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Intermolecular Photochemical Reduction of Aromatic Nitro-compounds

A.N.Frolov, N.A.Kuznetsova, and A.V.El'tsov

The current data on the intermolecular photochemical reduction of aromatic nitro-compounds under various conditions are considered and the mechanism of the primary stage of the photoprocess in neutral, acid, and basic media is discussed. The dependence of the photochemical reactivity of nitro-compounds on the characteristics of the structure of their excited state is examined.
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I. INTRODUCTION

The present review considers data on the intermolecular photochemical reduction of aromatic nitro-compounds (aliphatic nitro-compounds and intramolecular photochemical reduction of aromatic nitro-compounds have already been reviewed[1,2]).

The results of the first systematic studies on the photochemical reduction of nitro-compounds were published in the middle 1960s, [3-6] although isolated studies had been published before that[7-9]. Photochemical reduction of nitro-compounds is briefly considered in Morrison's review[1]. Numerous studies concerned with the synthetic aspects and mechanism of photochemical reduction have now been made and are discussed in the present paper.

It follows from the published data that the composition and yield of the products of the photochemical reduction of many nitro-compounds depend on the reaction conditions. These differences are associated with changes in the photochemical reduction mechanism. In Morrison's review[1], the mechanism of the photochemical reduction of nitro-compounds is treated as one involving the homolytic abstraction of a hydrogen atom from a solvent molecule excited by a molecule of the nitro-compound. However, this mechanism probably operates only in neutral alcoholic and ethereal solutions. There is reason to believe that in acid and alkaline media the process proceeds via a two-stage heterolytic mechanism with initial electron transfer followed by proton transfer. In the present review, it is shown how ideas have developed about the mechanism of the photochemical reduction of nitro-compounds in neutral, acid, and alkaline media.

II. PHOTOCHEMICAL REDUCTION OF NITRO-COMPOUNDS BY HYDROGEN DONORS (PHOTOCHEMICAL DEHYDROGENATION)

It has been established that aromatic nitro-compounds give rise to amino- and hydroxylamino-compounds on irradiation in protic solvents. When nitrobenzene is irradiated in 2-propanol by light at a wavelength of 366 nm, it is reduced to phenylhydroxylamine[3] with a quantum yield of 1.14×10^{-2}. As a result of the subsequent dark oxidation reactions and condensation with the reformed nitrobenzene, the final product is azoxybenzene. α-Nitrosonaphthalene is unreactive under these conditions[10], but is reduced on irradiation with light at a wavelength of 366 nm in benzene in the presence of a hydrogen donor stronger than 2-propanol, namely tri-n-butyltin[11]. The photochemical reaction product, α-naphthylamine, was identified from its fluorescence spectrum. In contrast to α-nitronaphthalene, the β-isomer is reduced in 2-propanol and β-naphthylhydroxylamine is formed with a quantum yield of 0.037.[12]

Nitrobenzoate esters are reduced to amines on irradiation in ethanol[13] and esterification and transesterification are observed; the yield of the amines is 13–40%. Other *p*- and *m*-derivatives of nitrobenzene undergo similar reactions[14,15]:

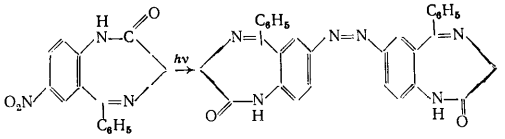
$$n\text{-R (R')}\,C_6H_4NO_2 \xrightarrow[313\ nm]{h\nu} \begin{cases} \longrightarrow n\text{-RC}_6H_4NH_2 \\ \longrightarrow n\text{-R'C}_6H_4NHOH \end{cases};$$

R=COOH, COOEt, CN; R'=H, CH_3, OCH_3.

The photolysis was carried out in 2-propanol in an atmosphere of nitrogen at room temperature. The quantum yield of the reaction, determined spectrophotometrically from the decrease in the amount of the initial nitro-compound, is 0.12–0.45 for electron-accepting substituents (R) and 0.02–0.03 for electron-donating substituents (R'). *p*-Nitrophenol and *p*-nitroaniline are not reduced under these conditions[15]; however, photochemical reduction does occur when the amino-group is acylated[15,16]. It has been shown[14,15] that the quantum yield in the photochemical reduction of substituted nitrobenzenes in 2-propanol is satisfactorily correlated with the Hammett σ constants.

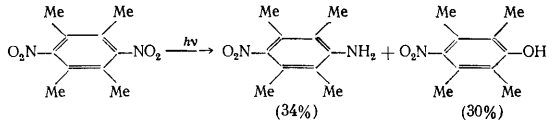
m-Dinitrobenzene and 1,3,5-trinitrobenzene are reduced photochemically in ethanol, the yield of the corresponding azoxy-derivatives not exceeding 2 %.[4] A similar process takes place in tetrahydrofuran. The final products were isolated by thin-layer chromatography. It has been established that ethanol is then oxidised to acetaldehyde[4].

On irradiation with light filtered through Pyrex glass in tetrahydrofuran, 7-nitro-5-phenyl-2,3-dihydro-1*H*-1,4-benzodiazepin-2-one gives a 10% yield of an azo-compound[16]:

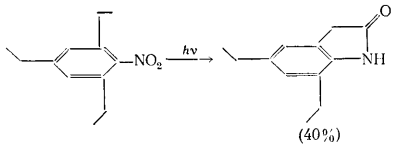


The reaction product was identified by its elemental composition and infrared, ultraviolet and mass spectra.

It is of interest that the photolysis in isopropyl alcohol of *p*-nitroacetophenone gives rise to a product resulting from the reduction of the nitro-group and not the keto-group, namely 4,4-diacetylazoxybenzene, in 31% yield[17]. The photochemical reduction of the sterically shielded nitro-group in 2-propanol has been investigated[18] and it has been shown that, together with the reduction process, the nitro-group is substituted by the hydroxy-group:



If the alkyl substituent in the *ortho*-position with respect to the nitro-group has a β-carbon atom, the photochemical reduction probably proceeds intramolecularly, for example[18]:



It has been reported[6] that 1,2,3,4-tetramethyl-5,6-dinitrobenzene is reduced photochemically in anhydrous ether to 1,2,3,4-tetramethyl-5-nitroaniline in 25% yield. The reaction was carried out with irradiation by the light of a 450 W mercury lamp at 2–6°C with stirring by a stream of nitrogen. The products were isolated by thin-layer chromatography and identified by ^{1}H NMR and from the elemental composition and mass spectra.

On irradiation with light filtered through Pyrex glass in ether, *p*-nitroanisole is reduced to *p*-anisidine (30%) and 4,4′-dimethoxyazoxybenzene (12%).[19] Under these conditions, nitrobenzene yields 44% of aniline, 2% of azobenzene, and 1% of 2-hydroxyazobenzene[19].

Heterocyclic compounds behave on photolysis similarly to nitro-compounds of the benzene series. It has been shown[5,20–22] that 4-nitropyridine *N*-oxide is converted quantitatively into the corresponding hydroxylamine on irradiation in absolute ethanol. Similar results were obtained for 4-nitro-derivatives of the *N*-oxides of α-picoline and 2,6-lutidine[5]. The experiments were performed in an atmosphere of nitrogen; after irradiation in the presence of oxygen, unidentified products having a different composition are formed.

Thus the photochemical reduction of nitro-compounds in a series of protic solvents proceeds comparatively readily. t-Butyl alcohol does not promote the occurrence of the reaction[13,19].

Qualitative aspects of the photochemical reduction by hydrogen donors have been considered in the studies described above. We shall now examine the available data concerning the nature of their reactive excited state and the mechanism of photochemical dehydrogenation.

1. The Multiplicity of the Excited State in the Photochemical Dehydrogenation Reaction

A characteristic feature of nitro-compounds is the comparative ease of the transition from the singlet to the triplet excited state and vice versa. The quantum yield in the formation of triplets is 0.6–0.8,[10,23] regardless of the configuration of the triplet state (n, π^* of π, π^*). Bearing in mind the longer lifetime of the triplet state compared with the singlet state, nitro-compounds in the triplet state are presumably involved in photochemical reduction.

This conclusion, based on the work of Brown and Williams[24], was reached in Morrison's review[1]. The evidence available at present for the involvement of the triplet state (T) in the photochemical reduction of nitro-compounds can be divided into two groups. They are based on (1) information about the chemical reactivity of nitro-compounds in the T state according to flash photolysis data[25] and (2) a comparison of data for the sensitisation or inhibition of the formation of the T state (from ESR [24] and phosphorescence spectra[26]) and the photochemical reduction reaction; in a number of studies the conclusions concerning the involvement of the T state in the reaction is based on experiments designed to investigate the influence of the donors and acceptors of the energy of triplet excitation on the quantum (chemical) yield of the reaction[3,12,19].

(1) The triplet–triplet absorption spectra of α- and β-nitronaphthalenes have been described[25,27,28]. Capellos and Porter[25] determined by the method of laser photolysis the rate constant for the abstraction of hydrogen from ethanol by α-nitronaphthalene (10^4 M^{-1} s^{-1}) and nitrobenzene (10^6 M^{-1} s^{-1}) in the T state. The photochemical dehydrogenation rate constant for nitrobenzene in the excited state[10], found from the dependence of the photochemical reduction quantum yield on the concentration of the alcohol (2-propanol), is 0.8×10^6 M^{-1} s^{-1}. The agreement between the constants determined by different methods is satisfactory and is consistent with the conclusion[10] concerning the triplet nature of the reactive state in photochemical reduction.

(2) Perfluoronaphthalene, the singlet level of which is higher and the triplet level (E_T = 56 kcal mole^{-1}) is lower than for nitrobenzene (E_T = 60 kcal mole^{-1}), has been used as an inhibitor of the photochemical reduction of nitrobenzene[24]. The irradiation was carried out with light at a wavelength >330 nm, which is not absorbed by perfluoronaphthalene, in degassed tetrahydrofuran solutions at room temperature. Following irradiation in the absence of inhibitors, the authors observed an ESR spectrum, which they attributed to the radical $C_6H_5N\dot{O}_2H$. In the presence of 0.1 M perfluoronaphthalene, the photochemical reduction of nitrobenzene did not occur. Under these conditions, the solution in tetrahydrofuran at −160°C gives rise to the ESR spectrum resulting from the formation of perfluoronaphthalene in the triplet state.

It has been shown[26] that 4-nitropyridine *N*-oxide (E_T = 52 kcal mole^{-1}) quenches the phosphorescence of diacetyl (E_T = 56.3 kcal mole^{-1}) in degassed solutions in ethanol and 2-propanol at room temperature. When a mixture of diacetyl and 4-nitropyridine *N*-oxide in alcohol is irradiated with light at a wavelength exceeding 400 nm, which is absorbed by diacetyl alone, the product is 4-hydroxyaminopyridine *N*-oxide. The results of the above studies[24,26] can be explained within the framework of the hypothesis of the triplet energy transfer leading to the T state of the nitro-compounds.

It has been concluded in a number of investigations that oxygen influences the photochemical reduction of nitro-compounds. Thus the quantum yield for the formation of phenylhydroxylamine by the reduction of nitro-benzene in 2-propanol is 1.14×10^{-2} in degassed solutions and 0.87×10^{-2} in air-saturated solutions[3]. The photochemical reduction of β-nitronaphthalene is also suppressed in the presence of oxygen[12].

According to Barltrop and Bunce's data[19], the yield of aniline in the photolysis of nitrobenzene (E_T = 60 kcal mole^{-1}) in ether in the presence of a fourfold excess of benzophenone (E_T = 69 kcal mole^{-1}), with almost complete absorption of the incident light by benzophenone, increases by a factor of six. Diacetyl and octafluoronaphthalene inhibit the photochemical reduction reaction[19]. Similar inhibition occurs also in the reduction of β-nitronaphthalene in the presence of cyclohexa-1,3-diene[12].

In the discussion of data based on the inhibition and sensitisation of a chemical process, one must bear in mind the multistep mechanism of the photochemical reduction (see below) and hence the possible influence of organic excitation energy acceptors or oxygen not only on the triplet state deactivation stage but also on the secondary thermal processes involving radical species. The above investigations did not yield unambiguous evidence showing that the sensitisation of the photochemical reduction reaction is in fact due to the triplet–triplet energy transfer. The conclusions concerning the triplet nature of the reactive state of nitro-compounds in photochemical dehydrogenation reactions, based on the above results[3,12,19], are therefore tentative.

2. The Photochemical Dehydrogenation Mechanism

Yet another feature is characteristic of nitro-compounds in the n, π^* excited triplet state. The structure of the nitro-group in this state is such that its chemical properties resemble those of a "biradical"[1], like the carbonyl group in the triplet state of ketones[29]. It has been shown for ketones[30,31], that the properties of the reacting triplet state and of the t-butoxy-radical vary in parallel in hydrogen abstraction reactions.

The mechanism of photochemical reduction in protic solvents, including as a primary step the abstraction of a hydrogen atom from the alcohol by the nitrogen-compound in the excited triplet state n, π^*, has been considered[1,3] in conformity with the foregoing considerations:

Scheme 1

$$C_6H_5NO_2 \xrightarrow{h\nu,\varphi_{ST}} C_6H_5NO_2^{3*} \quad ;$$

$$C_6H_5NO_2^{3*} + CH_3CH(OH)CH_3 \rightarrow C_6H_5\dot{N}O_2H + CH_3\dot{C}(OH)CH_3 \rightarrow$$

$$\rightarrow C_6H_5N(OH)_2 + CH_3C(O)CH_3$$

$$C_6H_5N(OH)_2 + CH_3CH(OH)CH_3 \rightarrow C_6H_5N\dot{O}H + CH_3\dot{C}(OH)CH_3 + H_2O$$

$$\downarrow$$

$$C_6H_5NHOH + CH_3C(\dot{O})CH_3 \quad ;$$

$$C_6H_5NHOH \xrightarrow{O_2} C_6H_5NO \rightarrow C_6H_5N{=}NC_6H_5 \quad .$$

$$\downarrow$$

$$O$$

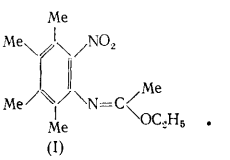
According to Scheme 1, phenylhydroxylamine is formed without a stage involving the formation of nitrosobenzene, which is believed[3] to be produced by the oxidation of phenylhydroxylamine by the dissolved oxygen.

It has been shown[19] that the photolysis of phenylhydroxylamine in ether leads to the formation of aniline in 42% yield. When an ethereal solution of nitrobenzene is irradiated with light filtered through Pyrex glass, aniline is again formed, but under these conditions nitrosobenzene is converted into azoxybenzene[19]. A similar result was obtained in the photolysis of nitrosobenzene in methanol[32]. These results lead to the conclusion, in agreement with Scheme 1, that nitrosobenzene does not constitute an intermediate stage in the photochemical reduction of nitrobenzene to phenylhydroxylamine.

However, it has been established recently that, when deoxygenated dilute (10^{-3}–10^{-5} M) solutions of nitrosobenzene in 2-propanol are irradiated, phenylhydroxylamine is formed with a quantum yield of 0.047.[33] The photolysis of concentrated nitrobenzene solution gave azoxybenzene. The latter process has probably been observed in earlier investigations[19,32]. In the light of these data, Scheme 1 may not reflect quite accurately the sequence of reactions involving the formation of the intermediates in the photochemical reduction.

We shall now consider data confirming qualitatively certain details of Scheme 1. The abstraction of a hydrogen atom from the solvent by an excited molecule of the nitroso-compound is indicated by the dependence of the quantum yield of the photochemical reduction of *p*-nitrobenzonitrile on the C–H bond energy of the reducing agent: the quantum yield of this reaction decreases on passing from 2-propanol to ethanol and hexane[15]. Similar data have been published for *m*-dinitrobenzene[34]. It has been established[34] that the efficiency of the photochemical reduction of *p*-dinitrobenzene decreases on passing from CH_3OH to CD_3OD, the isotope effect being $K_H/K_D \simeq 2.6$.

The photolysis of 1,2,3,4-tetramethyl-5,6-dinitro-benzene in ether yielded[6] compound (I), which is a product of the recombination of the radicals formed in the photochemical dehydrogenation of ether by the nitro-compound:



(I)

The structure of compound (I) was confirmed by infrared spectroscopy, ^{1}H NMR, and elemental analysis. Its formation is consistent with the radical mechanism for the primary step of the photochemical reduction in protic media.

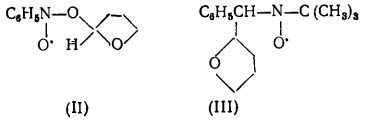
The formation of phenyl nitroxide $C_6H_5N\langle^{H}_{O\cdot}$ (Scheme 1) in the photolysis of nitrobenzene in secondary alcohols and tetrahydrofuran follows from a number of data[35–37]. When photolysed in the cavity of a microwave spectrometer, the ESR spectrum is identical to that of phenyl nitroxide obtained in the photolysis of nitrosobenzene[35]. When nitrobenzene is irradiated in primary alcohols, the product is the radical $C_6H_5N(\dot{O})R$, while in secondary alcohols (in 2-propanol) $C_6H_5N\dot{O}H$ is formed. The radical $C_6H_5N(\dot{O})C(OH)(CH_3)_2$ was detected in a later investigation[37] involving the irradiation of nitrobenzene in 2-propanol.

The detection of the primary photochemical reduction product, the $ArN\dot{O}_2H$ radical, would constitute direct confirmation of Scheme 1. Such confirmation has been obtained for the photochemical reduction of ketones. When benzophenone was irradiated with ultraviolet light in ethanol in the ESR spectrometer cavity, the simultaneous appearance of diphenyl hydroxymethyl and hydroxyethyl radicals was observed[38]:

$$(C_6H_5)_2CO^{3*} + CH_3CH_2OH \rightarrow (C_6H_5)_2\dot{C}OH + CH_3\dot{C}HOH \quad .$$

However, the analogous radical $C_6H_5N(\dot{O})OH$ derived from nitrobenzene has not yet been detected experimentally.

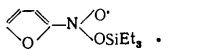
Ward[39] attributed the ESR signal obtained in the photolysis of nitrobenzene in tetrahydrofuran to the $C_6H_5N(\dot{O})OH$ radical. However, later studies[37,40] established that this signal is due to the $C_6H_5N\dot{O}_2R$ radical (II), which is formed when the tetrahydrofuryl radical reacts with nitrobenzene:



(II) (III)

When the tetrahydrofuryl radical is removed from the system with the aid of a spin trap (t-butyl phenyl nitrone), the characteristic spectrum of radical (III) appears instead of the ESR spectrum obtained by Ward.

A radical of the $ArNO_2R$ type has been detected[41] following the irradiation of 2-nitrofuran in triethylsilane:



The attempts to obtain the $C_6H_5N\dot{O}_2H$ radical by the photolysis of nitrobenzene in the presence of other effective hydrogen donors were unsuccessful[35,40]. However, the $ArN\dot{O}_2H$ radical has been detected in the reaction of atomic hydrogen with solid nitrobenzene[42] and also in the low-temperature radiolysis of nitrobenzene[43]. Evidently it is rapidly destroyed under the photolytic conditions.

It has been suggested[37] that a radical of type $ArN\dot{O}_2R$ undergoes monomolecular decomposition:

$$ArN(\dot{O})OR \rightarrow ArNO + R\dot{O}$$

leading, as with the $ArN\dot{O}_2H$ radical, to the formation of the final reaction products.

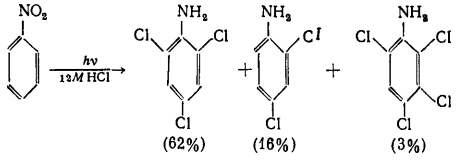
Thus the mechanism of the photochemical reduction, involving the abstraction of hydrogen from solvent molecules by the nitro-compound in the n, π^* triplet state, may be regarded as generally accepted.

The abstraction of hydrogen from alcohol molecules by nitro-compounds in the π, π^* triplet state was not observed until recently[1]. According to the latest data, 2-nitronaphthalene[12] and 4-nitropyridine N-oxide[26], which have the lowest π, π^* triplet level, are reduced on irradiation in 2-propanol. The quantum yield in the photochemical reduction of 2-nitronaphthalene is 0.037. Nitrobenzene in the n, π^* triplet state is reduced under these conditions with a quantum yield of 0.0114.[3] It is believed[12] that the rate of abstraction of hydrogen by 2-nitronaphthalene in the triplet state is lower by 3–4 orders of magnitude than for nitrobenzene, but the longer lifetime of the 2-nitronaphthalene triplets compensates the lower rate and leads to a comparatively high quantum yield in the photochemical reduction. Furthermore, one must bear in mind that the quantum yield is for the formation of the triplet states of 2-nitronaphthalene (0.83) is higher than for nitrobenzene (0.67).[10,23]

The low quantum yield in the conversion of nitrobenzene in 2-propanol into arylhydroxylamine [bearing in mind that the quantum yield in the transition of nitrobenzene to the excited state is 0.67 (Hurley and Testa[10]) and that the degree of conversion of $C_6H_5N(\dot{O})(OH)$ into C_6H_5NHOH is 100%] is evidently due to the fact that the deactivation of triplets predominates over the abstraction of hydrogen from the solvent. Thus it has been reported[11] that the lowest triplet state of nitrobenzene is of the n, π^* type and that the rate of abstraction of hydrogen atoms is high (0.8×10^6 mole^{-1} s^{-1}).[10] The low quantum yield in the photochemical reduction of nitrobenzene is therefore associated, according to the authors[10], with the high rate of deactivation of the triplet state ($\sim 10^9$ s^{-1}).

III. PHOTOCHEMICAL REDUCTION OF NITRO-COMPOUNDS IN AN ACID MEDIUM

Studies of the photochemical reduction of nitro-compounds in alcohols showed that the process proceeds more effectively when hydrochloric acid is added[44,45]. Thus the quantum yield in 50% aqueous isopropyl alcohol in an atmosphere of nitrogen increases from 1.14×10^{-2} in the absence of acid to 0.3 in the presence of 12 M HCl.[44] The initial product of the reduction of nitrobenzene in isopropyl alcohol in the presence of HCl is phenylhydroxylamine, which was determined polarographically[45]: the final products are aniline (40%), *p*-chloroaniline, and *p*-aminophenol. When nitrobenzene is irradiated in the presence of 12 M HCl but in the absence of alcohol, the reduction of the nitro-group is accompanied by the substitution of the hydrogen atoms in the benzene ring by chlorine[46]:



Similar results were obtained for *o*-, *m*-, and *p*-substituted nitrobenzenes[47]. The quantum yield in the photochemical reduction of nitrobenzene derivatives in water in the presence of 12 M HCl (determined from the decrease in the amount of the nitro-compound) depends only slightly on the electron-accepting properties of the substituent and decreases following the introduction of an electron-donating group into the ring[47].

On irradiation with light at a wavelength of 335 nm[48] in a hydrochloric acid–2-propanol mixture, α-nitronaphthalene is converted into α-naphthylamine in 70% yield. It has been shown[49] that the primary product of the photochemical reduction of α-nitronaphthalene under these conditions is α-naphthylhydroxylamine, which is converted in the presence of HCl into 4-chloro-1-naphthylamine. The latter is dechlorinated photochemically and yields α-naphthylamine. The quantum yield in the formation of 4-chloro-1-naphthylamine, identified from ultraviolet, infrared, and fluorescence spectra, increases in proportion to the concentration of HCl.[50] The maximum quantum yield was 1.28×10^{-2} for 6 M HCl in 50% aqueous 2-propanol solution, while in the alcohol in the absence of acid an appreciable photochemical reaction is not observed.

On irradiation in alcohol in the presence of HCl, 4-nitropyridine is converted into 4-hydroxyaminopyridine and 4,4′-azopyridine[51]. The quantum yield for the decrease in the amount of 4-nitropyridine rises to 0.94 with increase of HCl concentration[29,51]. According to the results of Cu and Testa[52], the limiting quantum yield in the photochemical reduction of 4-nitropyridine in 2-propanol in the presence of HCl is somewhat smaller, amounting to 0.65. The discrepancy between the quantum yields has been explained[52] by the difference between the two analytical methods used to determine the degree of conversion of the starting material (spectrophotometry[29] and polarography[52]).

Irradiation of 5-nitroquinoline in aqueous 2-propanol in the presence of HCl leads to the formation of 5-amino-6,8-dichloroquinoline[53]; the maximum quantum yield in the photochemical reduction is 5.44×10^{-2} at an HCl concentration ≥ 1 M.

The linear dependence of the quantum yield in the photochemical reduction of α-nitronaphthalene on the HCl concentration led[50,51] to a mechanism for the photochemical reduction of nitro-compounds by isopropyl alcohol in an acid medium (Scheme 2), including a stage in which the excited triplet state is protonated (aromatic nitro-compounds in the ground state are weak bases):

Scheme 2

$$ArNO_2 \xrightarrow{h\nu,\Phi_{ST}} ArNO_2^{3*} \quad ;$$

$$ArNO_2^{3*} + H^+ \rightleftarrows \overset{+}{ArNO_2}H^{3*} \quad ;$$

$$ArNO_2^{3*} \rightarrow ArNO_2 \quad ;$$

$$\overset{+}{ArNO_2}H^{3*} + (CH_3)_2CHOH \rightarrow ArN\dot{O}_2H + (CH_3)_2\dot{C}OH + H^+$$

$$\downarrow$$

reaction products.

The quantum yield in the photochemical reduction of nitrobenzene is independent of HCl concentration up to 3 M, after which it increases linearly. Evidently the protonation of nitrobenzene in the T state begins to an appreciable extent only at HCl concentrations exceeding 3 M.[44]

Using the method of pulsed laser photolysis, Capellos and Porter[25] determined the rate constants for the protonation of α-nitronaphthalene (1.85×10^7 M^{-1} s^{-1}) and nitrobenzene (4.4×10^7 M^{-1} s^{-1}) in the T state, the values obtained being much greater than the dehydrogenation rate constants (10^4 and 10^6 M^{-1} s^{-1} for α-nitronaphthalene and nitrobenzene respectively[25]). These results agree indirectly with Scheme 2).

The completion of the photochemical reduction of the protonated triplet state should include an electron transfer stage. This process is probably unlikely, since alcohols, the ionisation potentials of which are 11–12 eV, are weak electron donors[54]. Data which cannot be accounted for by the mechanism of acid catalysis (Scheme 2) have been published recently. It has been shown[53,55,56] that catalysis is observed in the presence of HCl but not H_2SO_4. Since the hydrogen sulphate anion undergoes one-electron oxidation with greater difficulty than the chloride anion, the authors[55] suggested that the protonation in the presence of HCl is preceded by electron transfer from the chloride anion to the excited triplet state of the nitro-compound (Scheme 3):

Scheme 3

$$ArNO_2 \xrightarrow{h\nu,\Phi_{ST}} ArNO_2^{3*} \quad ;$$

$$ArNO_2^{3*} + Cl^- \rightarrow [ArNO_2^{\cdot-} \ldots Cl^{\cdot}] \quad ;$$

$$[ArNO_2^{\cdot-} \ldots Cl^{\cdot}] + H^+ \rightarrow [ArN\dot{O}_2H \ldots Cl^{\cdot}] \quad ;$$

$$[ArN\dot{O}_2H \ldots Cl^{\cdot}] + CH_3CH(OH)CH_3 \rightarrow ArN\dot{O}_2H + HCl + CH_3\dot{C}(OH)CH_3$$

$$\downarrow$$

reaction products.

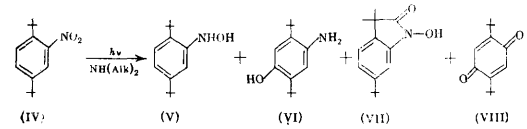
The conversion of the $ArN\dot{O}_2H$ radical into the final products can be described within the framework of Scheme 1.

An absorption spectrum with a maximum in the region of 440 nm has been obtained in the flash photolysis of degassed nitrobenzene solutions in aqueous 2-propanol in the presence of 6 M HCl. The authors attribute it[56] to the $C_6H_5N\dot{O}_2H$ radical formed on protonation of the radical-anion. A similar result was obtained for 4-nitropyridine[56]. The authors[56] are inclined to favour a photochemical reduction mechanism resembling Scheme 3, although they were unable to measure the spectrum of the pair $[ArNO_2^{\cdot-} .. Cl]$ or the radical-anion $ArNO_2^{\cdot-}$ in acid media. The reason for this is probably the high rate of protonation of the radical-anion (for example, the rate constant for the protonation of the α-nitronaphthalene radical-anion is approximately 10^{10} M^{-1} s^{-1}).[25] On the other hand, there are literature data[57] demonstrating one-electron transfer from the chloride anion of the nitro-compound in the ground state (m-dinitrobenzene and trinitrobenzene), resulting in the formation of radical-anions. Similar data for the reaction in the excited state are lacking.

IV. PHOTOCHEMICAL REDUCTION OF NITRO-COMPOUNDS IN AN ALKALINE MEDIUM

A series of studies on the photochemical reduction in alakaline media has shown that the composition of the reaction products and the kinetics are different from those in the photochemical reduction in neutral media. In alkaline media, the reduction process proceeds more effectively and the yield of products is higher than for the photochemical reduction in alcohols and ethers; instead of hydroxylamines and amines, final condensation products are obtained—azo- and azoxy-compounds. The yield of the azo-compound in the photolysis of 7-nitro-5-phenyl-2,3-dihydro-1H-1,4-benzodiazepin-2-one in diethylamine is higher than in tetrahydrofuran (40% and 10% respectively)[16].

There are data showing that, on irradiation in neutral solutions, 1-t-butyl-2-nitrobenzenes give rise to intramolecular products only, namely indolinones (VII),[58-61] while in solutions in aliphatic amines products of the intermolecular reduction of the nitro-group are formed, i.e. hydroxylamines (V) and amines (VI):[59-62]



In the latter case, indolines (VII) and quinones (VIII) are formed as side products. The hydroxylamines (V) are converted into azoxy- and azo-compounds[59-61] and can also condense with amine oxidation products[62].

The photochemical reduction of a series of mononitro-compounds in alkylamines has been investigated[19] and it has been shown that the composition of the reaction products is more varied than in photochemical reduction in neutral media: the yield of arylamines varies from 6 to 22%, that of azo-compounds from 2 to 20%, that of azoxy-compounds from 5 to 35%, and that of o-hydroxyazo-compounds from 10 to 30%.

Aromatic amines may be used as reducing agents[63]. When m-chloronitrobenzene is irradiated in a benzene solution of N-methylaniline in an atmosphere of nitrogen, 37% of m-chloroaniline is formed; in the presence of NN-dimethylaniline, the yield of m-chloroaniline is 25%. Under these conditions, α-nitronaphthalene is converted into α-naphthylamine (37%) [63] and arylamines are oxidised, N-methylformanilide (34%) and N-methylaniline (56%) being fromed from NN-dimethylaniline.

An increase of the yield of the reduction products compared with alcoholic media is also observed in an alkaline alcoholic medium. The photolysis of m-dinitrobenzene in ethanol yields not more than 2% of an azoxy-compound[4],

while irradiation in 50% aqueous methanol in the presence of 0.05 M NaOH gives a yield of reduction products up to 69%:[64,65]

$$NO_2C_6H_4NO_2 \xrightarrow[MeOH,\ NaOH]{h\nu} NO_2C_6H_4N{=}N{-}C_6H_4NO_2 + \underset{O}{\downarrow} \quad (44\%)$$
$$+ NO_2C_6H_4N{=}NC_6H_4NO_2 + NO_2{-}C_6H_4NH_2$$
$$(20\%) \qquad (5\%)$$

A number of other mono- and di-nitro-compounds of the benzene and naphthalene series are also reduced under these conditions[65]. The photolysis of 5-nitro- and 8-nitro-anthraquinone-1-sulphonic acids in alkaline aqueous alcoholic solutions gives an approximately 3% yield of amino-anthraquinonesulphonic acids[66].

The sequence in which the photochemical reduction products are formed in an alkaline medium has been described[19]. It has been shown that irradiation with light at a wavelength ≤ 290 nm leads to the formation of anilines, while irradiation with light at a wavelength ≥ 290 nm results in the formation of azoxy- and azo-products. The experiments were carried out in the presence of oxygen, since it has an insignificant influence on the yield of the final product[19]. The irradiation of azo- and azoxy-benzenes under the experimental conditions leads to the formation of hydrazobenzene[67] and 2-hydroxyazobenzene[68] respectively. Aniline is also formed in small amounts under these conditions[19], but the process is much slower than the formation of anilines from hydroxylamines. The authors[19] therefore believe that anilines are formed on photochemical reduction mainly from the corresponding arylhydroxylamines and not from azo- and azoxy-derivatives. It has also been suggested that a nitroso-compound is formed as an intermediate before the hydroxylamine formation stage. Arylhydroxylamines and nitroso-compounds are unstable in alkaline media and condense with formation of azo- and azoxy-compounds, which has been established by special dark experiments[19,65].

Indirect data consistent with the involvement of nitro-compounds in the triplet state in photochemical reduction in alkaline media have been published[65,69]. A study has been made of the sensitisation of the photochemical reduction of 4,4′-dinitrobiphenyl (E_T = 58 kcal mole^{-1}) by naphthalene (E_T = 61 kcal mole^{-1}) and benzophenone (E_T = 69 kcal mole^{-1}).[65] The relative singlet levels in these pairs is not known accurately but, judging from the long-wavelength limit of the absorption spectra, the energy of the singlet state, at least in naphthalene, is higher than in 4,4′-dinitrobiphenyl. Irradiation was carried out with light at a wavelength of 254 nm, the ratio of the donor and acceptor concentrations being such that the main bulk of the exciting light ($\geq 90\%$) is absorbed by benzophenone or naphthalene. Under these conditions, the quantum yield of the reaction, found from the decrease in the amount of the nitro-compound, is 0.056 in the absence of the sensitiser and 0.03 and 0.16 in the presence of naphthalene and benzophenone respectively.

The quantum yield and the photochemical reduction of 4-*NN*-diethylamino-4′-nitroazobenzene in butylamine increases from 4.2×10^{-4} to 0.14 when 0.27 M benzophenone is introduced[69]. These data can probably be accounted for by energy transfer via triplet levels. However, results have been published showing[69] that the sensitisation of the photochemical reduction of nitro-compounds by benzophenone may be to some extent also "chemical" sensitisation (for the description of its mechanism, see Monroe and Wamser[70]):

$$Ph_2CO \xrightarrow[RH]{h\nu} Ph_2\dot{C}OH \quad ;$$
$$Ph_2\dot{C}OH + ArNO_2 \rightarrow Ph_2CO + Ar\dot{N}O_2H$$
$$\downarrow$$
$$\text{reaction products.}$$

It has been suggested[19,63] that photochemical reduction in both amines and alcohols proceeds via a mechanism involving the dehydrogenation of the amine by the nitro-compound in the triplet state, which leads to the formation of the $ArN\dot{O}_2H$ radical. However, this hypothesis is inconsistent with the results of other studies[10,19,63], where it has been shown that α-nitronaphthalene is not reduced in alcohol[10] but is reduced in amines[19,63].

α-Nitronaphthalene is known to have a π, π^* lowest triplet state, which is relatively unreactive in hydrogen abstraction reactions[23,71]. Possibly the reduction of the π, π^* triplets of nitro-compounds in alkaline media is facilitated by the occurrence of the process via a mechanism different from that of photochemical dehydrogenation. In this respect, the photochemical reduction of nitro-compounds in alkaline media resembles the photochemical reduction of ketones. Electron transfer with subsequent proton transfer in secondary processes has been suggested as the first stage in the reduction by alkylamines of excited states of ketones, which are unreactive in hydrogen abstraction reactions[72]. This is indicated by the chemical polarisation of electrons[73], observed on irradiation of the benzophenone–triethylamine system, and also by the decrease in the rate of photochemical reduction with increase in the ionisation potential of the amine[72].

Pacifici et al.[69] were the first to suggest that the reduction of nitro-compounds in amines proceeds via electron transfer from the solvent to the nitro-compound in the triplet state. The authors observed that the direction of the photochemical reaction of 4-*NN*-diethylamino-4′-nitroazobenzene in amines is different from that in alcohols. A hydrazo-compound (resulting from the reduction of the azo-group) is formed in alcohols, while in butylamine the reduction involves the nitro-group, the product—4-*NN*-diethylamino-4′-hydroxyaminoazobenzene—having been identified from the ultraviolet spectrum and its conversion into an azoxy-compound. The following reaction mechanism was proposed:

$$ArNO_2 \xrightarrow[\varphi ST]{h\nu} ArNO_2^{3*} \quad ;$$

$$ArNO_2^{3*} + RNH_2 \rightarrow ArNO_2^{\cdot-} + RNH_2^{\cdot+} \quad .$$

The radical-anion of the nitro-compound abstracts a proton from the radical-cation of the amine:

$$ArNO_2^{\cdot-} + RNH_2^{\cdot+} \rightarrow Ar\dot{N}O_2H + R\dot{N}H \quad .$$

The $ArN\dot{O}_2H$ radical is subsequently converted into the final products.

A similar mechanism has been proposed in another investigation[62], the difference being that the radical-anion of the nitro-compound and the radical-cation of the amine are believed by the authors to exist in the form of an ion pair, where proton transfer takes place.

There are data showing that photochemical reduction in alkaline alcoholic media also proceeds with electron transfer in the primary step[65]. It has been established that the quantum yield of the photochemical reduction of nitro-compounds in absolute alcohol in the presence of sodium alkoxide and in alkaline aqueous alcoholic media increases with increased concentration of the alkoxide ion[34,65]. According to ESR data, there is a simultaneous

increase in the steady-state concentration of the radical-anions of the nitro-compounds[74]. These results have been explained by the participation of the alkoxide ion in the photochemical reduction, which involves one-electron transfer from the anion to the nitro-compound in the excited triplet state (Scheme 4):

Scheme 4

$$ArNO_2 \xrightarrow[\varphi_{ST}]{h\nu} ArNO_2^{3*} \quad ;$$

$$ArNO_2^{3*} + CH_3\bar{O} \rightarrow [ArNO_2^{\cdot-} \ldots CH_3\dot{O}] \quad ;$$

$$[ArNO_2^{\cdot-} \ldots CH_3\dot{O}] \rightarrow Ar\bar{N}O_2H + CH_2O \text{ (or } ArN\dot{O}_2H + e + CH_2O)$$

$$\downarrow$$

reaction products.

The radicals formed as a result of electron transfer are probably enclosed in a solvent cage, where hydrogen transfer takes place[65,74]. Hydrogen transfer may be promoted by the formation of the $CH_3\dot{O}$ radical in a non-equilibrium state, which has excess vibrational energy. This scheme is consistent with the absence of an isotope effect in the photochemical reduction by CH_3O^- and CD_3O^- ions[34,74]. In contrast to photochemical dehydrogenation, where the ratio $K_H/K_D = 2.6$ for *p*-dinitrobenzene, in photochemical reduction in an alkaline medium $K_H/K_D = 1$ for *m*-dinitrobenzene and 1.4 for *p*-dinitrobenzene[34,74]. In the reduction by the alkoxide ion, the C–H bond energy in the reducing agent probably plays a secondary role. This conclusion can be explained on the hypothesis that the rate of reaction of the excited state of the nitro-compound with the alkoxide ion is diffusion-controlled and reduces to electron transfer in the primary step; the transfer of a hydrogen atom (proton) takes place in subsequent stages of the reaction, which are not kinetically controlled[34].

Data demonstrating the formation of radical-anions when the charge of a strong base is accepted by the nitro-compound provide a qualitative confirmation of Scheme 4 for the photochemical reduction of nitro-compounds in alkaline media[75-77]. On irradiation, the probability of electron transfer increases markedly[78,79]. According to data obtained by ESR, alkylamines[69] and alkali metal alkoxides[74,79] can play the role of reducing agents in electron phototransfer[74,79].

It has been noted[65] that nitro-compounds are reduced by the formate anion as well as alkoxide ions. The limiting quantum yield in the photochemical reduction of *m*-dinitrobenzene by sodium formate in water is 0.01.[34] *m*-Dinitrobenzene is not reduced by sodium acetate in water[65]. The authors explain this by the fact that, in contrast to acetate anions, alkoxide and formate anions behave as hydride ion donors. The transfer of a hydride ion can in principle proceed in stages, and may include electron transfer followed by the transfer of a hydrogen atom.

V. INTERMOLECULAR PHOTOCHEMICAL DEOXYGENATION AS A VARIETY OF PHOTOCHEMICAL REDUCTION

Intermolecular photochemical deoxygenation can be regarded as a kind of photochemical reduction process in which the reduction products are formed via the abstraction by the reducing agent of an oxygen atom from the nitro-group in the excited nitro-compound. The photochemical deoxygenation of nitro-derivatives by triethyl phosphite has been described[80].

It has been observed recently that nitrobenzene and some of its derivatives react with the cyanide ion under the influence of ultraviolet light and are converted into nitroso-compounds[81-83]:

$$ArNO_2 + CN^- \xrightarrow{h\nu} ArNO + OCN^- \quad .$$

The reaction proceeds stoichiometrically and the quantum yield increases as the cyanide concentration rises to 1 M. Evidently nitrosobenzene is formed in the reaction of excited nitrobenzene with CN^-.[83]

The photochemical deoxygenation occurring when the nitrobenzene–BCl_3 complex is irradiated in cyclohexane has been described[84]; the quantum yield is 3.9×10^{-3}. The authors believe that electronic excitation leads to a weakening of the N–O bond of nitrobenzene and a strengthening of the O–B bond in the complex. The transfer of an oxygen atom from nitrobenzene to BCl_3 is accompanied by the liberation of a chlorine atom, which gives rise to a chain process resulting in the formation of chlorocyclohexane and H_3BO_3.

VI. SIDE REACTIONS ACCOMPANYING PHOTOCHEMICAL REDUCTION

The photochemical reduction of nitro-compounds is frequently complicated by side reactions, which may compete with the reduction process and sometimes become fully dominant. The photochemical reactions involving substituents in the nitro-compound (photochemical dehalogenation, photochemical rearrangement of benzoate esters, hydrolysis of the nitrile group, etc.) are not considered here. Under the conditions of "reducing photolysis", the nitro-group itself can undergo photochemical denitration, or photochemical substitution, or can be converted into a nitrite. These processes sometimes completely suppress the photochemical reduction of the nitro-group.

Photochemical denitration of nitro-compounds has been observed in the photolysis of isomeric chloro- and bromo-nitrobenzenes in an aqueous alcoholic solution of sodium nitrite[85]. Taking into account the results of El'tsov et al.[86], the nitro-group is presumably reduced under photolysis conditions to an amino-group, the latter is diazotised, and the diazo-group formed is substituted by hydrogen. Photochemical denitration by sodium tetrahydroborate has been observed in the photochemical reduction of certain nitro-compounds: α-nitronaphthalene 4-methoxy-1-nitronaphthalene, and 1-nitropyrene[82].

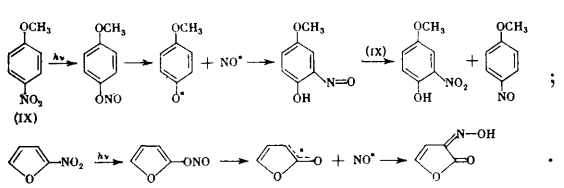
Certain aromatic nitro-compounds can not only reduce the nitro-group but can also participate in the photochemical substitution of the nitro-group by cyano-, methoxy-, hydroxy-groups, etc. Thus α-nitronaphthalene and *p*-nitroanisole are reduced to the amines on irradiation in aliphatic amines[19], while in the presence of CN^-, CH_3O^-, and OH^- ions they are involved in nucleophilic photochemical substitution reactions[81,87,88]. In the presence of HCl, 1-nitronaphthalene, 1,5-dinitronaphthalene, and 1,8-dinitronaphthalene in chloroalkanes are converted by the photochemical substitution of the nitro-groups by chlorine into the corresponding chloronaphthalenes[89]. At a concentration of 0.1 M in ethanol, 4-nitropyridine Λ-oxide is reduced to hydroxylamine[20]. Under the same conditions, at a concentration of the initial nitro-compound of 0.001 M, the nitro-group is replaced by a hydroxy-group; at moderate concentrations, the two photochemical reactions compete[20,90]. In the

presence of piperidine, the substitution leads to the formation of 4-piperidinopyridine *N*-oxide[91]. The nitro-group in α-nitroazulene is readily substituted photochemically[87,92]. The photochemical substitution of the nitro-groups in certain nitrocompounds by hydroxy-groups has been discussed in a review[93].

It has been suggested that photochemical substitution takes place with participation of the triplet state[92]. This hypothesis is based on the results of experiments on the sensitisation by benzophenone of the photochemical substitution of the nitro-group in *p*-nitroanisole[94] and 2,6- and 1,7-dinitronaphthalenes[95]. The quenching of the *T* state of α-nitronaphthalene by hydroxide ions has been reported[25]; the quenching rate constant, determined from the triplet–triplet absorption spectra in degassed ethanol solutions, is 1.73×10^{8} M^{-1} s^{-1}. (The quantity is equal to the sum of the rate constants for the quenching of the *T* state by hydroxide and ethoxide ions, since in ethanol solutions hydroxide ions are in equilibrium with ethoxide ions[34].)

The photochemical conversion of the nitro-group into a hydroxy-group can proceed intramolecularly via the intermediate formation of a nitrite group (the nitro–nitrite rearrangement). The nitro–nitrite rearrangement was first postulated by Chapman et al.[96] to account for the formation of anthraquinone and 10,10′-bianthrone in the photolysis of 9-nitroanthracene. They believe that the rearrangement is promoted by steric hindrance, which displaces the nitro-group from the plane of the aromatic ring. The overlap (in the excited state) of the *p*-orbital of the oxygen in the nitro-group with the *p*-orbital of the aromatic system leads to the formation of an oxaziridine ring, which is converted by a thermal reaction into a nitrite group. Other data[18,58] are consistent with this hypothesis. The hydrolysis of nitrites leads to the formation of hydroxy-derivatives, which are usually the final products of the photochemical reaction.

There are data indicating the intermediate formation of nitrites on irradiation of nitro-compounds which are not subjected to steric hindrance in the ground state. In this case, the displacement of the nitro-group from the plane of the aromatic ring is probably caused by the transition to the excited state. Thus the formation of 4-methoxy-2-nitrophenol and 3-hydroxyiminofuran-2(3*H*)-one on photolysis of *p*-nitroanisole[97] and 2-nitrofuran[98] respectively can be readily explained in terms of the nitro–nitrite rearrangement, the homolysis of the resulting nitrite into radicals, and their subsequent recombination:



The formation of 4-hydroxypyridine *N*-oxide in the photolysis of 4-nitropyridine *N*-oxide in isopropyl alcohol in the presence of HCl is explained by the intermediate rearrangement to the nitrite[90].

On photolysis of 8-nitroquinoline in benzene and alcoholic solutions, 8-hydroxyquinoline is probably formed also via the nitro–nitrite rearrangement. The intramolecular mechanism of the process is confirmed by the absence of a dependence of the quantum yield in the formation of 8-hydroxyquinoline on the concentration of hydroxide ions in the aqueous alcoholic solution and on the nature of the solvent (aqueous alcohol, benzene)[99].

It is suggested[90,97,99], that nitro-compounds are involved in this reaction in the triplet state. Thus triphenylene (E_T = 67 kcal $mole^{-1}$) sensitises the photochemical rearrangement of *p*-nitroanisole (E_T = 60.8 kcal $mole^{-1}$).[97] The conversion of 8-nitroquinoline (E_T = 58 kcal $mole^{-1}$) into 8-hydroxyquinoline is sensitised by benzophenone (E_T = 69 kcal $mole^{-1}$) and naphthalene (E_T = 61 kcal $mole^{-1}$).[99] Under conditions where the light flux (at a wavelength of 254 nm) is absorbed by the sensitiser (≥ 90%), the quantum yield, determined from the decrease in the amount of 8-nitroquinoline, was 4.38×10^{-3} and 1.25×10^{-3} in the presence of benzophenone and naphthalene respectively. On direct excitation of 8-nitroquinoline, the yield is 1.87×10^{-3}.

VII. THE INFLUENCE OF SUBSTITUENTS AND OF THE TYPE OF THE LOWEST TRIPLET STATE ON THE PHOTOCHEMICAL REACTIVITY OF NITRO-COMPOUNDS

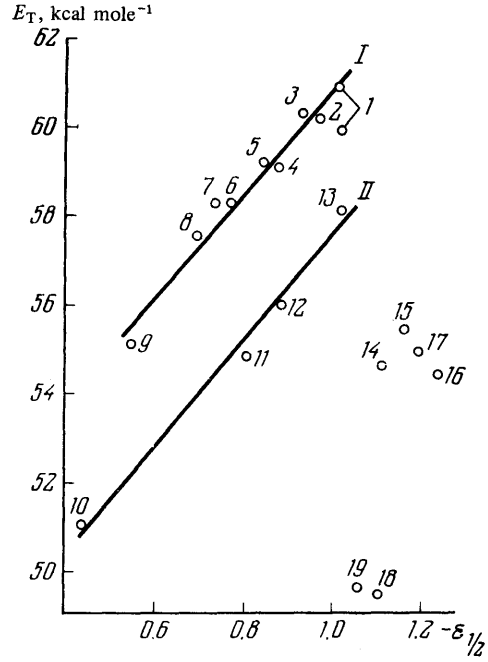
By analogy with the behaviour of ketones in photochemical reduction and on the hypothesis of the dominant role of the triplet state of nitro-compounds in these reactions, it has been suggested[82,100,101] that the reactivities of nitro-compounds in the excited state be classified in terms of their behaviour in photochemical reactions and of the type of the lowest triplet state. Nitrobenzene and its derivatives without strong electron-donating substituents are usually reduced photochemically by protic solvents. It is postulated that the reactive excited state of these compounds is of the n, π^* type[82]. The second group comprises α-nitronaphthalene and nitrobenzenes with electron-donating substituents. In the lowest excited π, π^* state, these compounds undergo photochemical substitution and reduction reactions; their ability to abstract hydrogen is diminished. Finally, the third group consists of nitro-compounds whose excited state includes a large contribution by the charge-transfer state (CTS); they are photochemically stable.

The existence of three types of nitro-compounds with different reactivities in the excited state has been confirmed by a study[101] in which a linear relation between the energy of the 0–0 transition to the triplet state and the potential of the one-electron polarographic reduction for aromatic nitrogen-compounds is reported. Similar relations have been described for aromatic hydrocarbons[102] and ketones[102–105]. In order to account for these correlations, the authors[103–105] represented the energy of excitation to the n, π^* and π, π^* triplet states by the differences between the energies of the n and π^* of the π and π^* orbitals:

$$E_T^{n\pi^*} = \varepsilon_n - \varepsilon_{\pi^*} \quad ;$$
$$E_T^{\pi\pi^*} = \varepsilon_\pi - \varepsilon_{\pi^*} \quad .$$

The introduction of substituents leads to an increase or decrease of the energy of the molecular orbital (MO). The energy of the highest occupied molecular orbital is the same for compounds of the given series (ϵ_n) or if it is linearly related to the energy of the lowest vacant molecular orbital (ϵ_{π^*}), one may expect a linear relation between the energy of the triplet state E_T and ϵ_{π^*}. Since ϵ_{π^*} varies linearly with one-electron reduction potentials[106] ($\epsilon_{1/2}$) (for nitro-compounds, this relation has been published[107]), one may expect also a linear relation between E_T and $\epsilon_{1/2}$, which is in fact the case for the various classes of compounds[101–105].

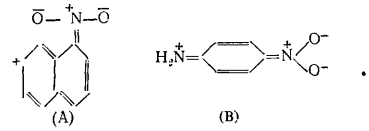
The data of Frolov et al.[101] indicate the existence of three types of relations between E_T and $\epsilon_{1/2}$ (see Figure), which corresponds to the different reactivities of nitro-compounds in the excited state: some are reduced on irradiation (the group of compounds corresponding to line I), others are difficult to reduce but undergo photochemical substitution reactions (group corresponding to line II), while unreactive compounds (nitroanilines and nitronaphthylamines) constitute an isolated group of data in the Figure.



Dependence of the one-electron polarographic reduction half-wave potentials ($-\epsilon_{1/2}$, V) in dimethylformamide on the energy of the 0–0 transition to the triplet state (E_T): *1*) *p*-nitroanisole; *2*) 2-nitrobiphenyl; *3*) nitrobenzene; *4*) 2-nitrofluorene; *5*) 4-nitrobiphenyl; *6*) *m*-nitroacetophenone; *7*) 4,4′-dinitrobiphenyl; *8*) 1,8-dinitronaphthalene; *9*) 1,5-dinitronaphthalene; *10*) 1,4-dinitronaphthalene; *11*) α-nitronaphthalene; *12*) β-nitronaphthalene; *13*) 8-nitroquinoline; *14*) 4-nitrodiphenylamine; [4-nitrobiphenylylamine?]; *15*) 4-nitroaniline; *16*) *NN*-dimethyl-4-nitroaniline; *17*) 2-methyl-4-nitroaniline; *18*) 1-amino-4-nitroaniline; *19*) 2-amino-1-nitronaphthalene; E_T^{I} (kcal mole^{-1}) = (13.6 ± 0.9) ($-\epsilon_{1/2}$) + (47.5 ± 0.1); E_T^{II} (kcal mole^{-1}) = (12.6 ± 0.9) ($-\epsilon_{1/2}$) + (45.4 ± 0.2).

In connection with the difficulties arising in the study of the phosphorescence spectra (low-intensity structureless spectra, frequently with superposition of the luminescence of an impurity) there are relatively few data concerning the nature of the lowest triplet state of nitro-compounds[108] and those available are contradictory. Judging from the lifetime of the triplet and the fine structure of the phosphorescence spectra, nitrobenzene, 2-nitrofluorene, *p*-nitrobiphenyl, and 1,5-dinitronaphthalene[10,109] are in the n, π^* state, while 4-nitropyridine *N*-oxide[26,110], 3- and 4-nitroquinoline *N*-oxides[110], and α- and β-nitronaphthalenes[12,23,111] are in the π, π^* triplet state. These data account for lines I and II in the Figure. However, it is believed[23] that the π, π^* configuration predominates in the triplet state of 1,5- and 1,8-dinitronaphthalenes.

It has also been suggested[101] that the tendency of nitro-compounds in the first group (line I in the Figure) towards reduction is due to the fact that the lowest triplet state is of the n, π^* type (or of the π, π^* type with a large n, π^* contribution). An increase in the energy of the n, π^* states and a decrease of the CTS level are probably characteristic of the nitro-compounds corresponding to line II in the Figure, so that there is an increase of the probability of the mixing of the lowest π, π^* and CTS levels [there is an increased contribution of the type (A) structure to the triplet state]:



An appreciable contribution of the charge-transfer state to the T state of α-nitronaphthalene is indicated by the marked dependence of the triplet–triplet absorption spectrum of α-nitronaphthalene on the nature of the solvent: the absorption maximum shifts from 525 nm in hexane to 580 nm in ethanol and 615 nm in *N*-methylformamide[25].

The triplet state of nitroanilines and nitronaphthylamines, constituting an isolated group, probably has the nature of an intramolecular charge transfer state [type (B)], characterised by a diminution of the electrophilic properties of the oxygen of the nitro-group as compared with the n, π^* and π, π^* states.

The different reactivities of the n, π, π, π^*, and charge-transfer triplet states of nitro-compounds in photochemical reduction reactions can be accounted for within the framework of the usual hypotheses adopted to explain the different photochemical reactivities of the triplet states of ketones[112]: owing to the repulsion between unpaired electrons, the excited molecule resembles a "biradical" and, like all free radicals, it abstracts a hydrogen atom[113] or an electron. The electrophilic nature of such a "biradical" and hence the probability of the abstraction of a hydrogen atom (or electron) decrease on passing from the n, π^* to the π, π^* and charge-transfer states, since n, π^* excitation entails the localisation of the positive charge on the n orbital of the oxygen in the nitro-group, while in the π, π^* state the positive charge is delocalised over the aromatic system. Intramolecular charge transfer (CTS) leads to the localisation of a negative charge on the oxygen of the nitro-group, which reduces its electrophilic properties to an even greater extent.

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The data discussed suggest that the reduction of nitro-compounds stimulated by ultraviolet radiation is complicated by photochemical substitution processes and photochemical rearrangement of the nitro-group. The photochemical reduction of nitro-compounds in acid and alkaline media cannot be described within the framework of the photochemical dehydrogenation mechanism, since

the quantum yield of the reaction in acid and alkaline media depends on the concentration of the acid or the alkaline reagent.

A number of problems arising in the study of the photochemical reactions of nitro-compounds have not been elucidated. Thus the available data permit only hypotheses concerning the changes in mechanism in the primary photochemical reduction step on passing from neutral to acid and alkaline media. The nature of the intermediate species in these processes is not clear. The data described are consistent with the orthodox view[1] concerning the dominant role of the triplet state of nitro-compounds in photochemical reduction reactions. With the exception of the study of Capellos and Porter[25], there is no direct evidence for the involvement of the triplet state of nitro-compounds in the reaction. The participation of the excited singlet state of nitro-compounds in the reactions considered has not been disproved experimentally.

The first attempts have been made to explain the influence of substrate structure on the photochemical reactivity of the nitro-group by a change in the nature of the reactive T state of nitro-compounds. Systematic studies of the influence of the structure of nitro-compounds on the competition of photochemical reduction and substitution processes and the nitro–nitrite rearrangement have not been made.

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