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The Electron Paramagnetic Resonance Method in the Study of Electron Phototransfer Reactions and Sensitised Photoreactions

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This review examines critically almost all available results of studies of electron phototransfer reactions and sensitised photochemical reactions. The unique possibilities provided by the electron paramagnetic resonance method in the study of photochemical processes are demonstrated. New work on two-quantum photochemical reactions is examined in particular detail. The important part played by electron phototransfer reactions in photochemistry is also emphasised. The bibliography contains 161 references

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I. INTRODUCTION

The possibilities provided by the fruitful utilisation of the electron paramagnetic resonance method (EPR method) for the study of elementary photoprocesses in photochemically active systems, namely the detection and study of intermediate products of the free radical and radical-ion type, were demonstrated fairly convincingly in several hundred papers published in the period 1954–1966 in the Soviet Union and other countries. In a review[1] devoted to the application of the EPR method to the study of photodecomposition reactions (photodissociation and photoionisation), we examined the chief results and conclusions reached by various workers in the study of the mechanisms and types of phototransformations undergone by various compounds with the formation of free radicals as intermediate products. In most instances the EPR method was used as a supplementary method to confirm various conclusions regarding a photoprocess which had previously been detected or discovered by other methods.

The most interesting results have been obtained by using the EPR method to study electron phototransfer reactions (photo-oxidation, photoreduction, and photodissociative electron attachment) and the photosenitisation of chemical transformations of a substance under the influence of near ultraviolet and visible light. Terenin devoted considerable attention to this aspect, in connection with the investigation of methods for the utilisation of light energy in the model systems of a photosynthesising apparatus, particularly in connection with the study of the primary photophysical and photochemical transformations undergone by pigments, dyes, and related compounds[2]. The EPR method can undoubtedly give important information even for such complex photosensitive systems as photosynthesising organisms. The possibilities provided by the EPR method are illustrated in the present review for the example of many original studies of electron phototransfer reactions and photosensitised chemical transformations of substances.

II. THE EPR METHOD IN THE STUDY OF ELECTRON PHOTOTRANSFER REACTIONS

1. Photo-oxidation

The result of the reaction of a photoexcited substance with electron donors or acceptors may be elementary photoreduction or photo-oxidation, that is the acceptance of an electron by one component and its simultaneous loss by another component of the photosensitive system, that is electron phototransfer. In some instances the elementary photo-oxidation process, carried out in solid matrices at low temperature under the influence of ultraviolet light, is accompanied by the formation of free radicals. An example of a photoreaction of this kind is provided by the photo-oxidation of ions of the iron group or halide ions in acid medium in the presence of water[3-6]:

$$[Fe^{2+} + H_2O\,(H_3O^+)]_{H_2SO_4} \xrightarrow{h\nu} [Fe^{3+} + OH^-\,(H_2O) + H^\cdot]_{H_2SO_4}$$

$$[I^- + H_2O\,(H_3O^+)]_{H_2SO_4} \xrightarrow{h\nu} [I^\cdot + OH^-\,(H_2O) + H^\cdot]_{H_2SO_4}$$

The EPR method provides a direct and convenient means of detecting the hydrogen atoms formed in this reaction, since they have a characteristic spectrum consisting of two narrow lines at a distance of 508 Oe from one another. Under ordinary conditions, however, as a result of the high mobility and high reactivity of the hydrogen atoms, they cannot be obtained in sufficient quantities for detection. Published data show that in solid matrices, including ice, hydrogen atoms diffuse readily even at 77°K, and to detect them it is necessary to carry out the studies at 4.2°K and 20°K.[7] In frozen aqueous and concentrated sulphuric, phosphoric, and perchloric acids, however, the hydrogen atoms do not recombine at 77°K.[8] This property of acid solutions was used by Bubnov and coworkers[9,10] to detect the hydrogen atoms produced during electron phototransfer

from metal ions with variable valency (V^{2+}, Cr^{2+}, Fe^{2+}, Mn^{2+}, Co^{2+}, etc.) and various anions (I^-, N_3^-, SH^-, SO_3^{2-}, etc.) in aqueous medium.

For example, when solutions of $FeSO_4$ in sulphuric and phosphoric acids, frozen at 77°K, were illuminated, an EPR signal consisting of a doublet with splitting 507 Oe was detected. This indicated unambiguously that hydrogen atoms are formed in the electron phototransfer reaction. To confirm this conclusion, experiments were carried out with solutions containing heavy water. The triplet signal of atomic deuterium was then detected in the EPR spectrum.

In another experiment, these workers showed that not only ions, but also the neutral molecules of aromatic compounds, can take part in photoreactions of this type. When solutions of benzene in aqueous sulphuric and phosphoric acids, frozen at 77°K, were illuminated, they observed the EPR lines of hydrogen atoms and the EPR spectra of various radicals formed from benzene derivatives ($\dot{C}_6H_6^+$, $\dot{C}_6H_7$, $\dot{C}_6H_5$), produced according to the scheme:

$$[C_6H_6 + H_2O]_{H_2SO_4} \xrightarrow{h\nu} [\dot{C}_6H_6^+ + OH^- + H^\cdot]_{H_2SO_4}$$

$$\dot{C}_6H_6^+ + OH^- \rightarrow \dot{C}_6H_5 + H_2O; \quad \dot{H} + C_6H_6 \rightarrow \dot{C}_6H_7$$

The positive benzene radical-ion $\dot{C}_6H_6^+$ was identified by Carter and Vincow[11] in solutions of benzene in H_2SO_4 at 77°K, irradiated with ultraviolet light. The EPR signal with $g \simeq 2.0$ also consisted of the superposition of the EPR spectra of several radicals. The seven-component spectrum of the $\dot{C}_6H_6^+$ radical-ion was resolved when the irradiated solution was heated. It was found that the $\dot{C}_6H_6^+$ radical-ion is relatively stable in the range 85–170°K, whereas the other radicals disappear in this temperature range. The authors cited confirmed the identification of the EPR spectrum using deuterated benzene (C_6H_5D and C_6D_6). They also obtained the EPR spectra of hexamethylbenzene and hexaethylbenzene, photoionised under the same conditions, and measured the hyperfine interaction constants and g-factor for these radical-ions.

We also detected hydrogen atoms by the EPR method in an electron phototransfer reaction when diphenylamine in aqueous sulphuric acid was illuminated with ultraviolet light[12]. The hydrogen atoms were produced according to the scheme:

$$[Ph_2\dot{N}H + H_2O]_{H_2SO_4} \xrightarrow{h\nu} [Ph_2\overset{+}{N}H + OH^- + H^\cdot]_{H_2SO_4}$$

The formation of the positive diphenylamine molecular ion in this photoreaction was confirmed by the production of a coloured product with absorption maximum at 680 nm[13].

The formation of alkyl radicals during electron phototransfer was observed by Bubnov and coworkers[14] when solutions of oxalic, acetic, and chloroacetic acids in various alcohols (methanol, ethanol, propanol, and butanol), frozen at 77°K, were illuminated with ultraviolet light. To explain the results obtained, the authors cited made allowance for the fact that in the system studied, partial protonation of the alcohol may take place in the presence of acids. In fact, if a certain amount of ROH_2^+ and X^- ions are formed in a system of the type ROH + HX (where ROH is a molecule of alcohol, and HX a molecule of acid), irradiation of the system with ultraviolet light will lead to electron phototransfer from the X^- anion to the ROH_2^+ cation, with the formation of an alkyl radical $\dot{R}$ according to the scheme:

$$ROHH^+ + X^- \xrightarrow{h\nu} \dot{R} + H_2O + X$$

In all instances the concentration of alkyl radicals $\dot{C}H_3$, $\dot{C}_2H_5$, $\dot{C}_3H_7$, and $\dot{C}_4H_9$ amounted to 0.01–0.03 times the concentration of acid.

Intracomplex electron phototransfer, leading finally to the production of free radicals, was studied by the EPR method by Shagisultanova and coworkers[15]. They give the results obtained by measuring the EPR spectra of solutions of complexes of the type $K_3[M(C_2O_4)_3]$, where M = Co, Fe, Cr, and Mn, and also $[Co(NH_3)_6]_2(C_2O_4)_3$, in dilute sulphuric acid (0.5–20%) or in aqueous alcohol at 77°K, irradiated with ultraviolet light (PRK-7). The concentration of the salts was varied in the range 2.5×10^{-3}–10^{-1} M. The doublet EPR signal of hydrogen atoms was detected in the irradiated solutions. It was found that the nature of the coordinated ligand and complex-forming metal has a marked influence on the production of hydrogen atoms: the intensity of the hydrogen doublet is maximal for the axalato-complex of Fe^{3+}, and minimal for the oxalato-complex of Cr^{3+}. In addition to the hydrogen doublet, the central section of the EPR spectrum at $g = 2.0036$ showed a slightly asymmetric line, with weak lines on both sides of it, belonging to the formyl radical $H\dot{C}O$. The authors cited consider that the primary step in the action of quanta of ultraviolet light on these coordination compounds is electron phototransfer between the ligand and metal, leading to the production of doubly-charged metal ions M^{2+} (Fe^{2+}, Co^{2+}, etc.). The formation of hydrogen atoms takes place by the reduction of the water molecules present in the hydration sheath of the complex, as a result of the charge in charge $M^{2+} \rightarrow M^{3+}$. It is possible, however, that under the influence of ultraviolet light the coordination complex undergoes photodissociation with the liberation of oxalate ions, which then reduce the water: $C_2O_4^{2-} + HOH \rightarrow C_2O_4^{-} + \dot{H} + OH^-$, as takes place in $K_2C_2O_4$ and $[Co(NH_3)_6]_2(C_2O_4)_3$.

Tollin and Green[16] used the EPR method to study a reaction which is very important for the solution of the problem of photosynthesis, namely electron phototransfer from chlorophyll A to various quinones (9,10-phenanthrenequinone, p-benzoquinone, coenzyme Q_6, *p*-chloranil, and *o*-chloranil) in solution (EPA mixture 8 : 3 : 5) at 268–100°K in a vacuum. Irradiation of the solution with light absorbed only by chlorophyll ($\lambda \geq 550$ nm) produced an intense EPR signal (10^{15}–10^{17} unpaired electrons per ml) of the corresponding quinone radical-anion, that is the semiquinone ion, in accordance with the photoreaction scheme:

$$ChI + Q \xrightarrow{h\nu} ChI^* + Q \rightarrow \begin{matrix}(ChI^+ \ldots Q^-)^* \\ \downarrow\uparrow \quad \downarrow\uparrow \\ ChI + QChI^+ + Q^-\end{matrix}$$

or:

$$ChI + Q \rightarrow (ChI \ldots Q) \xrightarrow{h\nu} \begin{matrix}(ChI^+ \ldots Q^-)^* \\ \downarrow\uparrow \quad \downarrow\uparrow \\ ChI + Q\,ChI^+ + Q^-\end{matrix}$$

Tollin and Green[16] postulated as intermediate product of the photoreaction an excited charge-transfer complex (CTC), capable of dissociating to form the positive chlorophyll radical-ion (Chl^+) and the quinone radical-anion (Q^-). It was found that the degree of dissociation is determined by the electron affinity of the quinone, temperature, and the polarity and viscosity of the solvent. Only the signals of the quinone radical-anion were detected by the EPR method. The positive chlorophyll radical-ions could not be detected. This is not a specific feature of this photochemical system: the EPR spectra of chlorophyll radical-cations in solutions has not yet been obtained, even at low temperatures.

2. Photodissociative Electron Attachment

Allen and Ingram[17] and Azizova[18-21] showed that ultraviolet irradiation of aqueous solutions of aromatic aminoacids at 77°K leads to their photoionisation with the production of the EPR singlet signals of the aminoacid radical-cations and hydrated electrons. In the presence of aliphatic aminoacids (glycine, alanine, valine, lysine, glyclyglycine, and alanylalanine), which do not absorb ultraviolet radiation directly in the range 240–290 nm, the action of ultraviolet light ($\lambda > 240$ nm) produced the multicomponent EPR signals of the corresponding aliphatic aminoacids. Ultraviolet irradiation of aqueous solutions of aliphatic aminoacids in the absence of aromatic aminoacids does not produce EPR signals. To investigate the mechanism of the free radical formation, the EPR method was used to study aqueous solutions of a mixture of aromatic and aliphatic aminoacids, irradiated with ultraviolet light, at 77°K and various pH values. It was found that at pH 12, when the aliphatic aminoacids are present in the form $RCH(NH_2)COO^-$, irradiation with ultraviolet light does not lead to the formation of free radicals. The formation of radicals of the aliphatic aminoacids takes place in acid medium (pH 0.5) when the aminoacids are present in the form $RCH(NH_3^+)COO^-$. This fact, and the decrease in the quantity of hydrated electrons in the specimen with increase in the concentration of aliphatic aminoacids, suggest that the free radicals are produced as a result of electron phototransfer according to the scheme:

$$\text{tryptophan}^+\ (\text{tyrosine}^+) + R{-}\underset{\displaystyle NH_3^+}{\underset{|}{CH}}{-}COO^- \xrightarrow{h\nu} \text{tryptophan}^+\ (\text{tyrosine}^+) + R{-}\dot{C}H{-}COO^- + NH_3$$

Thus the deamination of the aliphatic aminoacids, detected from the SPR spectra, takes place as a result of an electron phototransfer reaction.

The study of the deamination of aliphatic aminoacids by means of coloured compounds which absorb visible light, for example riboflavine or dyestuffs (trypaflavine, Acridine Orange, eosin), is of considerable interest. The irradiation of aqueous solutions of Acridine Orange (10^{-3} M) in the presence of alanine (10^{-1} M) produces the quintet EPR spectrum of the alanine free radical[22,23].

A large variety of aminoacids, peptides, and di- and tripeptides containing free amine groups in different parts of the molecule (gly-ala, ala-gly, ala-gly-gly, gly-met, gly-ser, leu-gly, etc.) have been studied. In the presence of readily ionisable additives, deamination takes place as a result of the transfer of an electron to the NH_3^+ group of the molecule.

The formation of free radicals from alkyl halides by electron phototransfer from a readily ionisable additive to the alkyl halide ($RX + e^- \rightarrow \dot{R} + X^-$) was demonstrated by Claridge and Willard[24] for the tetramethyl-*p*-phenylenediamine + alkyl halide system (methyl, ethyl, propyl, and butyl halides) in 3-methylpentane at 77°K. Alkyl radicals were detected by the EPR method. The alkyl halides, which exhibit diffuse absorption bands in the region of 250 nm, readily undergo photodecomposition in 3-methylpentane at 77°K with rupture of the C–I (Cl, Br) bond under the influence of ultraviolet light of $\lambda \leq 254$ nm. Tetramethyl-*p*-phenylenediamine in organic glasses at 77°K has an absorption maximum at 320 nm[25] with molar absorptivity 3×10^3, and on irradiation in this range it readily undergoes photoionisation, as indicated by the production of the characteristic colour of its radical-cation[26] and the corresponding EPR spectrum[27-30]. In the presence of alkyl halides, the action of light of $\lambda > 300$ nm produces not only the EPR spectrum of the tetramethyl-*p*-phenylenediamine radical-cation but also the distinct EPR spectra of the alkyl radicals $\dot{C}H_3$, $\dot{C}_2H_5$, n-$\dot{C}_3H_7$, i-$\dot{C}_3H_7$, n-$\dot{C}_4H_9$, and i-$\dot{C}_4H_9$; these authors assume that the latter are produced by the dissociative attachment of electrons, removed by photoreactions from tetramethyl-*p*-phenylenediamine, to the molecules of the corresponding alkyl halides, which have a positive electron affinity. The relative yields of the radicals for equal integral exposures ($\lambda > 300$ nm) are as follows: CH_3Cl 100%, CH_3Br 30 %, CH_3I 10%, C_2H_5Cl 40%, C_2H_5Br 25%, C_2H_5I 5%, i-C_3J_7Cl 20%, n-C_3H_7Cl 10%, i-C_4H_9Cl 20%, and n-C_4H_9Cl 10%.

3. Photoreduction

Ketones act as photosensitisers for the oxidation of various alcohols[31,32]. Although the mechanism of the sensitisation of this photoreaction is not completely clear[33,34], it has been established that unstable sensitiser semiquinones and solvent radicals are formed.[35] The overall scheme for the chemical transformations is:

$$AQ + h\nu \rightarrow AQ^*; \quad AQ^* + RH \rightarrow A\dot{Q}H + \dot{R};$$

$$A\dot{Q}H \xrightarrow{pH>8} A\dot{Q}^- + H^+; \quad 2A\dot{Q}H \rightarrow AQH_2 + AQ$$

where AQ is the quinone, and RH the solvent.

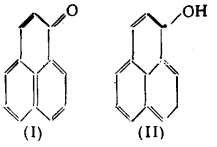
The production of semiquinones and radical-anions in this photoreaction was recorded from their optical absorption spectra by flash spectroscopy[33,36]. Their detection by the EPR method was of considerable interest.

Elschner and coworkers[37] used the EPR method to study the photoreduction of anthraquinone and its derivatives sodium anthraquinone-2,6-disulphonate, sodium anthraquinone-2-sulphonate, and 2,6-dichloroanthraquinone, at room temperature in alcohol. The structure of the EPR spectra of the semiquinones corresponds, as expected, to the interaction of an unpaired electron with two groups of equivalent protons. Solvent radicals were not detected, because of their low stability at room temperature.

The photochemical reduction of benzophenone in alcohols also involves an intermediate state[38]. Irradiation of a solution of benzophenone in propan-2-ol at −150° produced a structureless EPR signal, which disappeared when the temperature of the solutions was raised to −100°. Since the EPR signals in these experiments did not have a resolved hyperfine structure, their exact interpretation was difficult. Moreover, the experiment was carried out at −150°, and alcohol radicals were not detected.

Sharp and coworkers[39] used the EPR method to study the photoreduction of anthraquinone and benzophenone in methanol and propan-2-ol at room temperature and at low temperatures. EPR signals were not obtained when anthraquinone in methanol was irradiated at room temperature. When the temperature of the solution was lowered to −190°, however, a broad singlet without hyperfine structure was produced. The EPR signal disappeared with increase in temperature to −150°.

Under the influence of ultraviolet light, in degassed solvents such as methanol, ethanol, propanol, ethyl acetate, and acetone, which act as hydrogen donors, perinaphthenone (I) (absorption maximum at 359 nm)



(I) (II)

rapidly acquires a green colour ($\lambda = 650$ nm), which slowly

disappears in the dark[40]. It might be expected that this corresponds to the hydroxyperinaphthenyl radical (II), produced as a result of dehydrogenation of a solvent molecule by the photoexcited ketone. In fact, in degassed solutions of perinaphthenone irradiated with ultraviolet light (GEH-100 or Osram HBO-500 high-pressure mercury lamp) at 300°K, an intense EPR signal with hyperfine structure was obtained[41]. The hyperfine structure of the EPR spectrum of the radical formed is due to the interaction of the unpaired electron with the five protons of the equivalent hydrogen atoms in positions 3, 4, 6, 7, and 9, and with the three protons of the other equivalent hydrogen atoms in positions 2, 5, and 8. The same EPR signal was also obtained in solutions of perinaphthenone in dimethylformamide, irradiated with ultraviolet light, but the solution was not coloured. The green colour is apparently not due to the hydroperinaphthenyl radical.

Ayscough and Wilson, in a detailed study of the structure of aromatic ketyls[42-44] and radical-anions of aromatic nitro-compounds[45], used photoreduction of the starting materials (ketones and nitrobenzene derivatives) in concentrated alcoholic solutions of sodium methoxide or ethoxide at 20° in a vacuum as one method for obtaining negatively charged mono-ions.

The mechanisms by which these radical-anions are formed was investigated by Porter and Wilkinson[46]. On ultraviolet irradiation (λ = 330 nm), benzophenone is excited into a singlet state, from which it undergoes non-radiative transfer into a chemically active triplet state $Ph_2CO \xrightarrow{h\nu} Ph_2CO^* \rightarrow Ph_2CO_{T_0}$. Benzophenone in the triplet state removes a hydrogen atom from a suitable solvent, leading to the formation of the ketyl radical $Ph_2\dot{C}\overset{*}{O}_{T_0}$ + $RH \rightarrow Ph_2\dot{C}OH + \dot{R}$. In alkaline solutions, the radical-anion of the ketone (ketyl), familiar from its blue colour, is stabilised: $Ph_2\dot{C}OH + OH^- \rightarrow Ph_2\dot{C}O + H_2O$.

In Ayscough and Wilson's experiments, the source of ultraviolet light was a medium-pressure 250 W mercury lamp; the light from this lamp passed through a water filter to remove infrared radiation and was focussed by means of quartz lenses on the specimen situated in the resonator of the spectrometer. The photoreduction of benzophenone, 4,4-dichlorobenzophenone, and fluorenone, like electrolytic and chemical (by means of Na and K) reduction, led to the production of intensely coloured blue (benzophenones) or red (fluorenone) products. These coloured products gave well resolved spectra. These are the EPR spectra of the corresponding ketyls: Ph_2CO^-, Ar_2CO^-, and $C_{13}H_8O^-$. The maximal intensity of the EPR spectrum of the benzophenone ketyl is reached several seconds after the start of illumination. The ketyls of 4,4-dichlorobenzophenone and fluoroenone reached their maximal concentration 5–10 min after the start of illumination. The rates of disappearance of the ketyls in the dark correspond to the rates of their appearance. These spectra contain a larger number of components than the EPR spectra of the ketyls obtained by electrolytic reduction in acetonitrile. This is not due to better resolution of the spectrum as a result of narrowing of the individual components, however, but is due to a slight distortion of the distribution of the density of the unpaired electron in the ketyl as a result of a solvation effect. It is possible that an increase in the electron density of the unpaired electron in the aromatic ring is brought about by hydrogen bonding between the carbon–oxygen group of the ketyl and an alcohol molecule. Thus the ketyls in these systems should be regarded as Ph_2CO^-(solvated), Ar_2CO^-(solvated), and $C_{13}H_8O^-$(solvated).

The ketyls of benzaldehyde and acetophenone were obtained similarly. Their EPR spectra were observed several seconds after the start of ultraviolet irradiation. The short delay period is possibly due to the presence in the solution of uncontrolled impurities, which react with the radicals. For these ketyls, a solvation effect influencing the distribution of the density of the unpaired electron was also observed. It is revealed particularly clearly by comparing the splitting constants in alkaline methanol or ethanol solutions with the splitting constants in acetonitrile: all the splitting constants of the protons are decreased in acetonitrile. The stability of the ketyls also decreases in acetonitrile, due to the absence of a solvation sheath.

On ultraviolet irradiation of solutions of duroquinone in methanol, ethanol, or propan-2-ol in the presence of alkoxide ions, Cough and Symons[47] detected the EPR spectrum of durosemiquinone. Irradiation of solutions which did not contain alkoxide ions produced the EPR spectrum of the monoprotonated form of durosemiquinone[48]. Bridge and Porter[33] established that the mechanism of the formation of the radical-anions of quinones in alkaline solutions is the same as that in alkaline solutions of aromatic ketones. When strongly polar alcohols are replaced by less polar alcohols (quaternary pentanol), in which there is association of the radical-anion of the quinone (the semiquinone ion) with the alkali metal cation (Li, Na, or K) of the added alkoxide, the EPR spectrum of the semiquinone ion shows an additional structure, produced by the interaction of the unpaired electron with the nucleus of the alkali metal[49,50]. This indicates the formation of ion pairs. The magnitude of the hyperfine splitting is proportional to the effective density of the unpaired electron, which has 0.1–1% *s* character. By changing the polarity of the solvent, Cough and Symons altered the degree of association of the anion–cation pairs, and measured the rate constants for reactions of the type $M^+A^- \rightleftharpoons M^+ + A^-$ and $M^+A^- \rightleftharpoons A^-M^+$. Thus the EPR spectra of photoreduced aromatic ketones and diketones have been used to study not only solvation effects, but also the nature of ion association.

Ayscough and Wilson[44] detected solvation effects for the anions of aromatic nitro-compounds, obtained by photo-reduction in alcoholic solution in the presence of sodium methoxide or ethoxide. 16 para-substituted nitrobenzenes (*p*-alkoxynitrobenzenes, *p*-alkyl- and *p*-phenylnitrobenzenes, *p*-nitrobenzene alcohols, methyl *p*-nitrobenzoate, *p*-nitrobenzaldehyde, *p*-dinitrobenzene, and *p*-halogeno(Cl, Br, F)nitrobenzenes), *ortho*- and *meta*-fluoronitrobenzenes, and 2,6-dimethylnitrobenzene were subjected to photoreduction. The ease with which the aromatic nitro-compounds add an electron, and the stability of the resulting radical-anions, which give the solution a yellow-brown colour, permitted a detailed analysis of the EPR spectra and a comparison with the EPR spectra of the radical-anions of the corresponding nitrobenzenes, obtained chemically by reduction with glucose in alcoholic (ethanol or methanol) or aqueous-alcoholic medium in the presence of sodium ethoxide. The comparison showed that the spectra are identical. Most of the EPR spectra consist of three well resolved groups of lines, corresponding to the interaction of an unpaired electron with the nucleus of the nitrogen atom (a_N = 7.9–14.8 Oe), with the protons of the ring (a_{H_o} = 3.1–3.5 Oe; a_{H_m} = 0.78–1.2 Oe), and with the magnetic nuclei of substituents in the *para*-position (a_p = 0.26–8 Oe). Comparison of the EPR spectra of these radical-anions with the spectra of the same radical-anions obtained in an aromatic solvent shows that a proton-

donating solvent influences the distribution of the unpaired electron around the nitrogen atom, possibly as a result of the formation of a hydrogen bond with a solvent molecule.

Winkler and coworkers[51] showed by the EPR method that the radical-anions of various aromatic hydrocarbons can be obtained by photoreduction in the presence of phenyl-lithium. The action of ultraviolet light from a PL = 313 (70 W) high-pressure mercury lamp on solutions of biphenyl, terphenylene, naphthalene, phenanthrene, chrysene, pyrene anthracene, perylene, pentacene, and acenaphthene in diethyl ether at 20° gave coloured solutions, whose EPR spectra indicated the formation of radical-anions of the corresponding aromatic compounds. An additional hyperfine structure, due to the interaction of the unpaired electron with the lithium nucleus (^{7}Li, $I = 3/2$), was detected, indicating the existence of polyacene$^-$–Li$^+$ ion pairs under these conditions[52,53]. For example, the EPR spectrum of the anthracene radical-anion had the following characteristics: $a_\gamma = 5.35$ Oe, $a_\alpha = 2.45$ Oe, $a_\beta = 1.58$ Oe, and $a_{Li} = 1.70$ Oe. The mechanism of this photoreaction is being studied.

Charge transfer in molecular complexes, leading to the production of radical-anions, has been demonstrated by the EPR method for many charge-transfer complexes in the solid state. Lagercrantz and Yhland[54] showed that charge transfer can be induced by light in solutions of various organic charge-transfer complexes. An electron acceptor (chloranil, sym-trinitrobenzene, picryl chloride, or *m*-dinitrobenzene) was dissolved in an electron donor (tetrahydrofuran, *p*-dioxan, xylene, mesitylene, dimethoxyethane, or *o*-chlorophenol) and irradiated with ultraviolet light. Electron phototransfer was detected from the appearance of the EPR signals of the radical-anions of the corresponding electron acceptors. The maximal concentration of radical-anions amounts to 0.1% of the concentration of neutral molecules. The chloranil + tetrahydrofuran pair produces a single structureless EPR line, which disappears in the dark indicating that the phototransformations in the system are reversible. The EPR spectrum obtained on irradiation of the sym-trinitrobenzene + tetrahydrofuran pair has the hyperfine structure characteristic of the radical-anion of the electron acceptor.

Ward[55] observed the production of paramagnetism when a solution of nitrobenzene in tetrahydrofuran was illuminated, but the EPR spectrum of the paramagnetic centre contained a larger number of components than might have been expected for the nitrobenzene radical-anion. He was able to establish by means of deuterotetrahydrofuran that the additional splitting ($a_H = 0.38 \pm 0.04$ Oe) is due to the proton of the α-hydrogen of the tetrahydrofuran molecule. It may thus be assumed that under the influence of ultraviolet light, photoexcited nitrobenzene removes the α-hydrogen of the tetrahydrofuran molecule, and not the electron. The dehydrogenated tetrahydrofuran radical repidly dimerises or disproportionates, producing a non-paramagnetic compound. The conclusion that an uncharged nitrobenzene radical is produced on illumination of its tetrahydrofuran solution is confirmed by the absence of photoconductivity[56].

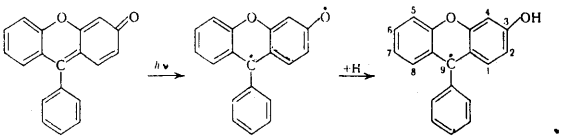
Tetracyanoethylene dissolves in most organic solvents to give solutions with an intense colour[57,58], due to the formation of a weak intermolecular complex with charge transfer[59-62] between the solvent molecule (the donor) and tetracyanoethylene (the acceptor). The production of a weak complex with charge transfer between tetracyanoethylene and tetrahydrofuran leads to the appearance of an absorption band at 318 nm[58]. The absorption band of the pyromellitic dianhydride + tetrahydrofuran complex lies in the range 330–385 nm[63]. Ward[56] showed that on illumination of their solutions the absorption band of the charge-transfer complex shows the EPR signals of the corresponding radical-anions: the eleven-component spectrum of the tetracyanoethylene radical-anion[64] and the three-component spectrum of the pyromellitic dianhydride radical-anion. The photogeneration of anion-radicals in these systems was confirmed by the production of photoconductivity. Analogous results were obtained on ultraviolet irradiation of solutions of tetracyanoethylene in methyltetrahydrofuran and *NN*'dimethylformamide. The photoreaction can be represented by the following scheme:

$$D + A \rightarrow D^{\delta+}A^{\delta-};\quad D^{\delta+}A^{\delta-} \xrightarrow{h\nu} D^+ + A^-\ .$$

As in the previous examples, proof of the existence of the positive tetrahydrofuran ion was not obtained.

Analogous results were obtained by Ilten and Calvin[65], who studied the photoinduced EPR signals and photoconductivity of solutions of tetracyanoethylene in tetrahydrofuran.

Bubnov and coworkers[66,67] used the EPR method to study the photoreduction of eosin. The photoreduction of eosin in the presence of a reducing agent involves the transformation of the dye into the leuco-compound. The mechanism of this reaction was previously studied by potentiometric and spectroscopic methods[68,69], and it was established that the reaction takes place in stages with the formation of intermediate product—the semiquinone of the dye. The lifetime of this intermediate product at room temperature amounts to several seconds. Illumination of eosin in pyridine in the presence of ascorbic acid (reducing agent) in fact leads to the production of the EPR signal of the corresponding semiquinone. The formation of the semiquinone in the photoreduction of eosin can be completely explained by Schenck's scheme[70].



eosin biradical semiquinone

The reversible photochemical reduction of chlorophyll by ascorbic acid is a model system for the photochemical stage of photosynthesis, in which light energy is stored in the photoproducts. Spectroscopic and electrometric measurements[71-73] have shown that the photoreduction involves the following elementary stages (Krasnovskii's reaction):

$$X + AH \xrightarrow{h\nu} X^* + AH \rightarrow X^{\cdot-} + \dot{A}H^+ \rightarrow \dot{X}H + \dot{A}$$

where X represents chlorophyll, and AH ascorbic acid.

The EPR method has been used to detect and study radical intermediate products formed on illumination of this model system[74,75]. Experiments on the photoreduction of chlorophyll and its analogues (pheophytin, haematoporphyrin, and magnesium phthalocyanine) were carried out in pyridine solutions in air and in a vacuum. The EPR signal produced in the illuminated solutions was found to be the same for all the pigments studied, and consisted of a doublet with a plitting equal to 1.8 Oe and $g = 2.004$. The spectra obtained belonged to the radical semi-oxidised form of ascorbic acid (monodehydroascorbic acid). In the system studied, the final stage involves the formation of a non-paramagnetic reduced form of the pigment and an

oxidised form of ascorbic acid. The EPR spectrum of the radical forms of the pigments could not be detected in any of the experiments, apparently because of their extremely high activity and correspondingly short lifetime in the system studied.

The semireduced semiquinone forms of the synthetic analogues of chlorophyll—the phthalocyanines—were detected by the EPR method during the dark reduction and photoreduction of these dyes in solutions in the presence of aliphatic amines or alkali metals[76,77]. Eigenmann[76] studied the photoreduction of copper phthalocyanine and phthalocyanine without metal in aqueous solutions in the presence of triethylamine and ethylenediamine. In the photoreduction of copper phthalocyanine, Cu^{2+} was converted into Cu^{+}, accompanied by a change in the intensity of the EPR signal. In the photoreduction of phthalocyanine without metal, which is a diamagnetic compound, a free radical whose EPR spectrum consisted of a narrow singlet was produced as intermediate product.

We showed[77] that the semi-reduced radical-ion form of Mg phthalocyanine and phthalocyanine without metal, produced by the reaction of the dye molecule with metallic sodium in tetrahydrofuran, is characterised by a structureless singlet EPR line with $g = 2.003$ and $\Delta H = 7$ Oe. These results show that the photoreduction of phthalocyanines takes place in an elementrary act involving the acceptance of one electron by the dye molecule.

Fujimori and Tavla[78] detected the formation of paramagnetic intermediate products in the photoreduction of chlorophylls *a* and *b* by hydroquinone in methanol under the influence of red light. Degassed solutions of $(4.5–4.9) \times 10^{-4}$ M chlorophyll and 10^{-2} M hydroquinone in methanol give two types of EPR signal on illumination. One has the hyperfine structure characteristic of the *p*-benzosemiquinone free radical, whereas the other is broad and is possibly due to the reduced form of chlorophyll. Measurements of the photovoltaic effect in these systems confirm the photoreduction of chlorophyll. The action of light apparently leads to electron phototransfer from hydroquinone to chlorophyll. Tollin and Banerjee[79] used the EPR method to study the reversible photoreduction of chlorophyll and pheophytin (*A* and *B*) by hydroquinone in alcohol solution in a vacuum (10^{-6} torr). They showed that the well resolved five-component EPR spectrum of benzosemiquinone is produced when a degassed solution of chlorophyll or pheophytin (7.3×10^{-5} M) and hydroquinone (2.2×10^{-2} M) in ethanol is illuminated with red light (duration of illumination from 30 min to 3 h). This photoinduced signal disappears very rapidly (< 1 s) on interruption of the illumination of the specimen, placed in the resonator of the spectrograph. Measurement of the optical absorption spectra of the solution before and after illumination showed that the electron transfer from the hydroquinone molecule to the photoexcited pigment is completely reversible. It was also found that oxygen effectively inhibits the oxidation of hydroquinone by reacting with the photoexcited pigment molecule[80,81].

It was found, however, that the addition of 0.1% pyridine (1.25×10^{-2} M) to this system increases the efficiency of the photoformation of the benzosemiquinone. Tollin and Banerjee suggest that this is due to the initial formation in solution of more readily oxidised non-paramagnetic complexes by the pyridinium ion and the hydroquinone anion, of the form $PyH^{+}...Q^{-}$. It is not excluded, however, that the addition of an organic base such as pyridine to the solution alters the pH of the medium and displaces the equilibrium for the reversible electron transfer towards the formation of the semiquonone.

The temperature dependence of electron transfer between hydroquinone and the photoexcited pigment molecule (chlorophyll or pheophytin) in the presence of pyridine was studied, and it was shown that electron transfer takes place even at −100°.

These results, and those given earlier, show that the photoexcited chlorophyll molecule, depending on the medium and its partners, may either take up or give up an electron with high efficiency, and this apparently determines its role in photosynthesis.

Rikhireva and coworkers[82,83] used the EPR method to detect chlorophyll molecules in the photoexcited triplet state, and also to study the free-radical forms of the pigment in ethanol solutions (5% HCl) at 77°K under the influence of visible light. Under these conditions a singlet EPR signal ($g \simeq 2$, $\Delta H = 9–11$ Oe) is produced in solutions of chlorophyll[83] and also of porphin and a number of prophyrins[84]. Similar singlet EPR signals were detected when solutions of chlorophyll in ethanol containing 20% water were illuminated with visible light at 77°K. The presence of reducing agents (ascorbic acid or phenylhydrazine) or oxidising agents (oxygen) in the solutions did not lead to intensification of the photoreaction at 77°K. Illumination of solutions of chlorophyll and pheophytin in ethanol, pyridine, piperidine, and 1 : 3 pyridine–ethanol mixtures at 300°K followed by rapid freezing ("fixation") of the solutions with liquid nitrogen leads to an increase in the intensity of the photoinduced EPR signals[85]. Under these conditions the concentration of paramagnetic photoproducts increases when oxygen, water, or a reducing agent are introduced into the solution. The authors cited[85] reached the following conclusion regarding the nature of the singlet EPR signal: the photoinduced EPR signal is due either to a charge-transfer complex formed by the photoexcited pigment molecule and the solvent molecule (with the participation of molecules of water and oxygen) or to a radical (radical-ion) form of the pigment.

Mauzerall and Feher[86] detected the EPR signals of the semireduced forms of various porphyrins, produced on illumination ($600 \leqslant \lambda \leqslant 700$ nm) of their degassed solutions in water, and also in aqueous glycerol at 25° in the presence of reducing agents. Three isomers of uroporphyrin and α,β-dihydroxyethyldeuteroporphyrin were studied. Ethylenediaminetetra-acetic acid, thiazolidine-4-carboxylic acid, NADH, and sparteine were used as reducing agents. The integral light intensity in the range 606–625 nm, corresponding to the long-wave absorption bands of the porphyrins, reached 10^{17} quanta $cm^{-2}s^{-1}$. Illumination produced singlet EPR lines of Gaussian form with $g = 2.0021 \pm 0.0001$ and $\Delta H = 5.4 \pm 0.2$ Oe. The EPR signal disappeared rapidly in the dark. Study of the kinetics of the disappearance of the EPR signal showed that the process involved in the disappearance of the paramagnetic centres is a second-order reaction. The processes taking place in these solutions can be described by the following scheme:

$$P + h\nu \xrightarrow{k_1} P^*$$

$$P^* \xrightarrow{k_2} P + h\nu_{fl.}\ (\text{heat})$$

$$P^* + R \xrightarrow{k_3} P^{\cdot} + R^{\cdot}$$

$$P^{\cdot} + P^{\cdot} \xrightarrow{k_4} P + \text{phlorin (dihydroporphyrin)}$$

$$R^{\cdot} + R^{\cdot} \xrightarrow{k_5} \text{product}$$

A possible reason for the absence of EPR signals from the radicals of the reducing agent ($\dot{R}$) may be that the rate constant $k_5 > k_4$, so that the steady-state concentration of $\dot{R}$ is too small for detection.

The formation of semireduced free-radical forms of various porphyrins on irradiation of their alcoholic solutions at 77°K by unfiltered light from a DRSh-1000 mercury lamp was detected by Gribova[87-91], who showed that the observed EPR spectrum of the free radicals consists of the singlet line of the free radical or porphyrin superimposed on the spectrum of the free-radical products of the decomposition of ethanol. It was also found that photoexcitation of porphyrins only in the long-wave absorption band (578 nm and 542 nm) leads to transfer of the chromophore molecule into the ground triplet state, but does not lead to the formation of free radicals. Comparison of the absorption spectra of a frozen solution of Mg etioporphyrin at 77°K before and after illumination with unfiltered light from a mercury lamp showed that in place of the characteristic absorption bands of porphyrin at 578 nm and 542 nm, an intense absorption band is produced at 686 nm, with a small maximum at 606 nm. Parallel qualitative comparison of the change in the concentration of the chromophore radical (singlet EPR line) and the absorption spectrum of the specimen with increase in temperature at 150°K showed that the decrease in the intensity of the absorption band at 686 nm corresponds to the decrease in the intensity of the EPR singlet line. According to these results, the absorption band at 686 nm can be assigned to the porphyrin free radical. As Gribova suggests, the porphyrin free radical may be produced as a result of the photoreduction of the chromophore molecule, existing in a high excited triplet state, by the solvent molecule.

4. Secondary Processes

The irradiation of salts of tervalent iron in alcoholic solutions with near ultraviolet or violet light leads to their reduction, with simultaneous oxidation of the solvent[92,93]. The basic elementary step in the photochemical reduction of tervalent iron in alcohols involves electron transfer within the complex:

$$Fe^{3+}Cl^- \xrightarrow{h\nu} Fe^{2+} + Cl^{\cdot}.$$

The chlorine atoms cannot be detected by the EPR method, but their formation is readily recorded from secondary processes—the chlorine atoms readily react with the alcohol, leading to the formation of free radicals:

$$RCH_2OH + Cl^{\cdot} \rightarrow R\dot{C}HOH + HCl.$$

Kryukov and coworkers[94] used the EPR method to detect and identify these radicals. To stabilise the alcohol radicals, the irradiation and the recording to the EPR spectra were carried out in methanol, ethanol, propan-1-ol, and propan-2-ol at 77°K. In all experiments a clearly defined EPR spectrum with hyperfine splitting was observed, indicating the presence of the free radical of the dehydrogenated alcohol in the system. The nature of the radicals is determined by the nature of the alcohol, and is independent of the nature of the iron complex.

Bazhin and coworkers[95], in a study of photoprocesses in an $H_2O + H_2SO_4 + FeSO_4$ mixture at 77°K in a vacuum, found that if the previously irradiated ($\lambda = 254$ nm) mixture is kept at 120°K and then cooled again to 77°K, the spectrum of the hydrogen atoms produced as a result of electron phototransfer disappears. This cannot be regarded as the result of recombination of the hydrogen atoms at 120°K, however. If the specimen is then subjected to irradiation again with visible light ($\lambda > 480$ nm), the doublet EPR signal of the hydrogen atoms is produced almost immediately on illumination. The formation of the "secondary" hydrogen atoms is observed if the second irradiation is carried out using red light ($\lambda > 600$ nm). These results show that the $H_2O + H_2SO_4 + FeSO_4$ photochemical system contains unique hydrogen atom traps, in which they are stabilised at 120°K. It is most probable that the hydrogen atoms at 120°K react with Fe^{2+} to form complexes of the type $(Fe^{2+}...H)$[96], which decompose under the influence of light with long wavelength ($\lambda > 260$ nm).

The use of the hydrogen atoms obtained in this way to study chemical reactions with various compounds at low temperatures is of considerable interest. Bazhin and coworkers[97] studied the reaction of hydrogen atoms with acetylene, ethylene, propene, allyl alcohol, and carbon monoxide at 90°K and 120°K. It was shown that at these temperatures the hydrogen atoms are capable of addition to these compounds with the formation of the corresponding radicals. Thus the reaction of hydrogen atoms with acetylene gives the vinyl radical ($H_2C=\dot{C}H$ (eight-component EPR spectrum with $a_\alpha = 16$ Oe, $a_\beta = 63$ Oe, and $a_{\beta_2} = 3.8$ Oe). The reaction of a hydrogen atom with ethylene gives the ethyl radical $\dot{C}_2H_5$. The reaction of a $\dot{H}$ atom with propene gives the isopropyl radical $CH_3\dot{C}HCH_3$. The reaction of a $\dot{H}$ atom with allyl alcohol $CH_2=CH-CH_2OH$ gives the radical $\dot{C}H_2-CH_2-CH_2OH$ (or $\dot{C}H_2-CH_2-CH_2OH_2^+$). The reaction of an $\dot{H}$ atom with CO gives the radical $H\dot{C}O$. Thus atomic hydrogen at 90–120°K can react with unsaturated compounds by addition to a double or triple bond or to a pair of unshared electrons (CO).

Whereas atomic hydrogen undergoes addition to unsaturated hydrocarbons at 90–120°K, in its reactions with saturated organic compounds in the same temperature range it removes a labile hydrogen atom. This was shown by Bazhin and coworkers[98], in a study of the reactions of atomic hydrogen with methanol, ethanol, propan-2-ol, ethylene glycol, isobutyric acid, malonic acid, and acetone. Bazhin and coworkers results[98] indicate that a "cold" $\dot{H}$ atom at 90°K is able to remove a labile hydrogen atom from the molecules of aliphatic alcohols, organic acids, and ketones.

Bazhin and coworkers[99] recently described the low-temperature reactions of hydrogen atoms with various aromatic compounds. They studied the reaction of atomic hydrogen in the $FeSO_4 + H_2O + H_2SO_4$ system irradiated with ultraviolet light ($\lambda = 254$ nm) with molecules of the following compounds: benzene, phenol, resorcinol, phloroglucinol, pyrocatechol, hydroquinone, guaiacol, 1,4-dimethoxybenzene, anisole, benzenesulphonic acid, benzyl alcohol, aniline, diphenylamine, and toluene. All the reactions at 90°K or 120°K produced radicals formed by the "attachment" of a hydrogen atom to the molecules of the aromatic compounds, characterised by an EPR triplet spectrum with a splitting of ~40–50 Oe for the protons of the $\diagdown CH_2$ group[100]. The additional splitting of the components of the triplet dependended on the position of the attached hydrogen atom relative to the substituent, and on the nature of the substituents. The EPR spectra of the radicals formed by the "attachment" of hydrogen atoms to the molecules of phenol, anisole, and benzenesulphonic acid show that 60–80% of the hydrogen atoms are attached in the ortho- or para-positions relative to the substituents. With resorcinol, the attachment of the hydrogen atom takes place chiefly in the ortho- or para-position relative to the OH groups. For pyrocatechol, hydroquinone, 1,4-dimethoxybenzene, and guaiacol, the EPR spectrum of the radicals formed by the "attachment" of a hydrogen atom consisted of a triplet of triplets, since in these radicals

the form of the EPR spectrum is independent of the position of attachment of the hydrogen atom. The observed EPR spectra for the radicals produced by the attachment of hydrogen atoms to the molecules of aniline, diphenylamine, and benzyl alcohol correspond to radicals with an H atom in the meta-position relative to the substituent.

Theoretical calculation[101] shows that the hydrogen atom should be attached chiefly in the ortho- or para-positions relative to the substituent, irrespective of the nature of the latter.

III. THE STUDY OF PHOTOSENSITISED REACTIONS OF ORGANIC COMPOUNDS BY THE EPR METHOD

1. Sensitised Photo-oxidation

The photo-oxidation and photoreduction of organic compounds, which require large quanta of energy, can be sensitised to the visible range of the spectrum by means of various dyes and pigments. A typical example of a photoreaction of this type is the photosensitised autoxidation of various aromatic compounds, studied by Ashkinazi and coworkers[102-104] by the EPR method.

When an ethanol solution of diphenylamine (10^{-2} M) at 293–295°K in the presence of chlorophyll *A* (10^{-5} M) and oxygen is irradiated with red light ($\lambda > 600$ nm), the colour of the reaction mixture changes in 10–15 min: the green solution first becomes reddish-brown, and then brown[102,103]. This is accompanied by a marked increase in the absorption in the range 400–560 nm. The same result is obtained when pheophytin *A* is used as senitiser. Prolonged irradiation of diphenylamine solutions freed from molecular oxygen does not change the absorption spectrum. The coloured product of the photoreaction was isolated in pure form. Its absorption spectrum is characterised by two maxima at 460 nm and 260 nm. The addition of a reducing agent (ascorbic acid, hydrazine, or hydroquinone) to a solution of this product instantaneously regenerates diphenylamine. This indicates that the autoxidation of diphenylamine sensitised by pigments gives a product which is not extensively oxidised. The authors cited[102,103] suggest that this product may be the diphenylnitrogen free radical $(C_6H_5)_2\dot{N}$. As confirmation of their suggestion, they give the EPR spectrum of the photoreaction product responsible for the colour; this spectrum consists of a triplet with component intensity ratio 1 : 1 : 1 and a splitting of 10–11 Oe. Ashkinazi and coworkers[103] suggest the following photoreaction scheme. A triplet molecule of the sensitiser reacts with the oxidation substrate (diphenylamine), removing an electron from it. This gives the diphenylamine radical-cation $[(C_6H_5)_2NH]^+$, which readily gives up a proton H^+ and is converted into the diphenylnitrogen radical $(C_6H_5)_2N$, which accumulates during the photoreaction. This scheme, however, ignores completely the part played by molecular oxygen in this photosensitised autoxidation. According to the above scheme, the photoreaction would take place with even greater efficiency under vacuum conditions, because of the quenching action of molecular oxygen on the triplet molecules of the sensitiser. Moreover, it is known that the diphenylnitrogen radical is extremely unstable in the presence of molecular oxygen and is rapidly converted in the dark into the diphenylnitroxide radical $(C_6H_5)_2\dot{N}O$, the EPR spectrum of which is extremely similar to the EPR spectrum of the diphenylnitrogen radical, showing only slight differences in the hyperfine interaction constants[105]. It may therefore be assumed that the accumulating free-radical product of the oxidation of diphenylamine, photosensitised by pigments (chlorophyll *A* or pheophytin *A*) is diphenylnitroxide. The diphenylnitrogen radical may be produced as a labile intermediate product of this photoreaction, as in the oxidation of diphenylamine by peroxo-compounds in the dark[106-108].

The formation of free-radical products was also detected by Ashkinazi and coworkers[103] in the autoxidation of *p*-phenylenediammonium chloride, photosensitised by pheophytin *A*, in alcoholic solution in the presence of molecular oxygen under the influence of red light. The photoreaction produced a reddish-yellow product (absorption maxima at 462 nm and 480 nm) with a singlet EPR signal and $\Delta H = 14$ Oe. The authors suggest that this product is the *p*-phenylenediamine radical-cation. The mechanism of the photoreaction is not discussed.

Ashkinazi and Dolidze[104] observed the autoxidation of α-naphthylamine, photosensitised by chlorophyll *A* and pheophytin *A*. In these experiments they observed a characteristic photo-after-effect: after the illumination of the system with red light was interrupted, the formation of an intensely coloured product (absorption maxima at 440 nm and 465 nm) continued for some time. The photoreaction does not take place in the presence of a reducing agent (ascorbic acid). EPR measurements showed that the photosensitised autoxidation of α-naphthylamine gives a free radical, the EPR spectrum of which consists of a singlet line with $\Delta H = 9$ Oe. The EPR signal disappears after several hours in the dark. Parallel measurement of the intensity of the absorption spectrum of the same specimen showed that the absorption increases so long as the EPR signal exists. This indicates that the free radical formed in the photoreaction takes part in a secondary reaction, leading to the production of a coloured product. The mechanism and nature of the intermediate product of the photoreaction have not yet been established.

The photo-oxidation of *NN*-diphenylamine, sensitised to visible light by eosin, in solution at room temperature was studied by Lagercrantz and Yhland[109] by the EPR method. They dissolved *NN*-diphenylamine in ethanol or pyridine (10^{-2} M), to which eosin was added (10^{-4} M). Illumination of the system with the visible part of the light from a xenon lamp (with a filter consisting of 5 cm of a 10% solution of $CuSO_4$ in H_2O) led to the immediate formation of a paramagnetic product, which disappeared under the influence of light in 5 min. This paramagnetic product is stable, however, in the dark in a vacuum. The EPR spectrum, recorded in the dark immediately after the attainment of the maximal concentration of the paramagnetic product, consisted of 37 components, situated in three main groups. It may be assumed that the photoexcited sensitiser (eosin) removes the hydrogen atom attached to the nitrogen atom of diphenylamine, leading to the production of the free radical $(C_6H_5)_2\dot{N}$, which is observed in the photoreaction. Unfortunately, the authors[109] did not study the optical absorption spectra of the photosensitive system before and after illumination. Precise identification of the paramagnetic product is therefore impossible.

Lagercrantz and Yhland[109] also detected the formation of a paramagnetic product in the photo-oxidation of phenothiazine, sensitised by eosin. Since the paramagnetic product is unstable in the dark, they were unable to obtain a complete well-resolved EPR spectrum. It was established, however, that the spectrum consists of three groups of lines, with a splitting of 9.5 Oe, due to the interaction of the unpaired electron with the nucleus of the nitrogen atom of phenothiazine. Each group contains a large number of

components. Although this EPR spectrum does not give complete information, it may be assumed that the phenothiazine free radical is produced as a result of the removal, sensitised by eosin, of a hydrogen atom from the bridging nitrogen atom.

The characteristic five-component EPR spectrum of *p*-benzosemiquinone was produced when alcoholic solutions of hydroquinone and *p*-benzoquinone (10^{-2} M) to which eosin had been added (10^{-3} M) were irradiated with visible light. The semiquinone appeared and disappeared as the light was switched on and off. Radicals were not detected when *p*-dimethoxybenzene was used as substrate. The reaction mechanism was not discussed. In these instances we undoubtedly have an example of oxidation or reduction of the substrate, photosensitised by the dye.

The EPR method has found application not only in sensitised photo-oxidation–photoreduction, but also in the polymerisation of a substrate, sensitised by dyes. Schenck and coworkers [110,111] showed that the cyclodimerisation of acenaphthalene (7×10^{-2} M), photosensitised by Bengal Rose (10^{-2} M), in methanol at room temperature gives as intermediate product a short-lived complex (adduct–product) of the photoexcited sensitiser molecule (Sens*) and acenaphthalene (Ace):

$$\text{Sens} \xrightarrow{h\nu} \text{Sens}^* \xrightarrow{+\text{Ace}} \text{Sens}^* \text{Ace} \xrightarrow{+\text{Ace}} \text{AceAce} + \text{Sens}$$

This complex is paramagnetic, and gives a three-component EPR signal, which differs from the EPR signal of the semiquinone of the sensitiser [66]. The authors cited point out that the photosensitised cyclodimerisation of acenaphthalene is an example of the photochemical transfer of energy from a sensitiser to the molecules of a substrate through a biradical complex [112].

2. The Photosensitised Decomposition of Organic Compounds

A unique position among photoreactions, sensitised to light of long wavelength, which have been studied by the EPR method, is occupied by the sensitised photodecomposition of saturated hydrocarbons, aliphatic alcohols, their esters, and various alkyl halides. These photoreactions provide examples of the chemical utilisation of light energy, transferred from a photoexcited sensitiser to substrate molecules (molecules of solvent or added substrate), in which is used in fairly high yield for the rupture of the weakest bond. There is now convincing proof that these photoreactions take place by a two-quantum mechanism with the participation of triplet molecules of the sensitiser (aromatic hydrocarbons, ketones, amines, dyes, and pigments).

Shelimov and coworkers [113-116] were the first to detect the sensitised formation of free radicals under the influence of ultraviolet light in transparent solutions of benzene in aliphatic hydrocarbons, frozen at 77°K. On ultraviolet irradiation ($\lambda = 254$ nm) in hydrocarbon media at 77°K, benzene is decomposed with rupture of a C–C bond of the benzene ring. Ultraviolet spectroscopy and gas chromatography showed that the product of the photochemical decomposition of benzene at 77°K is a substituted hexatriene.

Shelimov and coworkers [113-115] found by the EPR method that the reaction at 77°K gives not only hexatriene but also alkyl radicals (R̂), the formation of which did not fit into any of the schemes proposed to explain the formation of the substituted hexatriene. In their experiments, transparent solid solutions of benzene (1.8×10^{-3}–2.1×10^{-1} M) in methycyclohexane and 3-methylpentane were subjected to the action of light (PRK-7) at 77°K in a vacuum. Irradiation of these solutions with ultraviolet light ($\lambda > 230$ nm) produced free radicals, identified from the EPR spectra as methylcyclohexyl and 3-methylpentyl respectively. Alkyl radicals were also obtained by ultraviolet irradiation of hydrocarbon solutions of hexadeuterobenzene, toluene, ethylbenzene, isopropylbenzene, *o*-, *m*-, and *p*-xylenes, diphenylmethane, triphenylmethane [117], and naphthalene [118].

The fact that molecular hydrogen is formed on irradiation is extremely significant. The process leading to the simultaneous formation of alkyl radicals and hydrogen can only be the dehydrogenation of the aliphatic hydrocarbons, photosensitised by the aromatic hydrocarbons.

Shelimov recently † studied the dependence of the rates of formation of hydrogen (H_2) and alkyl radicals in solutions of benzene, toluene [117], and naphthalene [118] in 3-methylpentane on the intensity of the light. The quadratic dependence which he observed indicates that the photosensitisation is a two-quantum process. It should be noted that the rate of formation of the substiuted hexatriene is linearly dependent on the light intensity [121], that is this reaction is a one-quantum process. Shelimov and coworkers suggested [116] and demonstrated [117,122] that the intermediate state in the sensitisation is the triplet state of the aromatic hydrocarbon; in this state the hydrocarbon absorbs a second quantum of light with $\lambda < 370$ nm.

The ability of aromatic amines to bring about the photosensitisation of the dehydrogenation of aliphatic alcohols was observed by us in 1960 during an EPR study, carried out at the suggestion of A. N. Terenin, of the photoionisation of aromatic amines in an alcohol–ether mixture at 77°K. The publication of the results of this study [123] was stimulated by a paper published by Smaller [124] towards the end of 1962, on a study of the photodehydrogenating power of indole with respect to methanol at 77°K. In our experiments we studied solutions of the following amines: aniline, diphenylamine, triphenylamine, *p*-phenylenediamine, and tetramethyl-*p*-phenylenediamine; and the following heterocyclic compounds containing amine nitrogen: indole, carbazole, and 9,10-dihdroacridan. The solvents, which were purified by distillation, were methanol, ethanol, propan-2-ol, n-butanol, and 2-methylpropanol, and also diethyl, dipropyl, and dibutyl ethers. Control experiments showed that the solvents themselves do not decompose even on prolonged (3 h) irradiation with ultraviolet light ($\lambda \geq 300$ nm). Illumination of solutions of the aromatic amines and N-heterocycles (10^{-4}–10^{-1} M), frozen at 77°K, however, produced considerable concentrations of the free radicals of the solvent (alcohol or ether), formed by the removal of the labile α-hydrogen [123]. We made a detailed study of the dependence of this photoreaction on the duration and intensity of the ultraviolet irradiation, the spectral composition of the light source (DRSh-500), the temperature of the solution, and the presence of selective extinguishing agents for the triplet state of the sensitiser.

The inhibiting action of added naphthalene on the yield of the photoreaction in an ethanol solution of triphenylamine (carbazole) at 77°K provided convincing proof of the participation of triplet molecules of the amines in the photoprocess [123]. On the other hand, by means of the intermittent illumination method, we were able, like

† This study was undertaken by Shelimov and coworkers after the publication of papers by Bagdasar'yan and coworkers [119] and Terenin and coworkers [120], demonstrating the two-photon mechanism of the sensitised decomposition of aliphatic compounds.

Smaller for indole[124], to show that aromatic amines and N-heterocycles in the ground triplet state are not capable of dehydrogenating aliphatic alcohols at 77°K. The formation of free radicals took place only on irradiation and in the presence of triplet molecules of the sensitiser. We therefore suggested that the sensitisation photoprocess is a two-photon process[120]. An analogous suggestion that the sensitisation of the rupture of the C_α–H bond in methanol by photoexcited indole is a two-photon process was first put forward by Smaller[124]. In this instance the rate of formation of the radicals (dR/dt) should have shown a quadratic dependence on the intensity (I) of the light exciting the sensitiser, that is $dR/dt \sim I^2$. In fact, as shown by the measurements of Bagdasar'yan and coworkers[119,125,126] and results which we obtained[120], this relationship is observed fairly satisfactorily in experiments on the sensitisation by triphenylamine and diphenylamine of the dehydrogenation of methanol and ethanol at 77°K. It should be noted, however, that a quadratic dependence of dR/dt on I may be obtained both as a result of the absorption of two quanta of light by the sensitiser molecule (a two-photon mechanism) and also if the formation of free radicals of the solvent takes place through a photoactive intermediate compound (complex), which is produced under the influence of the first quantum of light and then absorbs a second quantum (a two-stage mechanism)[127-131].

To prove that the photoreaction is a two-photon process, it was necessary not only to obtain a quadratic dependence on the intensity of the light exciting the sensitiser, but also to prove that the absorption of the second quantum takes place in the photoexcited triplet-level of the sensitiser molecule (triplet–triplet absorption).

Bagdasar'yan and coworkers[125,126] studied the mechanism of this photoreaction by the method involving interrupted illumination of the specimens; by measuring the rates of the photoreaction with interrupted illumination ($t_{light} = t_{dark}$ = 0.5, 1.875, 3.75, and 7.5 s, duration of illumination 6–9 min) and continuous illumination (2 min) by light with λ = 313 nm, they estimated the characteristic lifetime of the intermediate state responsible for the absorption of the second photon in the diphenylamine + ethanol (5×10^{-4} M) and triphenylamine + ethanol (5×10^{-4} M) systems at 77°K. The agreement between this quantity (1.95–2.14 s for diphenylamine and 0.56–0.81 s for triphenylamine) and the lifetime of the sensitisers used in the triplet state (τ_{phosph} for diphenylamine = 1.9 s and τ_{phosph} for triphenylamine = 0.7 s[132]) must be regarded as providing quantitative confirmation of the earlier suggestion that the formation of alcohol radicals in these systems takes place as a result of an optical triplet–triplet transition of the amine molecule. Unfortunately, the positions of the short-wave and ultraviolet bands of the triplet–triplet absorption have not been established for aromatic amines and N-heterocycles. According to our data, they should lie in the range 260–340 nm, since it is this light which is photochemically active as the second quantum in the photoreactions involved in the dehydrogenation of primary and secondary alcohols at 77°K, sensitised by aromatic amines and N-heterocycles.

We obtained definite proof that the two-photon excitation of the sensitiser to high triplet states is a necessary stage in the sensitisation photoprocess in a study of the sensitised photodecomposition of t-butyl alcohol. t-Butyl alcohol $(CH_3)_3COH$ is an example of an alcohol which does not contain α-hydrogens. We showed[133] that by its sensitised photodecomposition it is possible, in the primary act of the photoreaction, to bring about rupture of a C–C bond with the formation of methyl radicals and the free radicals of the alcohol. When a solution of diphenylamine, triphenylamine, or indole (10^{-2}–10^{-3} M) in t-butyl alcohol at 77°K is irradiated with ultraviolet light ($\lambda \geqslant 320$ nm) corresponding to the long-wave edges of the absorption bands of the amines, the system after 5 min gives the EPR spectrum characteristic of the $\dot{C}H_3$ radical, and also an EPR spectrum identical to the spectrum of the radical of dehydrogenated propan-2-ol $(\dot{C}H_3)_2COH$. Similar spectra were observed on illumination ($\lambda \geqslant 300$ nm) of the solutions of naphthalene, phenanthrene, and biphenyl in t-butyl alcohol at 77°K, used as sensitisers. Of considerable interest in the rupture of the C–C bond in t-butyl alcohol, sensitised by dissolved naphthalene, for which the positions of the triplet–triplet bands, including the ultraviolet bands, are well known[134]. By illumination of specimens with monochromatic light from two sources, one of which (λ = 313 nm) was used to obtain high concentration of triplet molecules of naphthalene, whereas the light from the other corresponded to a given band of the triplet–triplet absorption of naphthalene, it was established that photochemically active conditions correspond to simultaneous subsidiary illumination of the solution by light with $\lambda > 365$ nm (the $T_0 \rightarrow T^*$ transition is brought about under the influence of light with λ = 415, 391, and 375 nm)[135].

Rupture of the C–CH_3 bond in t-butyl alcohol can be sensitised by means of various dyes. Acridine Yellow, Rhoduline Orange, and fluorescein (H^+ cation) were found to be extremely effective. The rate of production of free radicals shows a quadratic dependence on the intensity of the light exciting the dye[135,136]. By irradiation of solutions of the dyes by two light sources with different spectral compositions ($\lambda_1 > 400$ nm, $\lambda_2 < 400$ nm) it was established that the second photon is absorbed by a triplet molecule of the dye with its subsequent excitation to a high triplet state ($T_0 \rightarrow T_4^* - T_5^*$ -transition)[137,138].

Various biologically important compounds such as aromatic aminoacids (tryptophan, tyrosine, and phenylalanine) and nucleic acid bases (purine, adenosine, and guanosine), were found to have sensitising properties very similar to those of aromatic amines and N-heterocycles. Gribova and coworkers[87,89] studied the EPR of the triplet state of porphyrins and aromatic aminoacids (transition $\Delta m = \pm 2$) and found that during the ultraviolet irradiation of alcoholic solutions of aromatic aminoacids at 77°K the concentration of the latter in the triplet state decreases, with the simultaneous formation of free radicals of the dehydrogenated alcohol. The concentration of free radicals produced is proportional to the concentration of aromatic aminoacid molecules excited to the triplet state. A similar observation was made by Douzou and Ptak[139]. Azizova[18,20] found that brief (5 s) ultraviolet irradiation (unfiltered light from a DRSh-1000 mercury lamp) of a solution of tryptophan (2.5×10^{-3} M) in water in the presence of 2% ethanol at 77°K produces an EPR signal consisting of the superposition of the spectra of three paramagnetic products—the free radical $CH_3\dot{C}HOH$ (five-component spectrum), the positive tryptophan radical-ion, and an electron trapped in the matrix (singlet line). Subsequent prolonged irradiation of the solution by light with $\lambda \geqslant 320$ nm leads to a decrease in the intensity of the singlet EPR signal and to the appearance of components of the $\dot{C}H_3$ radical, produced as a result of photodecomposition of ethanol free radicals. The photosensitised decomposition of ethanol molecules also takes place in aqueous-alcoholic solutions of tyrosine and phenylalanine. The participation of the ground triplet state of aromatic amino-

acids in the photoreaction was confirmed by Gribova[87-91] in a study of the yield of free radicals obtained by interrupted and continuous irradiation of the specimens (tryptophan in ethanol, concentration 5×10^{-4} M) by light with the same intensity for the same total period of illumination. It was found that the yield of free radicals is smaller by a factor of 20 for interrupted irradiation (irradiation intervals 0.45 s, dark period 7 s). The participation of the excited triplet state of the aromatic aminoacids in the photoreaction was proved by the dependence of the yield of free radicals on the intensity of the incident light, which was found to be close to quadratic[89,91].

Helene and coworkers[140] found that purine, adenosine, and guanosine have a similar ability to sensitise the photodehydrogenation of aliphatic alcohols at 77°K. Ultraviolet irradiation ($\lambda > 250$ nm) of aqueous solutions of purine and adenosine (10^{-2} M) with 2% ethanol (0.35 M) at 77°K produced the five-component EPR spectrum of the $CH_3\dot{C}HOH$ radical, superimposed on a singlet EPR line‡. Subsequent irradiation of these solutions with visible light ($\lambda > 450$ nm) decreases the singlet signal, as a result of which the signal of the ethanol radical becomes more clearly defined. In aqueous solution containing 20% ethanol (3.5 M) or in pure ethanol solution, ultraviolet irradiation produced only the EPR signal of the ethanol radical $CH_3\dot{C}HOH$. At low intensities of the ultraviolet light, the rate of formation of the ethanol radicals remains unchanged with time and is proportional to I^2_{eff}, where I_{eff} is the intensity of the light absorbed by the molecules of the added sensitisers. At any moment of time, the rate of formation of the radicals is proportional to the concentration of triplet molecules of the sensitisers. The photosensitisation of the dehydrogenation of ethanol molecules by purine, adenosine, and guanosine evidently proceeds through an excited triplet state, produced by the two-photon photoexcitation of the sensitiser.

Irradiation of an ethanol solution of Mg etioporphyrin at 77°K by light from a superhigh-pressure mercury lamp (DRSh-1000) produces a large number of free radicals of the chromophore and ethanol $CH_3\dot{C}HOH$[87]. Gribova[88] showed by the EPR method that the irradiation of an ethanol solution of Mg etioporphyrin at 77°K by light with $\lambda =$ 578 nm, corresponding to the long-wave absorption band, produces only the EPR absorption due to molecules of the chromophore excited to the ground triplet state. The irradiation of frozen solutions by light with wavelength 248–365 nm for 5–10 min does not lead to the formation of free radicals, or produces them in very low yield. On simultaneous irradiation of solutions of Mg etioporphyrin in ethanol at 77°K by light from two sources (two DRSh-1000 lamps) with different spectral compositions, the yield of free radicals increases sharply (by a factor of 5–20) when the first source contains light of wavelength $\lambda = 578$ nm, leading to the formation of triplet molecules of the chromophore, and the second source has $\lambda < 322$ nm. Increase in the energy quantum from the second source increases the rate of formation of the free radicals. The EPR spectrum in this instance consists of the superposition of a single line due to the chromophore radical and a low concentration of free radicals of the alcohol $CH_3\dot{C}HOH$. From these results obtained by Gribova, it follows that the energy of a quantum of light of $\lambda = 578$ nm, absorbed by Mg etioporphyrin, is sufficient only for the excitation of its molecules to the ground triplet state, but is insufficient for the formation of free radicals; in the ground triplet state the chromophore is photochemically inactive in an ethanol matrix at 77°K. A high-energy quantum of light ($\lambda =$ 248–365 nm), however, is also insufficient for the dehydrogenation of ethanol in the absence of chromophore molecules excited to the ground triplet state. Free radicals of the chromophore and matrix are formed only on simultaneous irradiation by two quanta of light of $\lambda = 578$ nm and $\lambda < 322$ nm. The addition of glutathione, which was found to be a selective extinguishing agent for the triplet state of the chromophore, to an ethanol solution of Mg etioporphyrin led to a sharp decrease in the yield of radicals[89,91]. The participation of the ground triplet state as an intermediate state in the photochemical dehydrogenation of ethanol was proved by the dependence of the yield of free radicals on the intensity of the incident light; this dependence was found to be close to quadratic[89,91]. Direct proof of the participation of the ground triplet state of Mg etioporphyrin as an intermediate state in the photodehydrogenation of ethanol at 77°K was obtained by determining the influence of interrupted illumination on the yield of free radicals[90]. The solution was illuminated by unfiltered light from a DRSh-500 mercury lamp. The experiment was carried out at low light intensities. The periods of illumination were 1.8×10^{-2}, 9.0×10^{-3}, and 6.0×10^{-3} s, that is much less than τ_{phosph} for Mg etioporphyrin ($\tau_{phosph} = 1.83 \times 10^{-1}$ s [141]). The dark periods amounted to 1–2 s. Comparison of the yields of radicals for continuous and interrupted illumination for the same total periods of illumination showed that the concentration of radicals for continuous illumination is greater by a factor of 16 than for interrupted illumination with illumination intervals of 1.8×10^{-2} s, and greater by a factor of 25–30 than that for interrupted illumination with illumination periods of 9×10^{-3} s; this agrees with theoretical calculation and shows that a short-wave light quantum is absorbed by the chromophore molecule in the ground triplet state.

We noted in our first paper[123] that naphthalene, acting as sensitiser, can bring about the dehydrogenating of primary aliphatic alcohols at 77°K, but the yield of the photoreaction is lower by two orders of magnitide than that observed when aromatic amines and heterocycles with an amine group are used as sensitisers. Siegel and coworkers[142,143] made a detailed EPR study of the photodehydrogenation of ethanol, diethyl ether, and methylcyclohexane at 77°K, sensitised by naphthalene. They found that the rate of dehydrogenation also shows a quadratic dependence on the intensity of the light exciting the naphthalene. They also established that radiation with wavelength 270–300 nm is effective for the excitation of naphthalene molecules to the ground triplet state. Photochemical activity was observed, however, when the specimens were irradiated simultaneously with this radiation and by light of wavelength 250–260 nm. The naphthalene acting as sensitiser was not used up to a significant extent in the photoprocess. The observed decrease in the intensity of the EPR signal of the triplet molecules of naphthalene (transition $\Delta m = \pm 2$) was related to the decrease, by a factor of more than 100, in the lifetime of naphthalene in the triplet state as a result of the extinguishing action of the free radicals of the dehydrogenated solvent, produced on illumination. The formation of radicals of the solvent was not observed on illumination of non-degassed solutions of naphthalene at 100°K, that is under conditions where the

‡ In aqueous solutions of purine, adenosine, and guanosine, ultraviolet irradiation ionises the molecules $Pu \xrightarrow{h\nu} Pu^+ + e$. The singlet EPR signals actually consists of the signal of the Pu^+ radical-cation and the signal of electrons trapped by the matrix at 77°K.

steady-state concentration of the triplet molecules of naphthalene is low as a result of extinction by diffusing molecules of oxygen. The rate of appearance of free radicals of the dehydrogenated solvent increases significantly at 77°K when naphthalene is replaced by completely deuterated naphthalene, since the lifetime of the latter in the triplet state is greater by a factor of 5. [144] These results show that the groud triplet state of the naphthalene molecules is an intermediate state in the photosensitisation. The quadratic relationship shown by the rate of formation of the free radicals, and the fact that the range of photochemically active wavelengths coincide with the short-wave band of the triplet–triplet absorption of the naphthalene molecule ($\lambda \simeq 260$ nm) [134], enabled Siegel and Eisenthal to postulate that the sensitisation is a two-photon process, in which the final stage is the excitation of the molecule of the sensitiser (naphthalene) to a high triplet state.

West and coworkers [145,146] made a detailed optical study of the decomposition of alkyl iodides in hexane and ethanol at 300°K, photosensitised by naphthalene. We used the EPR method to study the primary processes taking place during the ultraviolet irradiation of solutions of alkyl iodides (methyl iodide and ethyl iodide) containing various sensitisers (diphenylamine, triphenylamine, naphthalene, biphenyl, phenanthrene, and benzophenone) at 77°K, and found that the sensitisation of the rupture of the C–I bond of the alkyl iodides is a two-photon process [147–150]. The spectral dependence of this photoreaction was studied for specimens containing naphthalene as sensitiser. The specimens were irradiated by two light sources. The light from one of these sources (a DRSh-500 superhigh-pressure mercury lamp) was filtered through a filter which picked out the 313 nm mercury line, necessary for the excitation of naphthalene to the triplet state. The light from the other source (DRSh-250), which was combined with an SZS-22 filter, contained the 365, 404, and 408 nm mercury lines, falling in the known range of the triplet–triplet absorption of naphthalene [134]. It was established beforehand that each source taken separately did not bring about the photodecomposition of the alkyl iodides at 77°K. Photodecomposition took place, however, under the simultaneous influence of both sources.

Similar experiments were carried out with specimens containing the dyes Acridine Yellow, Rhoduline Orange, fluorescein, and porphyrins as sensitisers. The only difference was that visible light ($\lambda > 400$ nm) was used to excite the dyes to the triplet state, and the triplet–triplet transitions were brought about under the influence of ultraviolet light with $\lambda < 400$ nm. The absorption spectrum of the triplet molecules of the dyes contains diffuse bands in the near ultraviolet range [137,138].

Siegel and Judeikes [151] used the EPR method to detect the decomposition of polydimethylsiloxane $[-O-Si(CH_3)_2-O-]_n$, photosensitised by naphthalene at 77°K. Methylsiloxanes are very stable to near ultraviolet light ($\lambda > 240$ nm) since neither the O–Si–O group not the $Si-CH_3$ group have absorption bands in this spectral range. In the presence of naphthalene, however, polydimethylsiloxane is decomposed at 77°K by light of $\lambda > 240$ nm, and the EPR spectrum shows two types of radical $\dot{C}H_3$ and $[-O(\dot{C}H_2)Si(CH_3)-O-]$. The quadratic dependence of the yield of $\dot{C}H_3$ radicals on the intensity of the incident light indicates that the sensitisation is a two-photon process. The naphthalene molecule is transferred to the ground triplet state under the influence of protons with $\lambda \leq 313$ nm. The simultaneous action of protons with $\lambda \simeq 250$–260 nm converts the naphthalene molecule into a high triplet state.

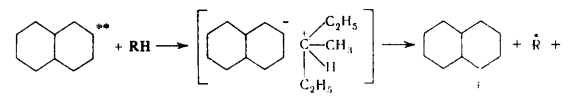
These results of the study of the photosensitised decomposition of substances to form free radicals at 77°K prove convincingly that the sensitisation of these processes takes place by a two-photon mechanism. It has been shown that the second quantum is absorbed by a triplet molecule of the aromatic compound, which acts as sensitiser. The least well-established feature is the final stage of the photoprocess—the mechanism of the interaction of the photoexcited sensitiser with the molecules undergoing photolysis. Three suggestions have been put forward regarding the type of interaction and the mechanism of the decomposition of the molecule undergoing photolysis to free radicals, recorded by the EPR method.

1. The formation of a complex of the charge-transfer type between a molecule of the sensitiser, photoexcited to a high triplet state, and a molecule of the dissociating substrate, followed by removal of a hydrogen atom [23,88,89,91] or decomposition with the formation of free-radical products [152].

2. Two-photon ionisation of the sensitiser molecule with subsequent dissociative attachment of an electron (solvated electron) to a molecule of the substrate [153,154].

3. Non-radiative transfer of energy from the photoexcited sensitiser to a molecule of the dissociating substrate with excitation of the latter to the decomposition state [120,135,136,140,142,155,156].

The first view is held by Bagdasar'yan [152], who suggested that photoexcited molecules of the sensitisers at 77°K can form complexes with the surrounding solvent molecules (substrate). These complexes, which are of the charge-transfer type but are formed only from excited molecules, have a short lifetime. Dissociation (predissociation) of this complex (reverse transfer of an electron to the substrate RH) may lead to decomposition of the solvent molecule (substrate) to free radicals. For example:



Gribova [23,88,89,91] proposed the following scheme for the two-photon dehydrogenation of ethanol by Mg etioporphyrin at 77°K. The chromophore molecule is converted into a lower triplet state under the influence of the first photon ($\lambda = 578$ nm). The second light quantum ($\lambda < 320$ nm), absorbed by the triplet molecules of the chromophore, transfers an electron of the triplet molecule of the chromophore to a state with higher energy. The strong coupling between the electrons forming the state of the chromophore with spin equal to 1 is weakened to such an extent that a labile biradical is produced (spin equal to 1/2). The chromophore molecule in this state is very active and adds on a hydrogen atom from neighbouring molecules of the matrix (ethanol), leading to the production of free radicals of dehydrogenated ethanol. Simultaneously, the Mg etieporphyrin molecule becomes a semi-reduced free radical. Study of the optical absorption spectrum of an irradiated frozen solution of Mg etioporphyrin in ethanol confirmed the formation of a free-radical form of the chromophore in this photochemical system.

Alfimov and coworkers [153] put forward yet another possible mechanism for the photosensitised dehydrogenation of alcohols by aromatic amines (diphenylamine or carbazole), involving two-photon ionisation of the amine molecules and interaction of the electrons produced with molecules of the alcohol. During the photodecolourisation of methanol solutions of diphenylamine and carbazole irradiated with ultraviolet light at 77°K, Alfimov and coworkers

found that the disappearance of the absorption band of the solvated electrons with λ_{max} = 600 nm is accompanied by a simultaneous increase in the concentration of alcohol radicals $\dot{C}H_2OH$. They therefore suggested that the formation of the $\dot{C}H_2OH$ radicals is associated with the disappearance of the centres absorbing light of λ = 600 nm, that is solvated electrons.

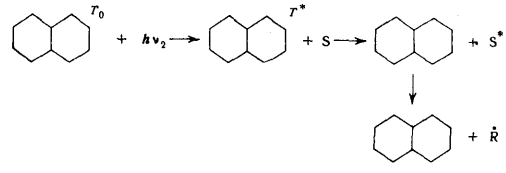
Shelimov and coworkers [154] tried to attribute the photosensitising action of aromatic hydrocarbons to the participation of ionic states formed by the action of ultraviolet light with short wavelength (λ < 300 nm) on their solutions in aliphatic hydrocarbons and alcohols at 77°K. For this purpose, they studied the decomposition of compounds with clearly defined electron-donating and electron-accepting properties in alcohol and hydrocarbons matrices, sensitised by aromatic hydrocarbons [154]. They carried out the photolysis of alcoholic solutions of naphthalene and phenanthrene in the presence of added compounds of the type R–Cl (n-propyl chloride, isopropyl chloride, benzyl chloride, methylene chloride, and carbon tetrachloride). In all instances with the exception of CCl_4, the formation of alkyl radicals $\dot{R}$ was observed. The rate of their formation was proportional to the square of the light intensity. If two-quantum photoionisation of naphthalene and phenanthrene [157] under the influence of ultraviolet light with λ = 254 nm is assumed, the formation of $\dot{R}$ radicals can be attributed to the dissociative attachment of an electron: $e + RCl \rightarrow \dot{R} + Cl^-$. The fact that the optical absorption spectra and the EPR spectra do not show the signals of the sensitiser radical-cations (A^+), which according to the photoreaction scheme should accumulate, was attributed by Shelimov to the disappearance of the greater part of these radical-cations by a "discharge" reaction: $A^+ + Cl^- \rightarrow A^* + \dot{C}l$. In the opinion of Shelimov and coworkers [154], the two-quantum formation of alcohol radicals during the illumination of solutions of aromatic compounds in ethanol at 77°K can also be explained by assuming photoionisation of the aromatic sensitisers followed by reaction of an electron with the oxonium ion ($CH_3CH_2OH_2^+$) or molecule of the alcohol ($CH_3-CH_2O^-H^+$). As confirmation of this suggestion, they give data on the observed increase in the rate of formation of alcohol radicals with decrease in the pH of the medium (increase in the concentration of $CH_3CH_2^+$ ions).

According to the suggestions which we put forward [120, 135,136,155], the final stage in the two-photon sensitisation of the rupture of the C_α–H and C–CH_3 bonds in alcohols and ethers and the C–I(Br, Cl) bonds in alkyl halides at 77°K involves the non-radiative transfer of energy from the photoexcited sensitiser in a high triplet state (aromatic amine, N-heterocycle, aromatic hydrocarbon, dye) to a molecule of the substrate (alcohol, ether, alkyl halide). We turned our attention [135,143,150] to the energetics of the photophysical stage of the two-photon sensitisation of the rupture of the C–I bond in alkyl iodides and the C–CH_3 bond in t-butyl alcohol at 77°K in the presence of aromatic compounds. It was found that the total energy of photoexcitation of the added sensitiser $E_{T_0} + h\nu_2$, where E_{T_0} is the energy height of the triplet level T_0 of the sensitiser, and $h\nu_2$ the photon absorbed by the sensitiser molecule in the triplet state, is always equal to or slightly greater than the energy of the photon $h\nu_{diss}$ bringing about the direct photodecomposition of the substrate molecules.

This energy relationship is a necessary condition for the non-radiative transfer of energy [158]. As a result of this resonance transfer of energy, the substrate molecule either is transferred directly to the repulsion potential curve of the bond being broken (C–H, C–CH_3, or C–I), which corresponds to excitation of a σ – or n-electron to a non-bonding orbital ($\sigma-\sigma^*$ or $n-\sigma^*$ transition) or decomposes by a predissociation mechanism. The efficiency of the transfer of energy to the substrate from the sensitiser photoexcited to a high triplet state is determined by the multiplicity of the electronic state of the substrate to which the energy is transferred [158–163]. The probability of energy transfer from an excited triplet level of the sensitiser (energy donor) to a triplet level of the substrate molecule (energy acceptor) should evidently be significantly greater than that for transfer to a singlet level, in accordance with the principle of preservation of the total spin of the system.

Since these intermolecular interactions have a limited sphere of influence [160–163], the dependence of the yield of radicals of the substrate on its concentration in a photochemically neutral matrix at 77°K at constant sensitiser concentration and constant experimental conditions, or, in principle, the magnitude of the radius of the sphere of influence of energy transfer, can be used to determine precisely the type of resonance energy transfer (triplet–triplet or triplet–singlet). We carried out these measurements [135,155] for two systems: naphthalene + t-butyl alcohol in ethanol and naphthalene + methyl iodide in ethanol at 77°K. The sphere of influence of the intramolecular energy transfer was taken as the averaged distance between the molecules of the energy donor and the energy acceptor, for which the probability of energy transfer from a molecule of the sensitiser (donor), excited to a high triplet state, to a molecule of the substrate (acceptor) was equal to the probability of intramolecular deactivation of the photoexcited sensitiser ($T^* \rightarrow T_0$ transition). The results showed that the characteristic radius of the sphere of interaction between the photoexcited sensitiser and the substrate is limited and is equal to 10–12 Å; this is characteristic of exchange-resonance interaction leading to triplet–triplet energy transfer [163].

Siegel and coworkers [142,143] reached a similar conclusion regarding the final stage of the mechanism of the two-photon sensitisation of the dehydrogenation of ethanol, diethyl ether, and methylcyclohexane, and also polydimethylsiloxane, by means of naphthalene. On the basis of their results they suggested that there is non-radiative resonance transfer of energy from a naphthalene molecule, photoexcited to a high triplet state, to a molecule of the solvent (ethanol, diethyl, or methylcyclohexane), followed by dissociation (rupture of the C–H bond). The proposed scheme for the two-photon sensitisation of the dehydrogenation of the solvent is as follows:



Douzou and coworkers [140] hold the same view regarding the mechanism of the two-photon sensitisation of the dehydrogenation of alcohols by aminoacids and nucleic acid bases.

Porter and coworkers [156] recently reproduced the experiments of Shelimov and coworkers on the two-photon sensitisation of dehydrogenation of unsaturated hydrocarbons by benzene derivatibes and various polycyclic compounds, and they also suggest that the final stage in

the sensitisation mechanism is the transfer of energy from the sensitiser, photoexcited to a high triplet state, to a molecule of the solvent (hydrocarbon), which is thus excited to a triplet decomposition state.

Since there is at present insufficient information for final resolution of the problem of the mechanism of the recently discovered two-quantum reactions of sensitised decomposition, it is necessary to carry out new and comprehensive studies in this direction by a combination of various physical methods of study (spectroscopy, EPR, mass spectroscopy, photoconductivity, etc.).

REFERENCES

1. V. E. Kholmogorov, Uspekhi Khim., **37**, 1492 (1968) [Russ. Chem. Rev., No. 9 (1968)].
2. A. N. Terenin, "Fotokhimiya Krasitelei i Rodstvennykh Soedinenii" (The Photochemistry of Dyes and Related Compounds), Izd. Akad. Nauk SSSR, Moscow–Leningrad, 1947).
3. B. Ya. Dain and E. A. Liberson, Dokl. Akad. Nauk SSSR, **28**, 228 (1940).
4. F. S. Dainton, and D. James, Trans. Faraday Soc., **54**, 649 (1957).
5. T. Rigg, and J. Weiss, J. Chem. Phys., **20**, 1194 (1952).
6. J. Weiss, Nature, **136**, 794 (1935).
7. M. S. Matheson and B. Smaller, J. Chem. Phys., **28**, 1169 (1958).
8. R. Livingston, H. Zeldes, and E. Taylor, Disc. Faraday Soc., **1955**, No. 19, 166.
9. N. N. Bubnov, V. V. Voevodskii, N. V. Fok, and B. N. Shelimov, Optika i Spektrosk., **11**, 78 (1961).
10. B. N. Shelimov, N. N. Bubnov, N. V. Fok, and V. V. Voevodskii, Dokl. Akad. Nauk SSSR, **134**, 145 (1960).
11. M. K. Carter and G. Vincow, Bull. Am. Phys. Soc., **10**, 374 (1965).
12. V. E. Kholmogorov and E. V. Baranov, Optika i Spektrosk., **14**, 827 (1963).
13. G. N. Lewis and D. Lipkin, J. Am. Chem. Soc., **68**, 1002 (1952).
14. N. N. Bubnov, N. M. Bezhin, and V. V. Voevodskii, Kinetika i Kataliz, **5**, 568 (1964).
15. G. A. Shagisultanova, L. N. Neokladnova, and A. L. Poznyak, Dokl. Akad. Nauk SSSR, **162**, 1333 (1965).
16. G. Tollin and G. Green, Biochem. Biophys. Acta, **60**, 524 (1962).
17. B. Allen and D. J. E. Ingram, Free Radicals in Biological Systems, Acad. Press, N.-Y.–L., 1961.
18. O. A. Azizova, Biofizika, **9**, 745 (1964).
19. M. K. Pulitanova and O. A. Azizova, Biofizika, **9**, 33 (1964).
20. O. A. Azizova and Yu. S. Malinin, in collected papers "Svobodnoradikal'nye Protsessy v Biologicheskikh Sistemakh" (Collected Papers on Free-radical Processes in Biological Systems), Izd. Nauka, Moscow, 1966, p. 247.
21. O. Azizova, Elektrochemische Methoden und Prinzipien in der Molekular Biologie (III. Jenaer. Symposium) Akademic Verlag, Berlin, 1966, p. 385.
22. O. A. Azizova, L. P. Kayushin, and M. K. Pulatova, Biofizika, **11**, 970 (1966).
23. O. A. Azizova, Z. P. Gribova, L. P. Kayushin, and M. K. Pulatova, Photochem. Photobiol., **5**, 763 (1966).
24. R. F. Claridge and J. E. Willard, J. Am. Chem. Soc., **87**, 4992 (1965).
25. A. C. Albrecht and W. T. Sympson, J. Am. Chem. Soc., **77**, 4454 (1955).
26. G. N. Lewis and D. Lipkin, J. Am. Chem. Soc., **64**, 2801 (1942).
27. S. I. Weissman, J. Chem. Phys., **22**, 1135 (1954).
28. T. R. Tuttle, J. Chem. Phys., **30**, 331 (1959).
29. J. R. Bolton, A. Carrington, and J. dos Santos-Veiga Mol. Phys., **5**, 615 (1962).
30. K. H. Hausser, Mol. Phys., **7**, 195 (1963–64).
31. H. L. Bäckstrom, Ztschr. phys. Chem., **25**, Abt. B, 99 (1934).
32. A. Berthoud and D. Porret, Helv. chim. acta, **17**, 694 (1934).
33. N. K. Bridge and G. Porter, Proc. Roy. Soc., **244**, 259, 276 (1958).
34. F. Wilkinson, J. Phys. Chem., **66**, 2569 (1962).
35. L. Michaelis, Chem. Rev., **16**, 243 (1935).
36. N. K. Bridge and M. Reed, Trans. Faraday Soc., **56**, 1796 (1960).
37. B. Elschner, R. Neubert, H. Berg, and T. Tressolt, Ztschr. Chem., **1**, 361 (1961).
38. J. N. Pitts, R. L. Letsinger, R. P. Taylor, J. M. Patpaterson, G. Reckenwald, and R. B. Martin, J. Am. Chem. Soc., **81**, 1068 (1959).
39. J. H. Sharp, T. Kuwana, A. Osborne, and J. N. Pitts, Chem. a. Ind., **1962**, 510.
40. H. Köller, G. P. Habold, K. Weiss, and T. Mukherjee, Proc. Chem. Soc., **1964**, 332.
41. G. P. Rabold, K. H. Bar-Eij, E. Reid, and K. Weiss, J. Chem. Phys., **42**, 2438 (1965).
42. P. B. Ayscough and R. Wilson, Proc. Chem. Soc., **1962**, 229.
43. R. Wilson, Canad. J. Chem., **44**, 551 (1966).
44. P. B. Ayscough and R. Wilson, J. Chem. Soc., **1963**, 5412.
45. P. B. Ayscough, F. P. Sargent, and R. Wilson, J. Chem. Soc., **1963**, 5418.
46. G. Porter and F. Wilkinson, Trans. Faraday Soc., **57**, 1686 (1961).
47. T. E. Cough and M. C. R. Symons, Trans. Faraday Soc., **62**, 269 (1966).
48. T. A. Ceaxton, T. E. Gough, and M. C. R. Symons, Trans. Faraday Soc., **62**, 279 (1966).
49. N. M. Atherton and S. I. Weissman, J. Am. Chem. Soc., **83**, 1330 (1961).
50. Iwaizumi, Isobe, Bull. Chem. Soc. Japan, **37**, 1651 (1964).
51. H. J. S. Winkler, H. Winkler, and R. Bollinger, Chem. Comm., **1966**, No. 3, 70.
52. A. Carrington, F. Dravnieks, and M. C. R. Symons, J. Chem. Soc., **1959**, 947.
53. A. Carrington, Quart. Rev., **17**, 67 (1963).
54. K. Lagercrantz and M. Yhland, Acta. chem. scand., **16**, 1043 (1962).
55. R. L. Ward, J. Chem. Phys., **38**, 2588 (1963).
56. R. L. Ward, J. Chem. Phys., **39**, 852 (1963).
57. R. E. Merrifield and W. D. Phillips, J. Am. Chem. Soc., **80**, 2778 (1958).
58. R. Vars, L. A. Tripp, and L. W. Pickett, J. Phys. Chem., **66**, 1754 (1962).
59. R. S. Mulliken, J. Chem. Phys., **19**, 514 (1961).
60. R. S. Mulliken, J. Phys. Chem., **56**, 801 (1951).
61. R. S. Mulliken, J. Am. Chem. Soc., **74**, 811 (1952).
62. A. N. Terenin, Uspekhi Khim., **24**, 121 (1955).
63. L. L. Ferstandig, W. G. Toland, and C. D. Heaton, J. Am. Chem. Soc., **83**, 1151 (1961).
64. W. D. Phillips, J. C. Rowell, and S. I. Weissman, J. Chem. Phys., **33**, 626 (1960).

65. D. F. Ilten and M. Calvin, J. Chem. Phys., **42**, 3760 (1965).
66. N. N. Bubnov, L. A. Kibalko, V. F. Tsepalov, and V. Ya. Shlyapintokh, Optika i Spektrosk., **7**, 117 (1959).
67. N. N. Bubnov, V. Yu. Tsepalov, and V. Ya. Shlyapintokh Izv. Akad. Nauk SSSR, Ser. Fiz., **23**, 1965 (1959).
68. V. F. Tsepalov and V. Ya. Shlyapintokh, Dokl. Akad. Nauk SSSR, **116**, 641 (1957).
69. V. F. Tsepalov and V. Ya. Shlyapintokh, Izv. Akad. Nauk SSSR, Ser. Khim., **4**, 637 (1959).
70. G. O. Schenck, J. Elektrochem., **56**, 855 (1952).
71. V. B. Evstingneev, Zhur. Fiz. Khim., **32**, 969 (1958).
72. A. A. Krasnovskii, Dokl. Akad. Nauk SSSR, **60**, 421 (1948).
73. A. A. Krasnovskii, Zhur. Fiz. Khim., **30**, 68 (1956).
74. A. A. Krasnovskii and A. V. Umrikhina, Biofizika, **3**, 547 (1958).
75. N. N. Bubnov, A. A. Krasnovskii, A. V. Umrikhina, V. F. Tsepalov, and V. Ya. Shlyapintokh, Biofizika, **5**, 121 (1960).
76. G. Eigenmann, Helv. chim. Acta, **46**, 298 (1963).
77. V. E. Kholmogorov and A. V. Shablya, Optika i Spektrosk., **17**, 298 (1963).
78. Fujimori, M. Tavla, Nature, **208**, 78 (1965).
79. A. K. Banerjee and G. Tollin, Photochem. Photobiol., **5**, 315 (1966).
80. G. R. Seely, J. Phys. Chem., **69**, 2779 (1965).
81. B. Evstigneev, Photochem. Photobiol., **4**, 171 (1965).
82. G. T. Rikhireva, Z. P. Gribova, L. P. Kayushin, A. V. Umrikhina, and A. A. Krasnovskii, Dokl. Akad. SSSR, **159**, 196 (1964).
83. G. T. Rikhireva, see Ref. 20, p. 258.
84. G. T. Rikhireva, A. V. Umrikhina, L. P. Kayushin, and A. A. Krasnovskii, Dokl. Akad. Nauk SSSR, **163**, 491 (1965).
85. G. T. Rikhireva, A. V. Umrikhina, L. P. Kayushin, and A. A. Krasnovskii, Biofizika, **11**, 796 (1966).
86. D. Mauzerall, G. Feher, Biochim. et biophys. Acta, **79**, 430 (1964).
87. Z. P. Gribova, R. P. Evstigneeva, A. F. Mironov, L. P. Kayushin, V. N. Luzgina, and A. K. Piskunov, Biofizika, **8**, 550 (1963).
88. Z. P. Gribova and L. P. Kayushin, Biofizika, **9**, 627 (1964).
89. Z. P. Gribova, see Ref. 20, p. 236.
90. Z. P. Gribova, V. A. Umrikhina, and L. P. Kayushin, Biofizika, **11**, 353 (1966).
91. Z. P. Gribova, see Ref. 21, p. 331.
92. G. J. Brcaley, N. Uri, J. Chem. Phys., **88**, 257 (1952).
93. A. Benrath, Ztschr. phys. Chemie, **74**, 115 (1960).
94. A. I. Kryukov and L. V. Nazarova, Ukrain. Khim., Zhur., **29**, 806, 812 (1963).
95. N. M. Bazhin, N. M. Likhacheva, N. N. Bubnov, and V. V. Voevodskii, Kinetika i. Kataliz, **6**, 1105 (1965).
96. G. Czapski, J. Jornter, and G. Stein, J. Phys. Chem., **65**, 956 (1961).
97. N. M. Bazhin, E. V. Kuznetsov, N. N. Bubnov, and V. V. Voevodskii, Kinetika i Kataliz, **7**, 161 (1966).
98. N. M. Bazhin, E. V. Kuznetsov, N. N. Bubnov, and V. V. Voevodskii, Kinetika i Kataliz, **7**, 732 (1966).
99. N. M. Bazhin, P. V. Schastnev, G. M. Zhidomirov, N. N. Bubnov, and V. V. Voevodskii, Kinetika i Kataliz, **7**, 999 (1966).
100. R. W. Fessenden and R. H. Schuler, J. Chem. Phys., **39**, 2147 (1963).
101. P. P. Schastnev and G. M. Zhidomirov, Kinetika i Kataliz, **8**, 203 (1967).
102. V. E. Karpitskaya, I. A. Dolidze, and M. S. Ashkinazi, Dokl. Akad. Nauk SSSR, **146**, 844 (1962).
103. M. S. Ashkinazi, V. E. Karpitskaya, and B. Ya. Dain, Zhur. Fiz. Khim., **38**, 2889 (1964) [Russ. J. Phys. Chem., No. 12 (1964)].
104. M. S. Ashkinazi and I. A. Dolidze, Zhur. Fiz. Khim., **39**, 2587 (1965) [Russ. J. Phys. Chem., No. 12 (1965)].
105. J. Pannell, Mol. Phys., **5**, 291 (1962).
106. J. R. Thomas, J. Am. Chem. Soc., **82**, 5955 (1960).
107. A. L. Buchachenko, M. S. Khloplyankina, and M. B. Neiman, Dokl. Akad. Nauk SSSR, **143**, 146 (1962).
108. A. L. Buchachenko, Optika i Spektrosk., **13**, 795 (1962).
109. C. Lagercrantz and M. Yhland, Acta. chem. Scand., **16**, 508 (1962).
110. G. O. Schenck and R. Wolgast, Naturwiss., **48**, 737 (1961).
111. G. O. Schenck and R. Wolgast, Naturwiss., **49**, 36 (1962).
112. G. O. Schenck, Naturwiss., **35**, 28 (1948).
113. B. N. Shelimov, N. N. Bubnov, N. V. Fok, and V. V. Voevodskii, in collected papers "Paramagnitnyi Rezonans" (Collected Papers on Paramagnetic Resonance), Izd. Kazansk. Univ., 1960, p. 37.
114. N. N. Bubnov, V. V. Voevodskii, N. V. Fok, and B. N. Shalimov, Optika i Spektrosk., **11**, 76 (1961).
115. S. P. Adintsova, B. N. Shelimov, N. V. Fok, and V. V. Voevodskii, Izv. Akad. Nauk SSSR, Ser. Khim., 572 (1963).
116. B. N. Shelimov, N. V. Fok, and V. V. Voevodskii, Dokl. Akad. Nauk SSSR, **144**, 596 (1962).
117. V. G. Vinogradova, B. N. Shelimov, N. V. Fok, and and V. V. Voevodskii, Dokl. Akad. Nauk SSSR, **154**, 188 (1964).
118. B. N. Shelimov, Kinetika i Kataliz, **7**, 543 (1966).
119. Kh. S. Bagdasar'yan, V. I. Muromtsev, and Z. A. Sinitsyna, Dokl. Akad. Nauk SSSR, **152**, 349 (1963).
120. V. E. Kholmogorov, E. V. Baranov, and A. N. Terenin, Dokl. Akad. Nauk SSSR, **152**, 1399 (1963).
121. S. Leach, E. Migirdicyan, and L. Grajcar, J. Chim. Phys., **56**, 749 (1959).
122. V. G. Vinogradova, L. M. Baider, B. N. Shelimov, and N. V. Fok, Dokl. Akad. Nauk SSSR, **168**, 134 (1966).
123. V. E. Kholmogorov, E. V. Baranov, and A. N. Terenin, Dokl. Akad. Nauk SSSR, **149**, 142 (1963).
124. B. Smaller, Nature, **195**, 593 (1962).
125. Kh. S. Bagdasar'yan, Z. A. Sinitsyna, and V. I. Muromtsev, Dokl. Akad. Nauk SSSR, **153**, 374 (1963).
126. Kh. S. Bagadsar'yan and Z. A. Sinitsyna, Dokl. Akad. Nauk SSSR, **160**, 625 (1965).
127. A. K. Piskunov, R. N. Nurmukhametov, D. N. Shigorin, V. I. Muromtsev, and G. A. Ozerova, Izv. Akad. Nauk SSSR, Ser. Fiz., **27**, 634 (1963).
128. Yu. I. Kozlov, V. I. Muromtsev, A. K. Piskunov, D. N. Shigorin, G. A. Ozerova, and N. V. Verein, Zhur. Fiz. Khim., **37**, 2800 (1963) [Russ. J. Phys. Chem., No. 11 (1963)].
129. A. K. Piskunov, V. E. Kholmogorov, D. N. Shigorin, N. V. Verein, and G. A. Ozerova, Dokl. Akad. Nauk SSSR, **154**, 910 (1964).
130. D. N. Shigorin, A. K. Piskunov, G. A. Ozerova, N. A. Shcheglova, and N. V. Verein, Dokl. Akad. Nauk SSSR, **158**, 432 (1964).

131. D. N. Shigorin, A. K. Piskunov, G. A. Ozerova, N. A. Shcheglova, and N. V. Verein, Zhur. Fiz. Khim., 38, 2279 (1964) [Russ. J. Phys. Chem., No. 10 (1964)].
132. V. L. Ermolaev, Optika i Spektrosk., 11, 492 (1961).
133. V. V. Ryl'kov, V. E. Kholmogorov, and A. N. Terenin, Optika i Spektrosk., 20, 524 (1966).
134. G. Porter and M. W. Windsor, Proc. Roy. Soc., 245, 238 (1958).
135. A. Terenin, V. Rylkov, and V. Kholmogorov, Photochem. Photobiol., 5, 543 (1966).
136. V. E. Kholmogorov, in collected papers "Elementarnye Fotoprotsessy v Molekulakh" (Collected Papers on Elementary Photoprocesses in Molecules), Izd. Nauka, Moscow–Leningrad, 1966, p. 163.
137. V. Zanker and E. Miehtke, Naturforsch., 12a, 385 (1957).
138. L. Pekkarinen and H. Linschitz, J. Am. Chem. Soc., 82, 2407 (1960).
139. M. Ptak and P. Douzou, Nature, 199, 1092 (1963).
140. C. Helene, R. Santus, and P. Douzou, Photochem. Photobiol., 5, 127 (1966).
141. R. S. Becher and J. B, Allison, J. Chem. Phys., 67, 2662 (1963).
142. S. Siegel and K. Eisenthal, J. Chem. Phys., 42, 2494 (1965).
143. S. Siegel and H. S. Judeikes, J. Chem. Phys., 43, 3638 (1965).
144. C. A. Hutchison and B. W. Mangum, J. Chem. Phys., 32, 1261 (1960).
145. W. West and W. Miller, J. Chem. Phys., 8, 849 (1940).
146. W. West, Ann. N.–Y.–Acad, Sci., 41, 203 (1941).
147. V. V. Ryl'kov, V. E. Kholmogorov, and A. N. Terenin, Dokl. Akad. Nauk SSSR, 165, 356 (1965).
148. V. V. Ryl'kov, V. E. Kholmogorov, and A. N. Terenin, Dokl. Akad. Nauk SSSR, 166, 913 (1966).
149. V. V. Ryl'kov and V. E. Kholmogorov, Zhur. Fiz. Khim., 40, 2900 (1966) [Russ. J. Phys. Chem., No. 12 (1966)].
150. V. V. Ryl'kov, V. E. Kholmogorov, and A. N. Terenin, Dokl. Akad. Nauk SSSR, 169, 1373 (1966).
151. S. Siegel and H. Judeikis, J. Chem. Phys., 43, 343 (1965).
152. Kh. S. Bagdasar'yan, Zhur. Vses. Khim. Obshch. im. Mendeleeva, 11, 216 (1966).
153. M. V. Alfimov, I. G. Batekha, and V. A. Smirnov, Kinetika i Kataliz, 7, 766 (1966).
154. B. N. Shelimov, V. G. Vinogradova, V. I. Mal'tsev, and N. V. Fok, Dokl. Akad. Nauk SSSR, 172, 655 (1967).
155. V. V. Ryl'kov and V. E. Kholmogorov, Dokl. Akad. Nauk SSSR, 171, 395 (1966).
156. B. Brocklehurst, W. A. Gibbons, F. T. Lang, G. Porter, and M. I. Savadatti, Trans. Faraday Soc., 62, 1793 (1966).
157. J. Joussot-Dubien and R. Lesclaux, Compt. rend., 258, 4260 (1964).
158. A. N. Terenin and V. L. Ermolaev, in collected papers "Pamyati S. I. Vavilova" (Collected Papers Dedicated to the Memory of S. I. Vavilova), Izd. Akad. Nauk SSSR, Moscow, 1952, p. 137.
159. V. Ermolaev and A. Terenin, J. Chim. Phys., 55, 698 (1958).
160. V. L. Ermolaev, Optika i Spektrosk., 6, 642 (1959).
161. V. L. Ermolaev and E. V. Sveshnikova, Izv. Akad. Nauk SSSR, Ser. Fiz., 26, 29 (1962).
162. V. L. Ermolaev and E. V. Sveshnikova, Dokl. Akad. Nauk SSSR, 149, 1295 (1963).
163. A. N. Terenin and V. L. Ermolaev, Dokl. Akad. Nauk SSSR, 85, 547 (1952).