-1}) proved to be almost equal to the rate constant of the gas-phase reaction for formation of AB in the reaction between PhN and PhA.[46]

Diaryltetraazadiene structures are generated under very mild conditions (20 °C) in exothermic reactions of aryl azides with transition metal complexes and are stabilised through formation of two metal—nitrogen σ-bonds with the N(1) and N(4) atoms. The reaction between a metal nitrene and azide at an intermediate stage has been suggested.[49]

The lithium salt of the DPTA dianion has some interesting properties. On treatment with methyl iodide it gives dimethyldiphenyltetrazine while proton solvents cause it to decompose to PhA and aniline:[69]



It follows from the data of X-ray diffraction analysis[69] that metal complexes with DPTA as the ligand are actually 2-tetrazene derivatives. For example, the following values of the bond lengths were for obtained for a palladium complex: 1.39 Å for N(1)—N(2); 1.26 Å for N(2)—N(3); and 1.37 Å for N(3)—N(4), which corresponds to two single and one double bond.

The formation of a fairly stable intermediate in reactions involving naphthylnitrenes is suggested by the data on the increase in yield in the dark of azo compounds when irradiated solutions are left to stand,[58] but there is no real evidence for a tetraazadiene structure. Hence, the second question—whether DPTA participates in the formation of AB—remains open.

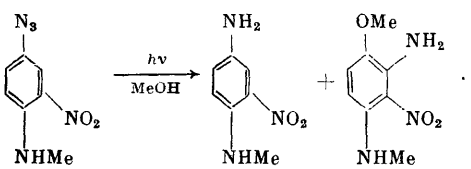
The structure of benzazirine that was widely discussed in earlier studies on the photochemistry of PhA is also not shown on the general scheme (Scheme 1) for interconversion of intermediates. The formation of condensed azirines during low-temperature photolysis of naphthyl azides was experimentally demonstrated from the appearance of bands in the region of 1700—1740 cm^{-1} in the IR

spectrum.[36] In similar studies of monocyclic aryl azides, the IR and UV spectroscopic data indicated the formation of DHA,[22,51,70] while UV and EPR spectroscopic data provided evidence for the formation of PhN^3.[13,17,19,51]

In order to resolve this contradiction, Leyva, et al.[51] suggested that the primary photolysis product is in fact PhN^3 and DHA is formed as a result of secondary photochemical reactions of nitrene. However, a recent examination of the results of low-temperature photolysis of PhA showed that this theory is only partly correct. In fact, on irradiation of PhA with light over a wide spectroscopic range ($\lambda > 210$ nm), including the region of PhN^3 absorption, the latter rapidly undergoes secondary reactions.[71] But photolysis with light at the region of the absorption minimum of PhN^3 (about 330 nm) also gave a mixture of DHA and PhN^3 in the ratio 1:4, whatever the concentration of PhA, matrix, or temperature. It was concluded that DHA, like PhN^3, is a primary photoproduct, namely at 12–45 K the proportion of "singlet" to "triplet" products formed at the same time is almost the inverse of that which occurs at 20 °C (we should recall that at 20 °C this proportion is equal to about 7:1).[27] An accurate knowledge of the composition of the photolysis products made it possible for Hayes and Sheridan[71] to record the IR spectrum of PhN^3 for the first time.

Thus, it is clear from the above that not a single method under any conditions has provided confirmation that benzazirine is formed during the photolysis of phenyl azide.

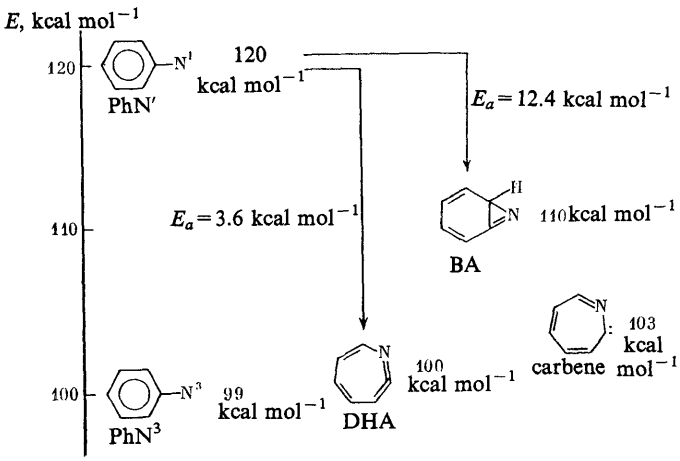
Indirect evidence for the existence of a benzazirine intermediate in the reactions of substituted PhA may possibly be provided by the results of a study by Nielsen and Buchardt,[72] in which during the photolysis of 3-nitro-4-methylamino-PhA migration of the nitrogen atom of the azide group to the *ortho* position of the benzene ring occurred and the corresponding isomeric anilines were isolated:



As was mentioned above, the most probable intermediate in this type of migration in a series of naphthyl azides is naphthazirine.[28,37] It should be noted that some of the findings of Nielsen and Buchardt[72] give rise to doubt. In the flash photolysis of PhA the authors did not succeed in detecting an intermediate with an absorption in the region above 300 nm, at variance with an earlier study[31] and more recent ones.[51,55,61]

Let us consider again the question of the tautomers of singlet PhA. After the unsuccessful attempts to find spectroscopic evidence for the formation of benzazirine, the only argument in favour of the existence of this intermediate was provided by the results of quantum-chemical calculations[34] which placed BA below DHA on the energy scale. Using this MNDO method[61] the potential energy surface for the interconversions of structures with the composition of PhN was calculated (Scheme 2).

Scheme 2



The calculated value of the singlet–triplet splitting (21 kcal mol^{-1}) is higher than the experimentally determined value of 4.3 kcal mol^{-1} for PhN, but Li, et al.[61] note that the MNDO method provides a reliable prediction of relative rather than absolute energy differences.

A more important result is that the calculated heat of formation of BA is 10 kcal mol^{-1} higher than that of DHA. Moreover, the energies of activation of the processes involving conversion of singlet PhN^1 to BA and DHA are equal to 12.4 and 3.6 kcal mol^{-1} respectively. Thus, calculations of both thermodynamic and kinetic criteria indicated the preference for a dehydroazepine structure as an intermediate, in complete agreement with the experimental results.

The reliability of this method was confirmed by calculations of the reaction route for 1-naphthylnitrene, for which it was found that, conversely (compared to PhA), naphthazirine is 10 kcal mol^{-1} more stable than the isomeric benzodehydroazepine and the activation barriers for their formation are equal to 3.1 and 13 kcal mol^{-1} respectively, which is also fully consistent with the experimental results.[36,37]

Li, et al.[61] subsequently considered the question of the possible structure of the intermediate "X" formed during interconversions of PhN^3 and DHA. It is generally assumed that the reaction occurs via PhN^1. In the opinion of the authors,[61] the intermediate conversion of DHA to a triplet carbene rather than PhN^1 is more probable. As an argument, use was made of the results of calculations in which it was found that the energy difference ΔE(carbene–DHA) = 3 kcal mol^{-1} was considerably less than the difference $\Delta E(PhN^1 - DHA)$ = 20 kcal mol^{-1}. The results of these calculations should evidently not be overrated. Starting from the experimentally determined value of the difference $\Delta E(PhN^1 - PhN^3)$ = 4.3 kcal mol^{-1}, $\Delta E(PhN^1 - DHA)$ should be less than 4.3 kcal mol^{-1}, i.e. singlet nitrene as well as triplet carbene could act as "X". We should note that even for the second excited singlet state of PhN the experimental difference $\Delta E(PhN^{*1} - PhN^3)$ = 8.8 kcal mol^{-1},[73] in other words, the calculated value for PhN^1 (21 kcal mol^{-1}) is considerably overestimated.

The quantum yield of dissociation of PhA under different conditions was determined by Budyka, et al.[74] It was shown that over a concentration range of $10^{-4}-10^{-1}$ M the value of Φ_{-PhA} stays equal to less than one (0.4–0.5), which is in agreement with the study of Reiser and Marley[33] and at variance with the data of

Waddell, et al.[1-8] Also, in contrast to the latter[1-8] but in agreement with the studies of Schuster, et al.,[55,61] the polymer was predominant amongst the photolysis products of concentrated solutions and the yield of AB did not exceed 20%.

Table 1. Effect of conditions of photolysis of phenyl azide on the quantum yield of photodissociation (Φ) and the ratio of reaction products (in an inert medium unless shown otherwise).

Solvent	[PhA], M	T, K	Φ	Yield, %*				Refs.
				AB	aniline	insertion product	polymer	
Benzene	0.1	298	—	5	—	—	p	[24]
Acetic acid	0.1	298	—	—	—	21	—	[24]
Hexane	—	298	0.53	—	—	—	—	[33]
Benzene	0.01	293	—	50±3	5±2	<3	50±1	[27]
Cyclohexane	0.01	293	—	51±3	4±2	<3	48±7	[27]
Methanol	0.01	293	—	5±3	7±2	~80	0	[27]
Benzene, acetonitrile	—	303	—	i	i	—	p	[75]
Hexane	1×10^{-4}	293	—	t	t	t	p	[31]
Piperidine	—	293	—	—	—	35	—	[76]
Acetonitrile	1.3×10^{-4}	293	0.58(O_2)—	—	—	—	—	[7]
	0.125	293	2920(O_2)	—	—	—	—	[7]
	0.722	293	15 300	—	—	—	—	[7]
	1×10^{-4}	293	—	45	—	—	—	[55]
	4.4×10^{-3}	293	—	9	—	—	p	[55]
Diethylamine	—	273	—	0	0	80	—	[51]
	—	77	—	44**	28	0	—	[51]
Phenyl azide		293	—	—	—	—	15	[68]
Cyclohexane	5×10^{-3}	293	—	15	—	—	p	[61]
Acetonitrile	2×10^{-4}	293	0.5(O_2)	i	i	—	—	[74]
	0.1	293	—	20	i	—	p	[74]
	0.1	293	0.4(O_2)	13	i	—	p	[74]

*Based on PhA reacted; i = insignificant quantity; t = traces; p = predominant product; absence of quantitative data indicated by lines: **After keeping at 195 K.

Thus, we may summarise our discussion of the photochemical properties of phenyl azide. In Table 1 the available data on the quantum yields of photodissociation of PhA and the ratio of the reaction products under different conditions have been arranged in chronological order (by insertion product is meant both substituted 3*H*-azepines and anilines that are substituted in the benzene ring—both are formed in reactions of isomers of singlet PhN with nucleophiles). It is clear from Table 1 that the total results can be divided into two groups: the first is made up by the results of Waddell, et al., and the results of the remaining research workers are in the second group. Despite the spread and frequent absence of values of the quantum and chemical (preparative) yields, on the whole the results of the second group are consistent with each other and are markedly at variance with the results of the first group. Up to the present time no one apart from Waddell, et al. has succeeded in observing a value of $\Phi > 1$ in the photodissociation of aryl azides and the quantitative formation of azobenzene in the reactions of PhA.

V. Photochemical chain reactions of azides

We shall now consider the available data on other photochemical chain reactions involving organic azides.

In 1963 it was found in a study of the photolysis of methyl azide in the gas phase that the quantum yield for liberation of nitrogen—the main gaseous product—varied from 1.7 to 2.3 on changing the wavelength of incident light from 313 to 254 nm (30 °C, 300 mm Hg), but it did not depend on the light intensity, temperature, or pressure. Radical "traps" inhibited the process and the composition of the condensate corresponded to a polymer with the general formula $(MeN)_n$.[77]

It was suggested that the methylnitrene which is formed at the first stage then reacts with the initial azide:

$$MeN_3 \xrightarrow{h\nu} MeN + N_2,$$
$$MeN + MeN_3 \rightarrow (MeN)_2 + N_2.$$

The resulting compound, presumably azomethane, also reacts with nitrene and at a higher rate than the azide since, firstly, azomethane was not present in the final products and, secondly, the addition of azomethane to the reaction mixture reduced the quantum yield:

$$MeN + (MeN)_2 \rightarrow (MeN)_3.$$

However, these two reactions of nitrene could only explain values of Φ up to 1.5, so the reaction of thermally excited ("hot") nitrene with azide to form two nitrenes was also introduced:

$$MeN^* + MeN_3 \rightarrow 2MeN + N_2.$$

Confirmation of the formation of nitrene in an excited state, in the opinion of Currie and Darwent,[77] was the dependence of Φ on the wavelength of radiation and the considerable excess of energy of the absorbed quantum of light over the energy of dissociation of the N–N bond. A similar explanation—reactions of nitrene in a "hot" state—was introduced to interpret the effect of the wavelength of exciting light on the ratio of the photolysis products of 4-cyanophenyl azide.[67]

A somewhat different interpretation of the values of Φ greater than 1 in the gas-phase photolysis of methyl azide was later put forward.[48] It was suggested that nitrene reacts with azide to form azomethane and also an aminonitrene, which on reacting with azide gives the trimer, etc., subsequently producing the polymer:

$$MeN + MeN_3 \rightarrow MeNHCH_2N + N_2,$$
$$MeNHCH_2N + MeN_3 \rightarrow (MeN)_3 + N_2,$$
$$MeN + (MeN)_3 \rightarrow (MeN)_4 \ldots$$

In contrast to the gas-phase reaction, the quantum yield of photodissociation of methyl azide (and hydrazoic acid) in methanol solution increased with an increase in concentration and reached a maximum value of 2.1 at a concentration above 1 M.[78] The dependence of the molar absorption index of these compounds on concentration suggested that molecules of azides were associating with each other or with molecules of solvent. On the basis of kinetic analysis Koch[78] assumed that the azide does not decompose in a

monomolecular reaction to nitrene, but existing for a sufficient time in an excited state, reacts with another, unexcited molecule of azide, solvent or intermediates. It is interesting to note that the quantum yield for ethyl azide under similar conditions did not depend on the concentration of azide and was equal to unity.[78]

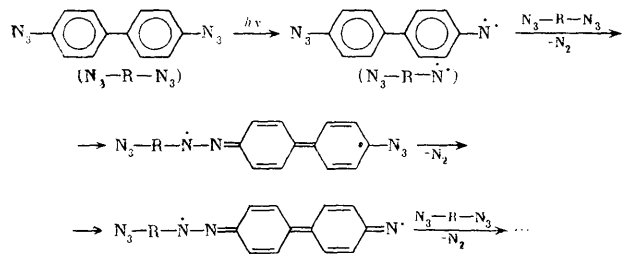
The thermolysis of PhA induced by chloromethyl radicals at 79.8 °C was autocatalytic in nature.[79] The sequence of stages of this reaction is similar to that proposed in the PACD reaction, if the radical nature of triplet PhN is assumed:

$$PhN_3+\dot{C}Cl_3 \rightarrow Ph-\dot{N}-N=N-CCl_3,$$
$$Ph-\dot{N}-N=N-CCl_3 \rightarrow Ph-\dot{N}-CCl_3+N_2.$$

Amongst the large number of nucleophilic substitution reactions known at present that are induced by electron transfer,[80] there are those that involve an azide. Thus, in the preparation of 4-nitrocumyl azide from the corresponding chloride and sodium azide it has been demonstrated that the substitution reaction is considerably accelerated when the reaction mixture is irradiated with light. The maximum quantum yield recorded was $\Phi \sim 6000$.[81] The dependence of Φ on the wavelength of incident light supported the conclusion that the first stage of the reaction is electron phototransfer within a charge-transfer complex between the cumyl chloride and azide ion followed by dissociation of the radical anion of the chloride and reaction with a second azide ion:

$$RCl+N_3^- \rightleftharpoons (RCl\cdot N_3^-),$$
$$(RCl\cdot N_3^-) \xrightarrow{h\nu} (RCl^{\cdot-}, N_3^{\cdot}),$$
$$RCl^{\cdot-} \rightarrow R^{\cdot}+Cl^-,$$
$$R^{\cdot}+N_3^- \rightarrow RN_3^{\cdot-},$$
$$RN_3^{\cdot-}+RCl \rightarrow RN_3+RCl^{\cdot-},$$
$$R=NO_2-C_6H_4-C(CH_3)_2- .$$

A polymer is formed in the photolysis of aromatic diazides in the crystalline stage. It has been suggested that the reaction may occur by a linear (nonbranching) chain mechanism, as, for example, that of diazidobiphenyl:[82]



Zelentsov, et al.[82] suggested that the conditions needed for this mechanism to occur are: firstly, a triplet state of the nitrene, which prevents the recombination of the adduct at the second stage of the reaction to an azo compound; secondly, a conjugation chain for intramolecular transfer of spin to the α-position of the second azide group; and thirdly, proximity of the nitrene to the azide group of the neighbouring molecule, which is determined by the packing of the diazide molecules in the crystal.

Theoretical calculation of the densest packing of the molecules of diazidobiphenyl in the crystal demonstrated the possibility for achieving a favourable molecular configuration. The fact that it is for this diazide (from the series of those studied), in which all three conditions are met, that the maximum yield of polymer occurred was considered to be experimental confirmation of a chain mechanism of decomposition.

In a study of the pyrene-sensitised photodissociation of 4-dimethylaminocarbonylphenyl azide in acetonitrile it was shown that the reaction is initiated by electron transfer from pyrene to azide with subsequent decomposition of the azide radical anion (Pyr = pyrene):[83]

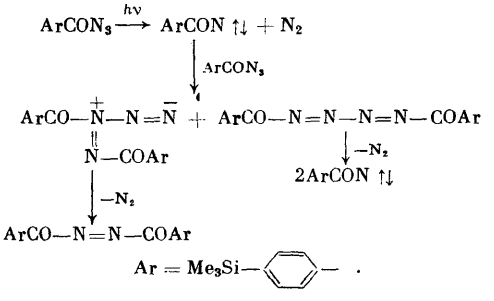
$$ArN_3 \xrightarrow{h\nu/Pyr} ArN_3^{\cdot-} \longrightarrow ArN^{\cdot-} + N_2,$$
$$Ar=Me_2NCO-C_6H_4- .$$

In order to account for the exclusive formation of an azo compound during the sensitised photolysis, Schuster, et al.[83] suggested that, in addition to dimerisation of nitrene, the nitrene radical anion may give rise to a chain reaction of azide decomposition.

A chain process initiated by 4-nitro-PhA radical anions was found in the electrochemical decomposition of this azide in the presence of weak methylene acids such as diethyl malonate.[84,85] Reaction resulted in the transfer of a diazo group from azide to ester to form aniline and diazoalkane, while the passage of not more 0.1 Coulomb mol^{-1} was sufficient for a quantitative yield of products:

$$ArN_3 + \bar{e} \rightleftarrows ArN_3^{\cdot-} \xrightarrow[-N_2]{SH} ArNH^-,$$
$$ArNH^-+H_2C(CO_2Et)_2 \rightleftharpoons ArNH_2+H\bar{C}(CO_2Et)_2,$$
$$ArN_3+H\bar{C}(CO_2Et)_2 \rightleftharpoons ArNH^-+N_2=C(CO_2Et)_2,$$
$$Ar = NO_2-C_6H_4- .$$

In 1989 the PACD reaction of an acyl azide—4-trimethylsilylbenzoyl azide—was reported. Abraham, et al.[86] found that the quantum yield of photodissociation of this azide in cyclohexane reached a value of $\Phi = 3-4$ at azide concentrations of 0.01–0.1 M; in dilute solution, as in the case of unsubstituted benzoyl azide, $\Phi < 1$ was obtained. With reference made to a study of Waddell, et al.,[5] the following reaction scheme was proposed:



In contrast to the earlier study,[5] the chain carrier was assumed to be singlet nitrene, although triplet is postulated as the ground state of nitrene (for a number of aroyl azides it was shown that singlet is the

ground state).[87,88] Isocyanate and cyclohexylamide, which were isolated as reaction products, are obtained from excited singlet azide and singlet nitrene. No products derived from triplet nitrene could be detected.

In support of their proposed reaction scheme, Abraham, et al.[86] refer to a study of Lwowski, et al.[89] in which photolysis of pure liquid ethyl azidoformate results in the isolation of an azo compound. However, it is shown by a special experiment in this study[89] that the reaction between thermally generated nitrene and azide does not result in the formation of an azo compound. It should be noted that in this case as well, there is no need to introduce this reaction in order to explain the values of $\Phi > 1$.

If it is assumed that the initiator of a chain process, if it exists, is triplet nitrene, it is possible that fluorinated PhA derivatives would be suitable substrates for the PACD reaction, since it has been demonstrated for them that singlet nitrene is not isomerised to DHA (or BA) but is quantitatively converted to the triplet state.[90] In studies of the chemical properties of fluorophenyl azides it was found that one of the main reaction products, and the predominant one in some cases, is the corresponding fluoroazobenzene.[91,92] However, there is no information about the quantum yields of photodissociation of these products.

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Thus, the literature data on the photoinitiated autocatalytic chain decomposition reaction of azides are contradictory, and it is evidently premature to say for certain that such a reaction may occur.

It can be stated that the main detected primary products of the photolysis of phenyl azide are dehydroazepine and triplet nitrene in the ratio of about 7:1 at 20 °C and about 1:4 below 77 K. Aromatic azo compounds may be formed both by dimerisation of nitrene and from its reaction with azide.

With regard to the reaction routes during photolysis of phenyl azide, it would appear that a complete picture of the possible intermediates and the ways in which they are interconverted has been built up, and the discussion about the photochemical properties of this compound can be brought to a close. However, new questions have arisen with the development and research application of novel physicochemical methods.

Recently high-resolution pulsed laser photolysis was used to study the rotational and spin structure of the electronic transition in the spectrum that was attributed to phenylnitrene,[93] and it was concluded that the data obtained were difficult to correlate with what was expected for phenylnitrene. Although the results of studies in the gas phase cannot be completely transposed to reactions in condensed media, Cullin, et al.[93] consider that with this lack of confirmation of a nitrene structure for the intermediate, it will be necessary to make a careful check of all the previously obtained data.

In our view, the aromatic azide with the simplest structure has proved to be probably the most complex in terms of its properties.

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