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Chapter 3

Kinetics and Mechanism of Photoconversion of N-Substituted Amides of Salicylic Acid

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Additional information is available at the end of the chapter

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Abstract

Studied using optical spectroscopy, stationary, and nanosecond laser photolysis (Nd:YAG laser 355 nm) conversion products in heptane of N-substituted amides of salicylic acid: N-(4-hydroxyhydro-3,5-di-tert-butylphenyl) amide 2-hydroxy-3-t-butyl-5-ethylbenzoic acid (1), 2-(4-hydroxy-3,5-hydroxybenzoic acid)-di-tert-butylphenyl) propyl] amide (2), N-(4-hydroxyphenyl) amide 2-hidroxy benzoic acid (3), and 2-hydroxy-3-t-butyl-5-ethylbenzoic acid N-[3-(4-hydroxy-3,5-di-t-butylphenyl) propyl] amide (4). It is shown that amides exist both in the unbound state and in complexes with intra- and intermolecular hydrogen bonding. Free phenolic groups of amides undergo photolysis, which leads to the formation of a triplet state and phenoxyl radicals RO·, presumably due to the absorption of the second photon by the excited singlet state. Triplet-triplet annihilation and recombination (kr ≈ $2.3 \cdot 10^8$ L mol^{-1} s) are the main channels for the decay of the triplet state and radicals RO·. UV irradiation of the compounds leads to the excitation of amide groups, and radical products are not formed due to ionization of the NH bond. The process of initiated UV oxidation of the model substrate (methyloleate) in the presence of amides 1–4 was compared with the known antioxidants (AO): dibunol (2,6-di-tert-butyl-4-methylphenol) (5) and α-tocopherol (6-hydroxy-2,5,7,8-tetramethyl-2-phytyl chromane) (6). It has been shown that all amides of salicylic acid (I–IV) effectively inhibit the oxidation of methyl oleate, initiated by UV irradiation. The mechanism of the inhibitory effect of compounds has been established, which is associated with the possibility of direct interaction of phenols with free radicals (antiradical activity). Testing of antiradical activity of amides (I–IV), estimated by the method of chemiluminescence, made it possible to determine the range of reaction rate constants with peroxyl radicals $RO_2^{\cdot}$ k_7 = (0.52–6.86) • 10^4 m L^{-1} s^{-1}. The interrelation of antioxidant properties of amides of salicylic acid (I–IV) and features of their structure is established. It was shown that the introduction of o-tert-butyl substituents and the separation of aromatic fragments by three methylene groups lead to a significant increase in antioxidant activity.

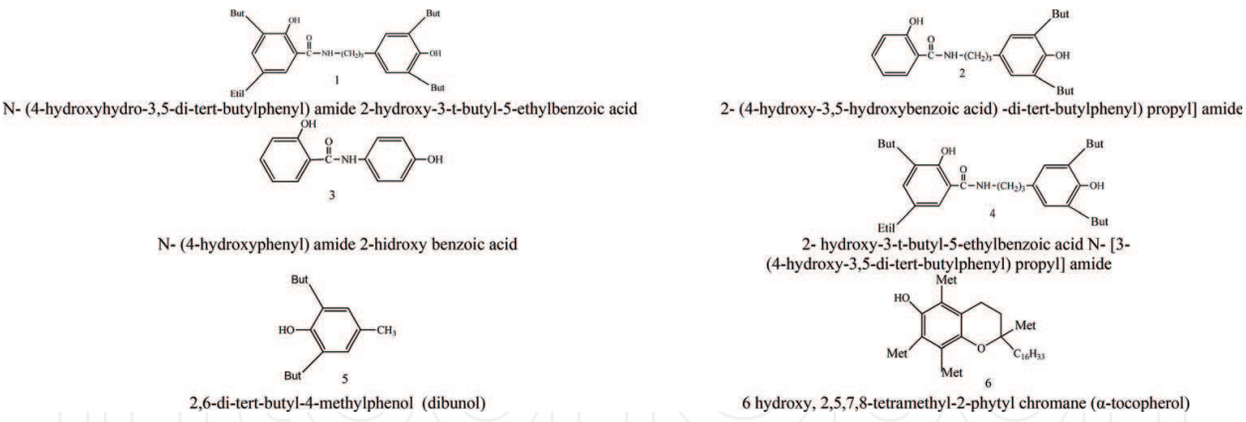
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Keywords: salicylic acid amide, photolysis, phenyl radical, recombination, TR and UV spectroscopy, hydrogen bond, deuteration, UV-initiated oxidation, antioxidant, antiradical activity

1. Introduction

It is known that UV irradiation is a destructive factor that accelerates the oxidation of organic materials: polymers, rubbers, fuel, food, and technical oils. The effect of UV rays is the cause of erythema and skin burns, can cause DNA fragmentation, and leads to melanoma. The mechanism of the destructive effect of UV rays is associated with the activation of free radical oxidation processes as a result of the formation of singlet oxygen [1]. Salicylic acid and its esters, the characteristic feature of which is maximum absorption in the range of 300 nm [1–3], are used to protect the skin from ultraviolet irradiation (methyl salicylate) and as promising photostabilizers of polymeric materials [4] and dyes [5]. Some N-substituted amide derivatives of salicylic acid serve as inhibitors of oxidation in the photo-irradiation of substrates and exceed in the efficiency of known synthetic and natural antioxidants [4]. The photochemical reactions of salicylic and 4-sulfosalicylic acid have been studied [6–8]. Therefore, it is interesting to study the features of the photochemistry of new amide derivatives of salicylic acid and their antioxidant properties in comparison with known synthetic and natural antioxidants. For the compounds studied, similar studies have not been conducted previously (**Structure I**).



Structure I. Structures of the test compounds.

2. Experimental

Optical spectra were recorded on an H P 8453 spectrophotometer (Hewlett Packard). IR spectra were measured on a Specord-75IR spectrophotometer. A laser stationary photolysis technique using excitation with a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (355 nm, pulse duration 5, bright area 0.03 cm^2, energy at a pulse 2 mJ (66 mJ cm^{-2})

was used. The principal scheme of the system is similar to that described earlier [6]. The power of laser radiation was measured using a known procedure [9] with potassium ferrioxalate as a chemical actinometer.

Stationary photolysis of solutions of amides in heptane was carried out by a series of laser pulses for 4 minutes or by irradiation with a DRSh-250-3 mercury lamp (313–365 nm) in a closed cell (d = 0.4 cm) remote from the source and spherical mirror at equal distances (10 cm).

Deuteration was conducted by the dissolution of the compound in CD_3OD followed by the evaporation of alcohol at 40–50°C.

Amides 1 and 2 were synthesized at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry (Siberian Branch of the Russian Academy of Sciences) and used without additional purification. The scheme of the synthesis and spectral characteristics of the products are published [9].

Carbon tetrachloride and heptane (reagent grade) were used for the preparation of solutions. All experiments were carried out at 298 K in a cell with an optical path length of 1 cm, except for specially indicated cases.

Oxygen was removed from solutions by argon bubbling. The kinetics of oxidation of methyloleate (0.67 mol L^{-1}) in the presence of amides of salicylic acid was studied in modified Warburg-type installations, fixing the amount of absorbed oxygen along the course of the reaction [4, 10]. As inert to the oxidation of the solvent, chlorobenzene purified by the simple distillation method was used. The temperature of the experiments is (60 ± 0.2)°C [3, 10]. From the kinetic curves, the period of induction (τ) was determined as a segment on the time scale, cut off by a perpendicular dropped from the point of intersection of the tangents. Initiation was carried out by preliminary irradiation of the substrate with a mercury lamp (λ = 313–365 nm) for 20 min at room temperature. The initiation rate was determined by the inhibitor method [11] using 6 as the control AO. The antiradical activity of salicylic acid amides was estimated from the rate constants in the elemental reaction with peroxyl radicals (k_7) by the chemiluminescent (CL) method with the initiation of cumene (isopropylbenzene) oxidation [12]. Chemiluminescence occurs as a result of the recombination of peroxyl radicals ($RO_2^{\bullet}$), since this reaction is very exothermic to excite luminescence in the visible region. When the antioxidant reacts with $RO_2^{\bullet}$, the intensity of chemiluminescence (CL) decreases to zero, which leads to a decrease in CL intensity. The consumption of antioxidant (AO) leads to an increase in the intensity of CL to the initial level. From the slope of the kinetic curves of CL, the rate of consumption of the antioxidant was determined [12]. The studies were carried out at a constant rate of generation of $RO_2^{\bullet}$ due to the thermal decomposition of azobisisobutyronitrile. The initiation rate was determined using a reference chromane inhibitor C_1 (2,2,5,7,8-pentamethyltocol). Oxidation of the substrate was carried out in a glass cell located in a light-tight chamber of a photometric block equipped with a photomultiplier FEU-29. The emitted light was focused on a photomultiplier using a system of spherical mirrors. To enhance the luminescence, 9,10-dibromanthracene was used in a concentration of $5 \cdot 10^{-4}$ M L^{-1}, which did not affect the kinetics of oxidation. The value of the constant k_7 was determined with the help of dependencies [12]:

$$\sqrt{I_0/I} = 1 + \left[k_7 \times [InH]/\sqrt{k_6 \times W_i}\right] \quad (1)$$

$$[d(I/I_0)/dt]_{max} = (0,22 \pm 0,02) \times k_7 \times \sqrt{W_i}/\sqrt{k_6} \quad (2)$$

where I and I_0 are the luminescence intensity in the presence of the antioxidant and without it, respectively, Wi is the initiation rate, and k_6 is the rate constant of the chain termination in the known liquid-phase oxidation scheme of hydrocarbons [1].

To avoid the influence of antioxidant conversion products and the possibility of disturbance of the stationary process, the value was extrapolated $[d(I/I_0)/dt]_{max}$ to zero antioxidant concentration.

3. Results and discussion of IR spectra of native compounds for examples 1 and 2 and their photolysis products

It is known that salicylic acid and its derivatives in organic aprotic solvents form both intramolecular and intermolecular hydrogen bonds between the phenolic hydroxyl and the neighboring carbonyl group [13–16]. We note that the intramolecular hydrogen bond is predominantly formed at low concentrations and the intramolecular hydrogen bond at high concentrations [14–16]. During the presence of an intramolecular hydrogen bond in salicylic acid, the stability of monomeric complexes was confirmed by molecular modeling. A comparative analysis of IR spectra of salicylic and acetylsalicylic acids and methyl salicylate showed that the absorption band of OH groups participating in intramolecular hydrogen bond is 3230 cm^{-1} and the complex spectrum in the range 2500–3300 cm^{-1} characterizes the absorption of dimers [14–17]. The mechanism of formation of dimeric products from an intermediate reactive compound obtained as a result of disproportionation is discussed [17].

The formation of intra- and intermolecular hydrogen bonds was previously proven by several independent methods for the derivatives of salicylic acid [18–21].

The formation of an intramolecular hydrogen bond for salicylic aldehyde and o-nitrophenol (-O-H … O = C- and -O-H … O = N-, respectively) was demonstrated. This coupling exhibits an intense maximum at 3200 cm^{-1} and a fairly strong shift of the v (OH) band to low frequencies. The vibration band v (OH) on an intermolecular hydrogen bond usually has a complex structure with a maximum in the 3400–3560 cm^{-1} range and is characterized by a half-width of ~ 400 cm^{-1} (see 10 and 13). Intermolecular hydrogen bond (O-H … O =) between phenol (a-tocopherol) and quinone (ubiquinone Q10) appears in the IR spectrum as a band with a maximum at 3545 cm^{-1} (see 14) [22].

To reveal specific features of the molecular structures of amides **1** and **2**, we examined the IR spectra of solutions in $CC1_4$ in a range of 1600–4000 cm^{-1} (**Figure 1**). The indicated range contains the band of stretching vibrations of the unbound phenol group (v(OH) = 3644 cm^{-1}) and the band with a maximum at 3454 cm^{-1}, which is due to the presence of the v(NH) amide group usually observed near 3450 cm^{-1}. For stationary photolysis of amide **1** in $CC1_4$, the IR spectra exhibit a decrease in the intensity of stretching vibration bands of isolated OH

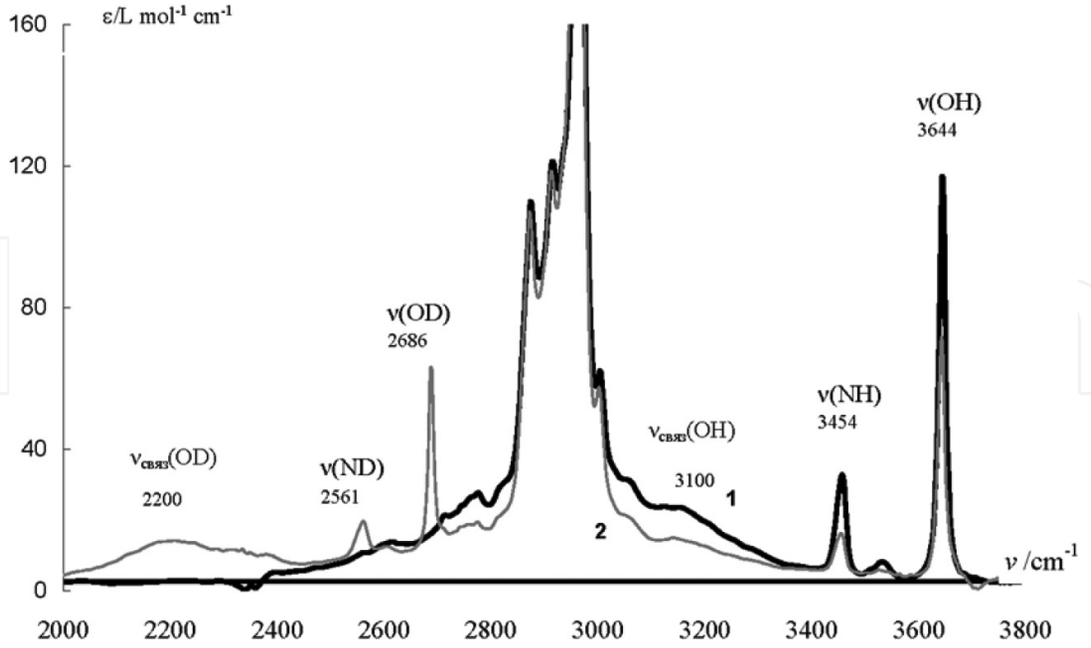


Figure 1. IR spectra of amide **1** (10^{-2} Mol L^{-1}) in $CC1_4$: (1) initial compound and (2) initial compound partially deuterated at the OH and NH groups.

(v(OH) = 3644) cm^{-1} and NH groups (v(NH) = 3454) cm^{-1} (**Figure 2**). Upon the irradiation of the solution for more than 3 min, a band with a maximum at ~3424 cm^{-1} assigned possibly to the absorption band of the product appears and increases in the spectrum of amide **1**.

We studied the possibility of formation of hydrogen bonds of different natures in structures **2** and **3.** The IR spectra of amides **1** and **2** exhibit a broad complicated band at 2300–3400 cm^{-1}. According to literature data, the phenol group (v(OH)) involved in intra- and intermolecular hydrogen bonds can absorb in this range. However, the identification of hydrogen bonds is impeded by the fact that an intense absorption of =C-H and C-H bonds is observed in a range of 2800–3100 cm^{-1}. The most intense absorption concerns just this range in the spectra studied. It is noteworthy that a broad doublet band with maxima at 3045 and 3150 cm^{-1} appears in the spectrum at a shoulder of the absorption band of the =C-H and C-H bonds in a range of 2300–3400 cm^{-1}.

To reveal the question about the existence and nature of hydrogen bonds, amides **1** and **2** were deuterated, and then a comparative analysis of the spectra of the initial and partially deuterated molecules was carried out. It is seen upon the superposition of the indicated spectra (for amide **1**; see **Figure 1**) that the absorption bands of the unbound OH (3644 cm^{-1}) and NH (3454 cm^{-1}) groups do not change their position, but their intensity decreases. At the same time, new bands assigned to the unbound OD and ND groups (frequencies 2686 and 2561 cm^{-1}, respectively) appear in the spectrum of the deuterated molecules. The low-frequency spectral range contains a new doublet band with maxima at 2250 and 2175 cm^{-1}. The appearance of this band indicates hydrogen OD bonds and is due to the resonance Fermi interaction and totally difference transitions involving low-frequency vibrations of the D bond [23]. It is known that the ratio between positions of the bands of the OH groups involved in the

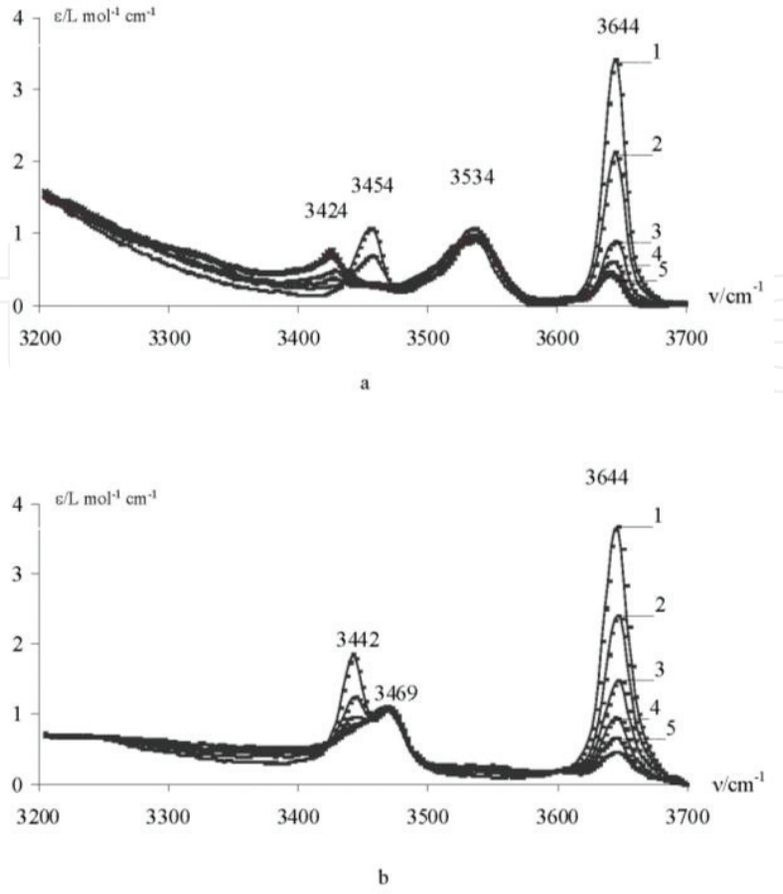


Figure 2. IR spectra for stationary photolysis of salicylic acid amides 1 (a) and **2** (b) ($5 \cdot 10^{-3}$ Mol L^{-1}) in $CC1_4$ after 1, 2, 3, 4, and 5 min (curves 1–5, respectively) of irradiation.

formation of structures with a hydrogen bonds and the OD group in a similar complex is $v_c(OH) \approx \sqrt{2}v_c(OD)$. It follows from the calculation by this formula that in the initial non-deuterated structure the OH groups involved in the hydrogen bond absorb at 3045 and 3150 cm^{-1}. These results coincide with experimental data: as indicated above, two maxima are observed in this range at the shoulder of the intense absorption of the =C-H and C-H groups. As a result of deuteration, the intensity of this doublet decreases, which additionally proves the presence of hydrogen bonds. The band intensity remains nearly unchanged with the temperature change in a range of 25–70°C, indicating a high strength of the formed intra- and intermolecular hydrogen bonds.

The change in the concentration of amides 2 and 3 in the range $1.0 \bullet 10^{-2}$–$25 \bullet 10^{-4}$ mol^{-1} did not affect the shape of IR spectra. To correctly compare the intensities of the absorption bands of solutions of different concentrations, they were normalized per unit concentration and unit thickness of the absorbing layer:

$$\varepsilon = \frac{\ln {}^{I_0}\!/_{I}}{c \bullet l} \tag{3}$$

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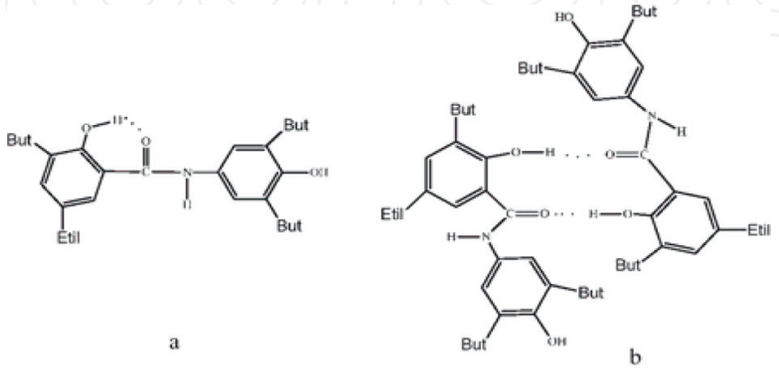
where C is the concentration of the substance in the solution and l is the thickness of the absorbing layer. As a result, there was an insignificant decrease in the intensity of the absorption bands v (= C-H, -C-H) and v (OH), referred to complexes with hydrogen bond, which also indicates the strength of the formed complexes.

It is known that amides and secondary amines are weaker proton donors in hydrogen bonding than hydroxyl-containing compounds. The v(NH) band is shifted over the band of the monomer from 14 to 74 cm^{-1} upon the formation of a complex of the N-H…O=C- type [10]. It is seen from **Figure 1** that no substantial shift of the v(NH) bands is observed in the spectral of the studied compounds. It is most likely that no hydrogen bond is formed at the amide groups and carbonyl of the N-H…O=C type in amides **1** and **2.**

Thus, an analysis of the spectral absorption distribution suggests that the following structures are most probable for the studied amides. Amides **1** and **2** exist predominantly as complexes with the structure I) and intermolecular hydrogen bond (**Structure II**) formed by the phenol and carbonyl groups. The phenolic OH groups arranged in the adjacent position with the C = 0 group are involved in complexes. It is most probable that sterically hindered phenol groups are free in both complexes with an intramolecular hydrogen bond and in structures with an intermolecular hydrogen bond. Therefore, our investigations were continued by the study of the kinetics of phototransformation of the studied amides at the absorption bands of the unbound v(OH) and v(NH) groups.

Analysis of IR spectra for stationary photolysis of amides **1** and **2**. An analysis of stretching vibrations for stationary photolysis of amides **1** and **2** shows that the intensity of the band v (OH) = 3644 cm^{-1} regularly decreases under UV radiation. These changes indicate the ionization of free phenolic hydroxyls.

The intensity of the band in the range of stretching vibrations of the NH group (v(NH) 3454 cm^{-1} (1) and 3442 cm^{-1} (2) decreases with an increase in the UV irradiation time (see **Figure 2**). The band with a maximum at 3424 cm^{-1} which can be attributed to the v(NH) vibration of long-lived intermediates appears and increases in the spectrum of amide **1** (see **Figure 2a**). For amide **2**, the indicated band is smoothened and exists as a shoulder (see **Figure 2b**).



Structure II. Intramolecular (a) and intermolecular (b) hydrogen bonds, on the model, amide structure 4.

The position and intensity of bands at 3534 and 3469 cm^{-1} remain almost unchanged after UV irradiation. They can be assigned to stretching vibrations of the C-H bonds of the aromatic fragments of amides **1** and **2,** respectively. The bathochromic shift of the indicated component of the spectrum related to a higher degree of delocalization is observed for amide **1**. In structure 1 both benzene rings, amide group, and phenolic hydroxyls are involved in the general system of conjugation, whereas in structure 2, the residue of salicylic acid amide and the fragment of sterically hindered phenol are separated by three methylene groups.

An analysis of the IR spectra allows one to conclude that during photolysis amides transform into the excited state, but no radical products are formed upon the cleavage of the N-H bond. Free phenolic hydroxyls that do not participate in hydrogen bonding undergo ionization. Thus, the formation of phenoxyl radicals should be expected for the photolysis of the studied structures. Most likely, no radical products at the amide groups are formed.

4. Analysis of UV: Vis spectra for stationary photolysis of amides 1 and 2

The UV spectrum of amide **1** (**Figure 3a**) exhibits absorption maxima at 225 and 325 nm responsible for the π-π^* and n-π^* transitions, respectively. For stationary photolysis (irradiation with a mercury lamp, 313–365 nm), the intensity of the absorption bands at 325 and 225 nm decreases, and new bands with maxima at ~255 and ~295 nm appear in the spectrum. An absorbance at 370–400 nm in the form of a shoulder also increases.

These new absorption bands belong to the products of phototransformations of amide **1**. The band of the π-π^* transition (225 nm) undergoes the bathochromic ("red") shift ($\Delta\lambda \approx 25$ nm), and the band of the n-π^* transition (325 nm) experiences by the hypsochromic ("blue") shift ($\Delta\lambda \approx 39$ nm) (see **Figure 3a**, **b**).

In amide **2** (see **Figure 3b**), the bands of electron transitions of the native and phototransformed molecules experience the hypsochromic shift compared to amide 1 caused by a lower degree of electron density delocalization. After irradiation, the intensity of the absorption bands of molecule **2** at 311 nm (n-π^* transition) and 220 nm (π-π^* transformation) decreases, and new bands with maxima at ~250 and ~ 300 nm and a shoulder in a range of 330–400 nm appear in the spectrum.

The pattern of spectral change in solutions of amide 1 in heptane upon irradiation with pulses of a neodymium laser (for 4 min) is nearly identical to that observed upon lamp photolysis (**Figure 4a**). The UV spectra also demonstrate a decrease in the absorption band intensity of the initial compound at 325 nm (band of the n-π^* transition) and 226 nm (band of the π-π^* transition) and the appearance of new bands with maxima at 255, 285, and 370 nm, which can be assigned to photoproducts (**Figure 4a**, **curve 5**). The band of the π-π^* transition experiences the bathochromic ("red") shift ($\Delta\lambda \approx 9$ nm), whereas the band of the n-π^* transition undergoes the hypsochromic ("blue") shift ($\Delta\lambda \approx 39$ nm).

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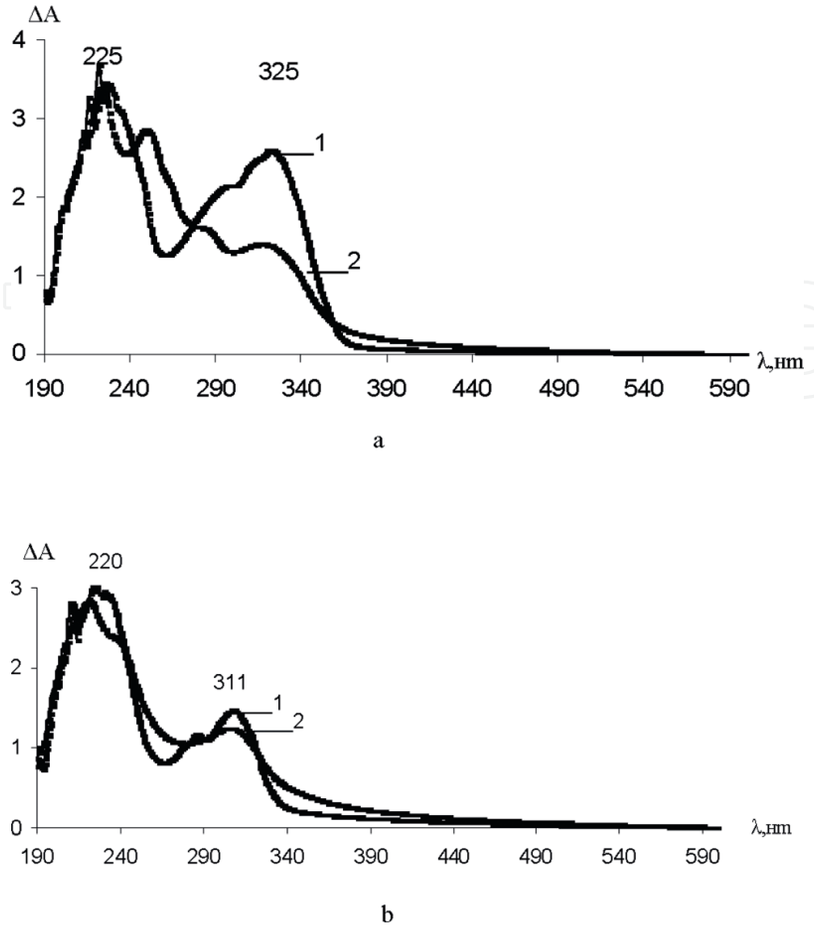


Figure 3. Optical absorption spectra for stationary photolysis of salicylic acid amides 1 (a) and 2 (b) (5 • 10–^{4} mol L^{-1}) before (1) and after (2) irradiation in heptane for 5 min.

($\Delta\lambda \approx 25$ nm) of the n-π^* transition (325 nm) experiences by the hypsochromic ("blue") shift (see **Figure 3a**, **b**) ($\Delta\lambda \approx 39$ nm).

In amide **2** (see **Figure 3b**), the bands of electron transitions of the native and phototransformed molecules experience the hypsochromic shift compared to amide **2** caused by a lower degree of electron density derealization. After irradiation, the intensity of the absorption bands of molecule 2 at 311 nm (n-π^* transition) and 220 nm (π-π^* transformation) decreases, and new bands with maxima at ~250 and ~ 300 nm and a shoulder in a range of 330–400 nm appear in the spectrum.

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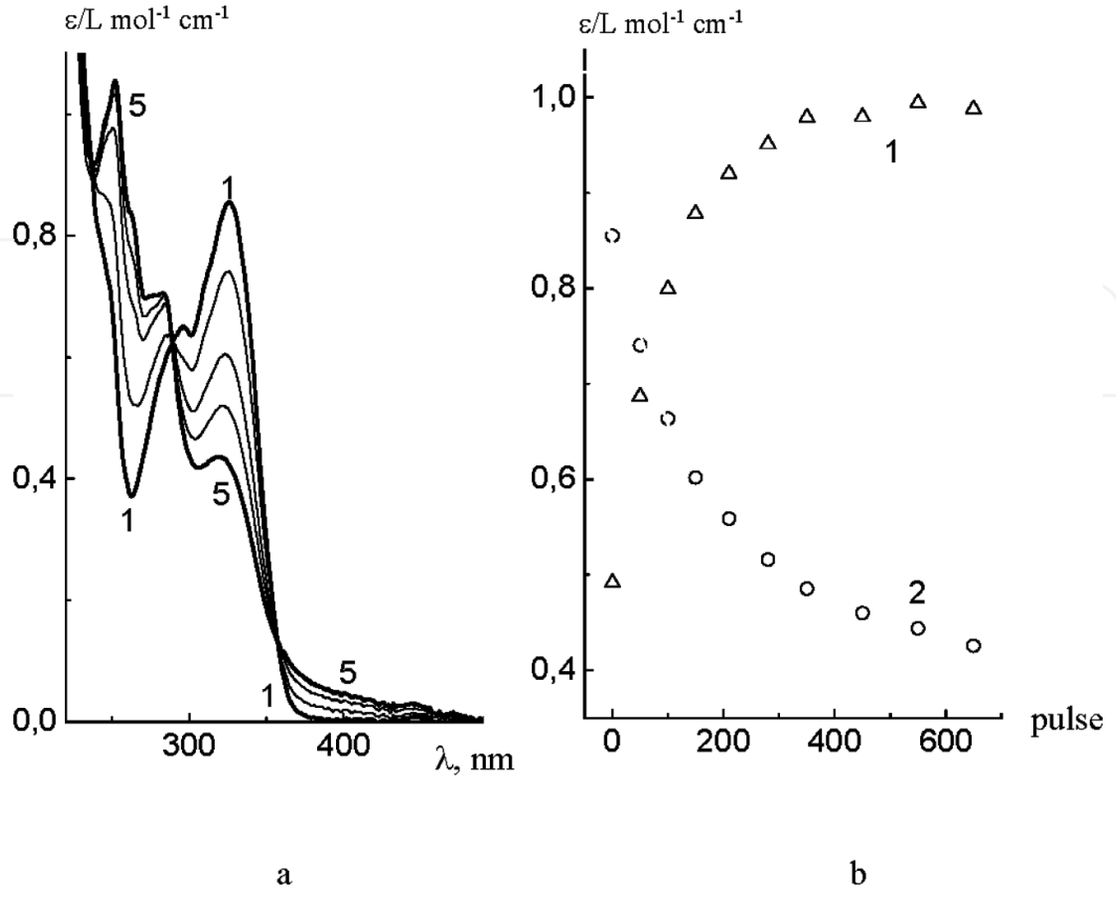


Figure 4. (a) Optical absorption spectra of a solution of amide 1 (3.45•10–^{4} Mol L^{-1}) in heptane after 0 (1), 50 (2), 110 (3), 180 (4), and 250 (5) laser pulses. (b) Change in the absorbance at the wavelengths 255 (1) and 325 nm (2) during photolysis.

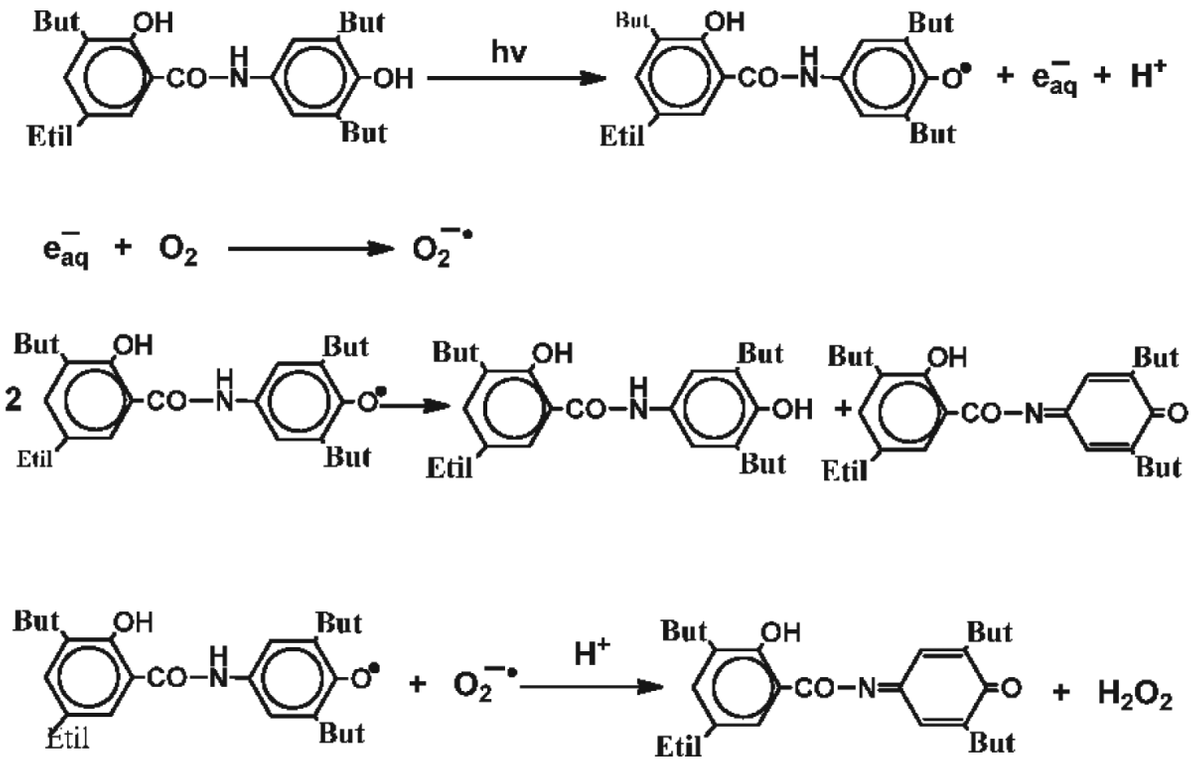
It should be mentioned that during photolysis of amide **1** isosbestic points at 238, 290, and 357 nm are retained, indicating a low photoactivity of the final products compared to the initial compound. The mentioned qualitative changes in the spectra of the substances under irradiation with a mercury lamp and a neodymium laser indicate the phototransformation of molecules accompanied by the formation of fairly stable products with the electron density redistribution in the system of *(π-π*)* and (n-π*) conjugation.

We also studied the dependence of the absorbance of amide 1 at 255 and 325 nm attributed to the photolyzed and native molecules, respectively, on the number of laser pulses fed to the sample (see **Figure 4b**). It is seen from **Figure 4b** that after 650 pulses 100% of the initial compound transform into photolysis products.

The combined interpretation of the data on pulse and stationary photolysis suggests the structure of the main final photochemical products and reactions of its formation (**Scheme 1**).

The formation of the compound with the quinoid structure (iminoquinone) corresponds to the disappearance of stretching vibration bands of the OH and NH groups (see **Figure 2**) and the disappearance of the absorption bands at 240–290 nm characteristic of quinones and iminoquinones [23–24]. The presence of bulky substituents in the *ortho*- and *para*-positions of

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Scheme 1. The formation reactions and structure of the main products of the photochemical conversion of salicylic acid amides.

the iminophenol fragment prevents the recombination of phenoxyl radicals with the formation of dimeric products.

Laser pulse photolysis of amide **1**. The excitation by a laser pulse (308 nm) of deoxygenated aqueous solutions of salicylic acid amides results in an intermediate absorbance consisting of two bands with maxima at 380 and 510 nm (**Figure 5a**), which disappear with significantly different rates (**Figure 5b**). These data indicate the formation of several intermediate species after a laser pulse. The lifetime of the band at 510 nm decreases substantially in the presence of oxygen, which indicates that the band belongs to the absorbance of amide 1 from the triplet T: state. The main channel of triplet state decay is triplet-triplet annihilation. It is known that the triplet-triplet absorption band of salicylic acid in cyclohexane has a maximum at 440 nm.[1] The bathochromic shift of the absorption band of amide **1** at 70 nm is caused, most likely, by an additional conjugation due to the introduction of the phenol substituent at the amide group of salicylic acid and to other types of the solvent.

In the presence of oxygen, the triplet state of amide **1** rapidly disappears during quenching, which makes it possible to detect one more, longer-living intermediate, whose optical spectrum consists of two absorption bands with maxima at 480 and 380 nm (**Figure 6a**). The kinetics of the disappearance of this absorbance is presented in **Figure 6b**. The absorbance amplitude at 380 nm (ΔA^{380}) depends nonlinearly on the laser pulse intensity (**Figure 7a**) and can be expressed by the following equation:

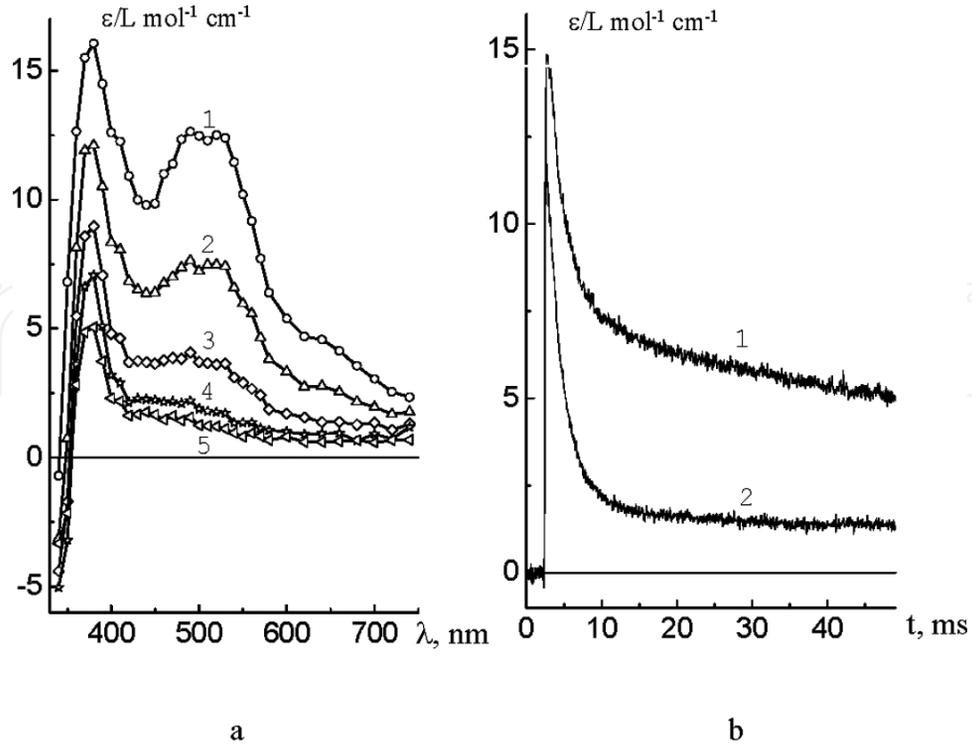


Figure 5. (a) Intermediate absorption spectra for stationary photolysis of a deoxygenated solution of amide 1 ($3.45 \bullet 10^{-4}$ Mol L^{-1}) in heptane; *1–5* spectra in 0, 1.6, 4, 10, and 48 ⁞is after a laser pulse (2.2 mJ $pulse^{-1}$), respectively. (b) Kinetic curves of a change in the absorbance at 380 (1) and 510 nm (2).

$$\Delta A^{380} = 1.6 \times 10^{-4} \times I + 1.4 \times 10^{-5} \times I^2 \tag{4}$$

where ***I*** is the laser pulse intensity, mJ cm^2. These data indicate that the long-lived intermediate is formed in both one- and two-quantum processes. The product of the quantum yield of the one-quantum process (cp) by the absorption coefficient of the long-lived intermediate at 380 nm (g^{380}) can be estimated as (g^{380} = 80 mol L^{-1}) cm^{-1}:

$$\mathrm{ROH{-}hv} \rightarrow \mathrm{RO}^{\bullet} + e^{-}_{solv} + \mathrm{H}^{+} \tag{5}$$

Phenoxyl radical can also be formed upon the absorption of the second quantum of light by the excited singlet or triplet states of phenols. For example, two-quantum photoionization for the absorption of the second quantum by the excited singlet state of these compounds to form a pair hydrated $RO^{\bullet}$ electron-organic radical was observed [5–7] in the study of photochemistry of aqueous solutions of salicylic and sulfosalicylic acids. These data suggest that the long-lived intermediate observed for photolysis of amide 1 is the phenoxyl radical formed in the one- (3) and two-quantum processes **(4):**

$$^{S1}\mathrm{X{-}hv} \rightarrow \mathrm{RO}^{\bullet} + e^{-}_{solv} + \mathrm{H}^{+} \tag{6}$$

$$\mathrm{ROH{-}hv} \rightarrow {}^{S1}\mathrm{X{-}hv} \rightarrow \mathrm{RO}^{\bullet} + e^{-}_{solv} + \mathrm{H}^{+} \tag{7}$$

The solvated electron in heptane absorbs in the IR range (a maximum at 1600 nm [8]) and cannot be detected using the system used in the work. It should be mentioned that the

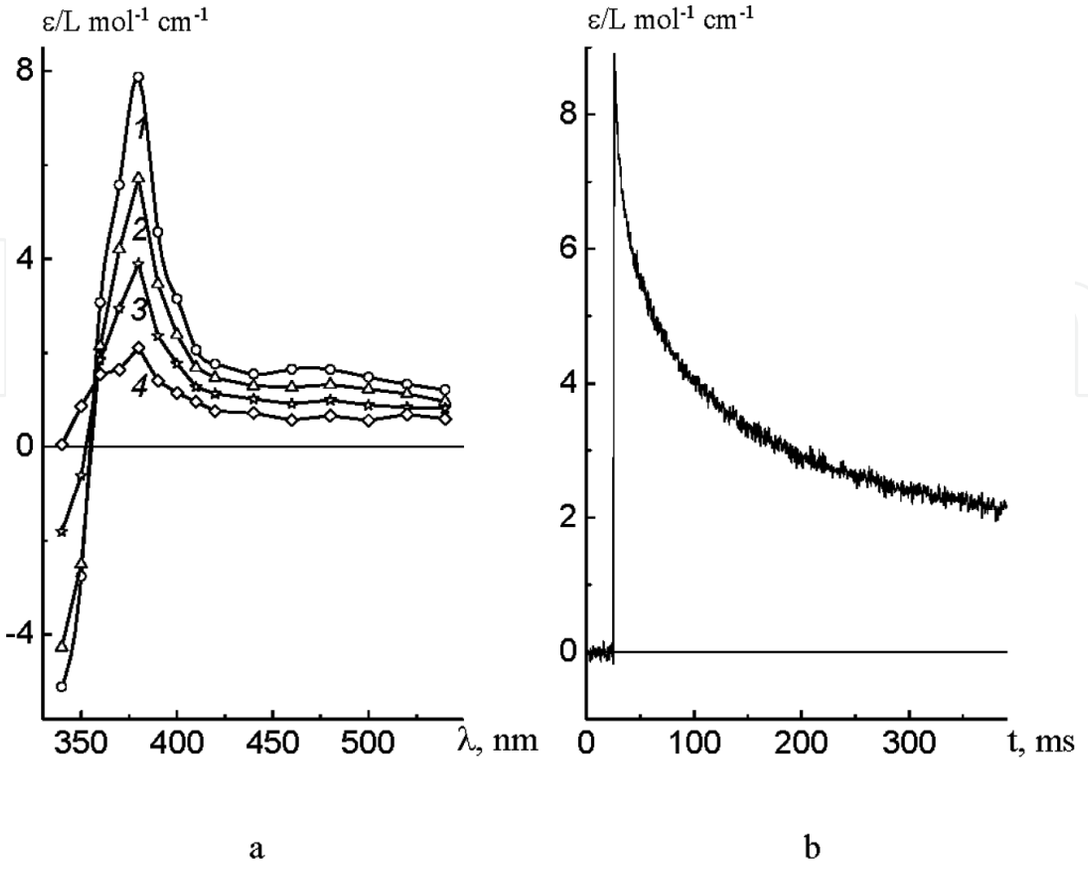


Figure 6. (a) Intermediate absorption spectra for stationary photolysis of a solution of amide 1 (3.45•10–^{4} Mol L^{-1}) in heptane at an oxygen concentration in the solution of 3•10^{-3} Mol L^{-1} (**1–4**) spool ra in 3, 12, 90, and 380 (is after a laser pulse, respectively. (**b**) Kinetic curve of a change in the absorbance at 380 nm. It is known that one of the intermediate products of photoionization of phenols (ROH) is the corresponding phenoxyl radical (see refs. 17 and 18) Formed in the reaction.

absorption band maxima of radical RO$^{\bullet}$ of amide 1 (380 and 480 nm) are shifted to the red range compared to the unsubstituted phenoxyl radical (290 and 400 nm) [25, 26]. This is due to the iminophenol substituent in molecule 1. It is known that the introduction of aromatic substituents results in the bathochromic shift of the absorption bands of phenoxyl radicals, in particular, ongoing from the unsubstituted phenoxyl radical to radicals of 4-phenylphenol and 4,4′-biphenol, the long wavelength band maximum shifts from 400 nm by 560 and 620 nm, respectively [27].

It should be mentioned that phenoxyl radicals decay predominantly in recombination reactions [26, 27]. The kinetics of the disappearance of the absorbance of radical RO$^{\bullet}$ (380 nm) is described rather well by the second-order law. The linear dependence of the observed rate constant (k_{app}^{380}) on the absorbance amplitude (**Figure 7b**) makes it possible to determine the ratio of the recombination rate constant of phenoxyl radicals, $2k_{pek}/\varepsilon^{380} = 1.6 \cdot 10^{5}$ cm s-^{1}. The kinetics of radical decay was determined in solutions containing oxygen (to accelerate the disappearance of the absorbance of the triplet state of amide 1), and, therefore, the section cut in the ordinate (see **Figure 7b**) corresponds, most likely, to the reaction of RO$^{\bullet}$ with oxygen. Under normal conditions, the concentration of oxygen in a heptane solution is 3· 0^{-3} mol L^{-1} [24], which makes it possible to estimate the rate constant of the reaction with oxygen,

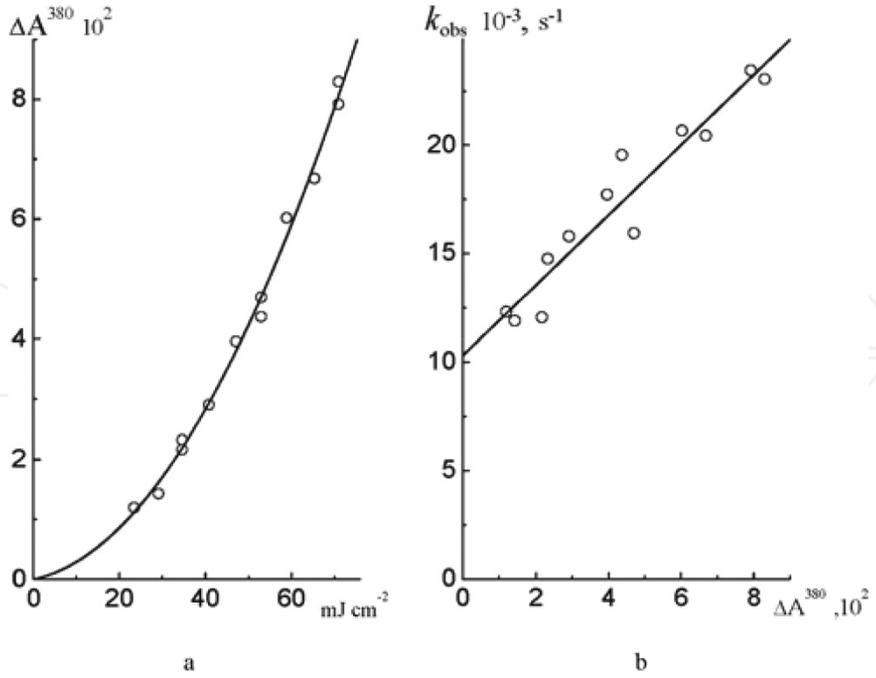


Figure 7. (a) Absorbance amplitude (Δa^{380}) и laser pulse intensity (the initial absorbance at the wavelength 355 nm is equal to 0.44). (b) Reaction rate constant (A'_{obs}) for the disappearance of the absorbance of radical $RO^{\bullet}$ of amide 1 ($3.45 \bullet 10^{-4}$ Mol L^{-1}) from signal amplitude at 380 mil.

$k_{Q2} \approx 3.4 \cdot 10^6$ L mol^{-1} s^{-1}. The value of rate constant is more than three orders of magnitude lower than the diffusion rate constant in this solvent. Low rate constants for the reaction with oxygen are characteristic of phenoxyl radicals [19, 27]:

$$A = A_0 + \frac{\phi_{app} N_{abs} (A_\infty - A_0)}{N_a C_X V} N_{pulse} \tag{8}$$

At the initial stage of photolysis, the change in the absorbance of the sample can be expressed by the equation where φ_{app} is the apparent quantum yield of photolysis of amide 1 at a given intensity of a laser pulse, N_{abs} is the number of quanta absorbed by the sample, N_a is Avogadro's number, V is the volume of the sample, N_{pulse} of laser pulses, C_1 is the initial concentration of amide 1, and A_0 and A_∞ are the initial and final absorbances of the sample. The latter value can be estimated from the data of **Figure 4b** assuming 100% conversion of amide 1 to photolysis products. Accordingly, knowing the value of A_∞, one can estimate the apparent quantum yield of photolysis of amide **1** by Eq. (8). For a laser pulse intensity of 60 mJ cm^{-2}, the apparent quantum yield of photolysis of amide 1 is 0.09.

Assuming that at this intensity the main mechanism of $RO^{\bullet}$ decay is recombination, the absorption coefficient of $RO^{\bullet}$ at a wavelength of 380 nm and, correspondingly, the recombination constant of radicals can be estimated from the value of the signal of intermediate absorbance at 380 nm at the given intensity. The obtained value of the absorption coefficient of phenoxyl radicals of 1 ($\varepsilon^{380} \approx 2.9 \bullet 10^3$ cm s^{-1}) is close to that presented for $RO^{\bullet}$ of salicylic acid (ε^{390} = (2.5 + 0.3) • 10^3 cm s^{-1} in an aqueous solution).[5] It is known that the absorption

coefficients of phenoxyl radicals depend slightly on their structure and in a range of 2.9–4.0 • 10^3 cm s^{-1}. The recombination rate constant of $RO^{\bullet}$ radicals of 1 was $2k_r \approx 4.6 \bullet 10^8$ L mol^{-1} s^{-1}. The obtained value corresponds to literature recombination constants for phenoxyl radicals that form relatively unstable dimers [28]. The recombination rate of unsubstituted salicylic acid is substantially higher than $2k_t \approx (1.8 + 0.3) \bullet 10^9$ L mol^{-1} s^{-1} (in an aqueous solution) [7], and the order of magnitude of the rate constant is typical of the bimolecular decay of phenoxyl radicals [24, 29]. The decrease in the activity of phenoxyl radicals of UV-substituted amides in dimerization processes is due to steric factors and the use of other solvents.

Thus, UV irradiation of UV-substituted salicylic acid amides organized in complexes with intra- and intermolecular hydrogen bonds induces the phototransformation of free phenolic hydroxyls with the formation of phenoxyl radicals $RO^{\bullet}$, which decay in recombination following the second-order law with the rate constant $k_T \approx 2.3 \cdot 10^8$ L mol^{-1} s^{-1}. The NH groups undergo excitation, but no radical products are formed. The dimerization products of amides 1 and 2 are relatively stable under the photolysis conditions. With phenoxy radicals, oxygen reacts at a relatively low rate [29, 30].

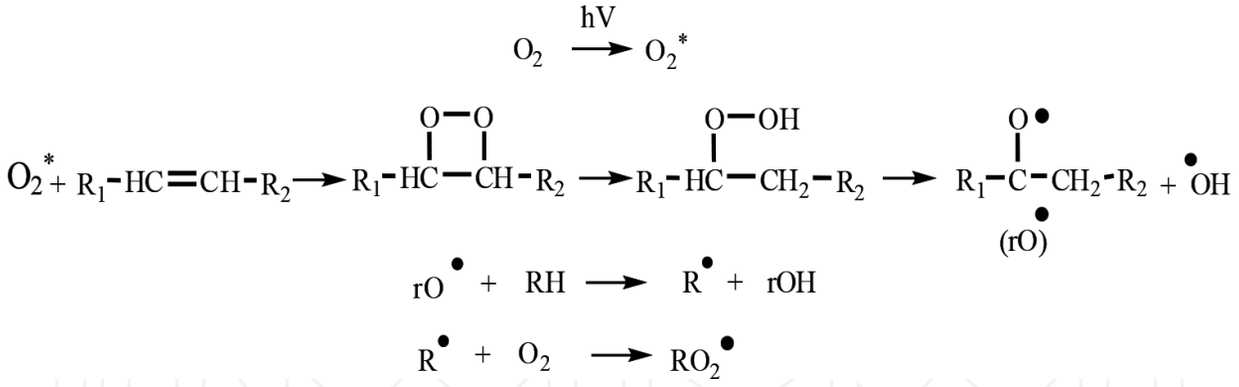
5. Study of the kinetics of inhibition of the oxidation process by N-substituted amides of salicylic acid

In the present work, the inhibitory and photostabilizing properties of compounds that are amide derivatives of salicylic acid, characterized by the conjugation of the electron density and the degree of spatial screening of the phenolic hydroxyls (structure 1) are investigated.

It is known that salicylic acid and its derivatives are capable of absorbing UV rays in the range of 301–305 nm [3, 8]. It can be assumed that the modified structures studied by us can also absorb UV rays in this range, which is dangerous for the development of skin cancer. The compounds can potentially exhibit antioxidant and antiradical activity, due to the presence of two phenolic groups in their chemical structure.

It is known that ultraviolet irradiation leads to the formation of singlet oxygen O_2^*, which joins the double bond of unsaturated lipids [11, 12]. As a result of further isomerization of cyclic peroxides and photochemical decomposition of hydroperoxides, hydroxyl (OH•) and alkoxy radicals (rO•·) are formed which react with the substrate RH in an oxygen atmosphere to form peroxyl radicals RO_2• (**Scheme 2**).

To study the possibility of photostabilization of oxidation processes caused by the action of UV rays, it was considered necessary to study the electronic spectra of N-substituted amide derivatives of salicylic acid (**1–4**) in comparison with **5** (**Figure 3**). The presence of intense absorption bands in the UV range (190–350 nm) for all amides of salicylic acid has been established. The most effective UV rays absorb compounds 1 and 2. This absorption is absent in **5**. Thus, the absorption of UV rays that initiate the process of lipid oxidation is one of the mechanisms of photostabilizing action of N-substituted amides of salicylic acid (**Figure 8**).



Scheme 2. Scheme of peroxyl radical $RO_2^{\bullet}$ formation during UV irradiation during the reaction of singlet oxygen O_2^{*} with unsaturated compounds.

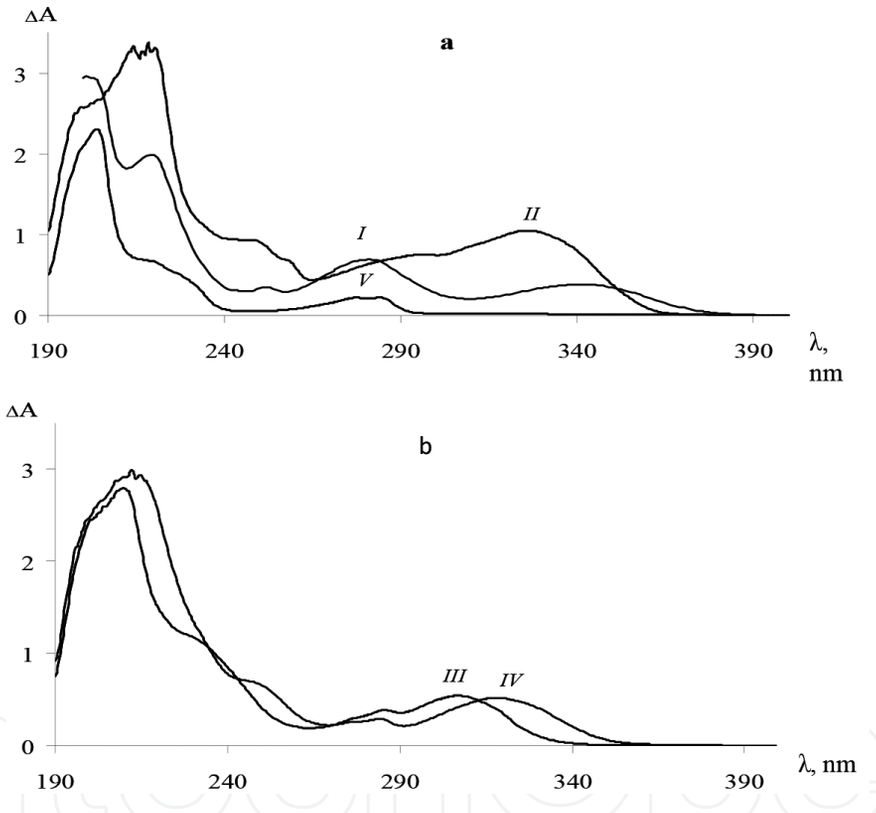


Figure 8. UV spectra of amides: (a) I is 3, II is 4, and V is 5; (b) III is 2, IV is 1, and in heptane c = 5 · 10^{-4} Mol L^{-1}, d = 0.2 cm.

The mechanism of the complex multistage process of free radical oxidation of the substrate is described by a conventional scheme [11, 12]. The oxidation process is carried out by.

peroxyl radicals reacting with a substrate with a rate constant k_2 [29].

$$RO_2^{\bullet} + RH \xrightarrow{k_2} ROOH + R^{\bullet} \quad (9)$$

In the presence of an antioxidant (InH), free radicals are killed according to reaction 7 to the conventional scheme [24, 25].

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$$RO_2^{\bullet} + InH \xrightarrow{k_7} ROOH + In^{\bullet} \quad (10)$$

In the presence of an antioxidant, induction periods (τ) appear, and the magnitude of which depends on their number. In this paper, the photostabilizing effect of N-substituted salicylic acid derivatives, differing in electron density conjugation and the degree of spatial screening of phenolic hydroxyls (structure 1), was studied. The antioxidant activity of amides of salicylic acid was evaluated by the value of induction periods (τ) with UV-induced oxidation of the model substrate, methyloleate. The kinetic curves of oxygen absorption by methyl oleate in the presence of test compounds are shown in **Figure 9**. As can be seen from **Figure 9**, all the amides (1–4) studied effectively inhibit the oxidation of the substrate. With comparable concentrations of AO, the magnitude of induction periods provided by different amides is significantly different. Differences in the inhibitory effect of compounds are determined by the peculiarities of their chemical structure. The most effective oxidation inhibitors are amides 1 and 2, which are sterically hindered diatom phenols, in the structure of which the conjugated fragments are separated by three methylene groups. In this case, both phenolic groups can interact with free radicals independently of each other. The presence of bulk tert-butyl substituents prevents the possibility of adverse reactions that reduce the effectiveness of the antioxidant. Compared with amides **1** and **2**, amides **3** and **4** exhibit a lower inhibitory effect.

In these compounds, both aromatic moieties form a general conjugation system with an amide group. The difference between amides **3** and **4** is the degree of spatial screening of phenolic groups (-OH). In structure **3** there is no tert-butyl substituents, which significantly increases the activity of oxidation products of phenols in the side processes of oxidation, in particular, in reaction with the substrate. This reaction leads to the continuation of the oxidation chains and

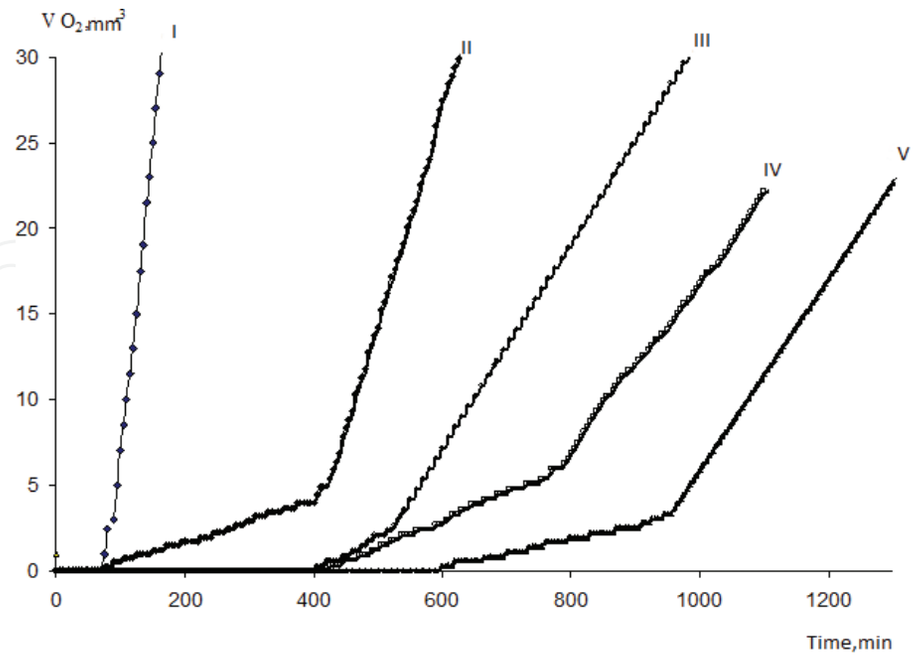


Figure 9. Kinetic curves of oxygen absorption of MO in the chlorobenzene medium upon initiation of the oxidation reaction by UV irradiation: I, substrate (S) (control); II, S + 3; III, S + 4; IV, S + 1; V, S + 2. Concentration of AO is $1.5 \cdot 10^{-4}$ mol L^{-1}, T = 60°C.

significantly reduces the effect of the antioxidant [31, 32, 34–36]. In the amide structure **4,** one of the two phenolic groups is spatially screened with bulky substituents, which provides a higher inhibitory effect 4 compared to **3**.

The kinetics of oxygen absorption in the oxidation of methyl oleate in the presence of amides 1–4 was studied in the range of concentrations (0.5–2.0) $\cdot 10^{-4}$ mol L^{-1}; the effectiveness of the antioxidants studied was compared with dibunol (**5**) and α-tocopherol (**6**) (**Figure 9**). The linear character of the dependence of the period of induction on the concentration of amides, described earlier for most synthetic antioxidants, is established. For natural antioxidants, extreme dependence on concentration is observed; at relatively high concentrations, the inhibitory effect may decrease and a prooxidant effect may be observed [33]. It has been shown that the action of N-substituted amides of salicylic acids **1** and **2**, which are spatially hindered diatomaceous phenols, is comparable to the efficiency of monohydric phenol-5 and exceeds the gross inhibitory effect of a natural antioxidant **6**. Amide 1, which includes in its structure two phenolic groups, exceeds the monatomic phenol 5 in terms of the induction period by no more than 20%. Amides **3** and **4**, which differ in the highest degree of conjugation of the electron density, are significantly inferior to amides **1** and **2** and also amide **5** (**Figure 10**).

It is known that the chemical structure has a significant effect on the antioxidant properties of oxidation inhibitors. An important stage of the present study was the establishment of the relationship between the features of the chemical structure of a series of amides of salicylic acid and the mechanism of their antioxidant action.

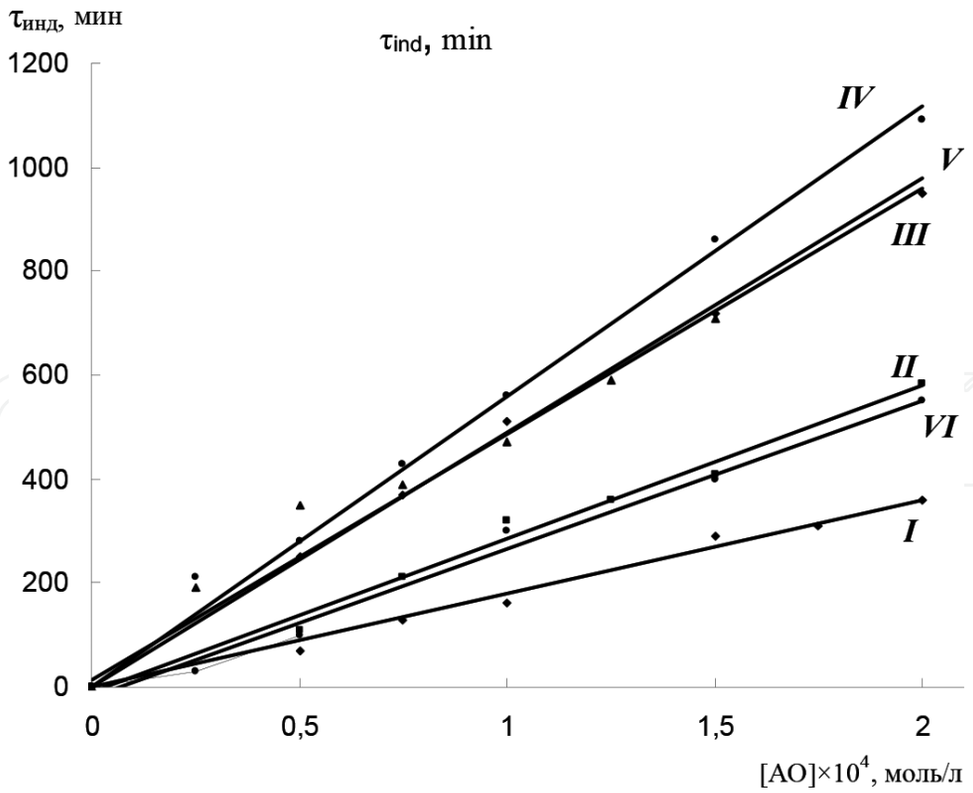


Figure 10. Dependence of the period of induction on the concentration of amides: I-3, II-4, III-2, IV-1, V-5, and VI-6 under UV-initiated oxidation of MO (w_i = 0.6 •10^{-8} Mol L^{-1} s^{-1}).

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The relatively low values of induction periods for N-substituted amides of salicylic acid (diatom phenols **1–4**) are found in comparison with monatomic phenols **5** and **6**. These differences are explained by the fact that compounds (1–4) form intra- and intermolecular hydrogen bonds (structure 2), in which some OH groups cannot participate in the reaction with peroxy radicals.

The effectiveness of amides of salicylic acid in the elemental reaction with peroxyl radicals $RO_2^{\bullet}$ is determined by the rate constant of the elementary reaction (k_7) (antiradical activity) estimated by the chemiluminescence method [12].

It has been established that all the derivatives of salicylic acid exhibit a high antiradical activity (**Table 1**).

Table 1 shows that the highest antiradical activity is found in natural antioxidant **6** (α-tocopherol), the efficacy of which is more than 400–460 times higher than that of compounds (**1–4**). The absence of bulky substituents in structure **5** provides this compound the highest antiradical activity. Note that all amides of salicylic acid have k_7 values of the same order as the known synthetic sterically hindered antioxidant (dibunol) (**5**). In the group of amides of salicylic acid, the highest values are characteristic for **3** and **4**, in the structure of which phenolic OH groups are included in the common conjugation system, which binds both benzene rings. For amides **1** and **2**, the conjugation system is "destroyed" by a bridging fragment containing three methylene groups, which contributes to a decrease in the value of k_7. The antiradical activity of amides of salicylic acid is comparable with the antioxidant activity of most known sulfur-containing and nitrogen-containing bifunctional oxidation inhibitors [36, 37].

It is known that the presence of phenolic OH groups with ortho-t-butyl substituents leads to a significant decrease in antiradical activity. Thus, the greatest value of k_7 was observed for compound **3**, which in its structure has two unsubstituted phenolic hydroxyls. The substituted analogue (amide **4**) is inferior to the **3** amide in **4**, 1 times, which is explained by the spatial difficulties in the interaction of antioxidant molecules with peroxy radicals. It is known that classical oxidation inhibitors interact, as a rule, with two free radicals (the stoichiometric inhibition coefficient for **5** and **6** is 2) [12, 36, 37]. The presence of two phenolic hydroxyls in N-substituted amides of salicylic acid theoretically should lead to an increase in the value of f to 4.0. However, the stoichiometric inhibition coefficient f approaches 4 only in two compounds (1 and 2) (f = 3.6–33), which kinetically reflects the presence of two OH groups in the molecule and indicates that both phenolic hydroxyls are interdependent during oxidation, and the difference in the value (f = 3.3–3.6) from 4.0 kinetically reflects the partial participation of

The subject compound	**1**	**2**	**3**	**4**	**5**	**6**
$k_7 \times 10^4$, $M^{-1} \times c^{-1}$	0.85	0.52	6.86	1.69	1.40	360.0
f	3.6	3.3	2.4	2.6	2.0	2
T = 333 K, Wi = $2.3 \bullet 10^{-8}$, mol L^{-1} s^{-1}, C = $1 \bullet 10^{-3}$ mol L^{-1}						

Table 1. The values of the constant k_7 in the reaction of N-substituted amides of salicylic acid with peroxyl radicals ($RO_2^{\bullet}$).

phenolic groups in the formation of complexes with a hydrogen bond, which cannot participate in the reaction with free radicals. For amides 3 and 4, a high degree of π-π and n-π conjugation and a low degree of screening of the phenolic groups with tert-butyl substituents reduce the inhibition rate to (f = 2.4–2.6). It is known that spatially uncomplicated phenols easily penetrate into side reactions, which significantly reduces their overall antioxidant effect. One of the most significant adverse reactions is the interaction of phenoxy radicals with the substrate. Therefore, the weaker inhibitory ability of amides **3** and **4**, as well as the lower stoichiometric inhibition coefficient, indicates the occurrence of side reactions, in particular the possibility of the interaction of phenoxy radicals with the oxidation substrate.

6. Conclusions

1. Comparative analysis of the spectral absorption of native and partially deuterated molecules showed that amides of salicylic acid exist as complexes with an intramolecular hydrogen bond or an intermolecular hydrogen bond. Complexes are formed with the participation of phenolic and carbonyl groups located in neighboring positions. Spatially hindered phenolic groups, in all likelihood, do not participate in the formation of complexes.

2. During photolysis, N-substituted amides of salicylic acid pass into an excited state, which leads to the appearance of triplets and the formation of phenoxy radicals, presumably as a result of absorption of the second quantum of light by the excited singlet state. The triplet-triplet state is the main channel for the death of the triplet state of annihilation and recombination of phenoxy radicals ($k_{rek} = 2.3 \cdot 10^8$ L mol^{-1} s^{-1}). With UV irradiation of N-substituted amides of salicylic acid, amide groups also become excited; however, radical products are not formed in this case.

3. On the basis of a joint interpretation of pulsed and stationary photolysis data, stable photochemical conversion products of amides are established, which are compounds of the quinoid structure (iminoquinones). The presence of bulky substituents in the ortho- and para-positions prevents the recombination of phenoxy radicals with the formation of dimers. Iminoquinones are the final products of the photolysis reaction.

4. It is shown that all amides of salicylic acid are highly effective inhibitors of UV-induced oxidation of the model substrate (methyloleate). The inhibitory effect is directly proportional to the concentration of the compound, as for most known synthetic antioxidants.

5. Investigation of the relationship between the chemical structure and the antioxidant properties of a number of N-substituted amides of salicylic acid showed that the greatest inhibitory effect is manifested in compounds 1 and 2, in the structure of which the aromatic fragments are separated by three bridging groups –CH_2- and in ortho-position with respect to the phenolic group there are tert- butyl substituents.

6. It was found that the mechanism of photostabilizing action of N-substituted amides of salicylic acid is due to their ability to absorb ultraviolet rays in the range (190–350 nm), which creates prospects for using these compounds to protect the skin from melanoma

and to prevent the destruction of various materials under UV irradiation. It is shown that in the presence of amides of salicylic acid, the rate of initiation of the oxidation process is significantly reduced.

7. It is proven that the mechanism of action of N-substituted amides of salicylic acid is determined by their high activity in the reaction with free peroxy radicals. The value of the death constant for the radicals is ($k_7 = 0.52–6.86 \cdot 10^4$, L mol c^{-1}). The highest antiradical activity in amides 3 and 4 is noted, in the structure of which phenolic OH groups are included in the general conjugation system, covering both benzene rings. For amides 1 and 2, the conjugation system is "destroyed" by a bridging fragment containing three methylene groups, which contributes to a decrease in the value of k_7.

8. The inhibition factor f, showing the amount of free radicals dying on the antioxidant molecule, for compounds **1** and **2** approaches 4.0 (f = 3.6–3.3), reflecting the presence of two OH groups in the molecule, and indicates that both phenolic hydroxyls in the oxidation process act independently. Some of the phenolic groups are linked to complexes with a hydrogen bond and do not participate in the reaction with free peroxide radicals. Amides **3** and **4** show a high degree of π-π and n-π conjugation and a lower screening effect of bulky substituents. As a result, the inhibition coefficient decreases to (f = 2.4–2.6), and a significant role is played by side reactions, in particular the possibility of incorporating phenoxy radicals into the reaction with the substrate.

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