ENERGETICS AND STRUCTURAL MECHANISMS OF PHOTOCHEMICAL PROCESSES IN MOLECULES OF ALDONITRONE VINYLOGS

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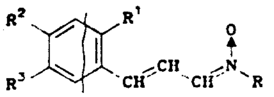
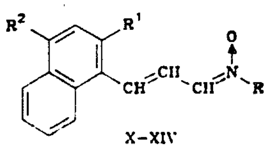
Depending on the multiplicity of the excited state, alternative photoreactions are realized in methoxy and acetoxy derivatives of aldonitrone vinylogs: diabatic nitrone–oxazypyridone rearrangement in the first excited singlet state and E–Z isomerization involving the C=N bond in the triplet state. In the case of aldonitrone vinylogs with an o-hydroxy group in the a-aryl ring one observed adiabatic proton transfer from the hydroxy group to the azotoxido group with a subsequent diabatic reaction involving cyclization to the 2H-chromene structure. The same transfer is also realized in the triplet state. The quantum yields were determined, and the energies of activation of the photoreactions and the reverse thermal processes were evaluated.

We have previously observed [1] the photochemical activity of aldonitrone molecules in solution, an activity that is associated with intramolecular photoreactions. As it turned out, the character of these photoreactions is strictly specific for individual classes of the investigated molecular structures.

In the present communication we have, by steady-state spectral-absorption and luminescence kinetic methods, made detailed investigations of the relationship between the energic and structural mechanisms of photoreactions in solutions of aldonitrile vinylogs I-XIV.


I-IX


X-XIV

	R	R^1	R^2		R	R^1	R^2
I	CH_3	H	OCH_3	VIII	$PhCH_3$-*p*	OH	H
II	Ph	H	OCH_3	IX	PhBr-*p*	OH	H
III	PhBr-*p*	H	OCH_3	X	Ph	H	$OCOCH_3$
IV	Ph	$OCOCH_3$	H	XI	Ph	$OCOCH_3$	H
V	CH_3	OH	H	XII	CH_3	OH	H
VI	Ph	OH	H	XIII	$CH(CH_3)_2$	OH	H
VII	$PhCH_3$-*p*	OH	H	XIV	Ph	OH	H

* I—VII, IX R^3=H, VIII R^3=Br.

In the case of UV excitation of solutions (in CCl_4, dioxane, ethanol, etc.) of aldonitrile vinylogs that do not contain an o-hydroxy group (I-IV, X, XI) we have observed photoinitiated (λ_{exc} 365 nm) irreversible changes in the electronic absorption spectra (Fig. 1). These changes are characteristic [2] for the extremely efficient photoreaction ($A_E \xrightarrow{h\nu} D$) involved in the formation of the oxaziridine structure (D), which absorbs in the shorter-wavelength region of the spectrum (λ 250-290 nm) than

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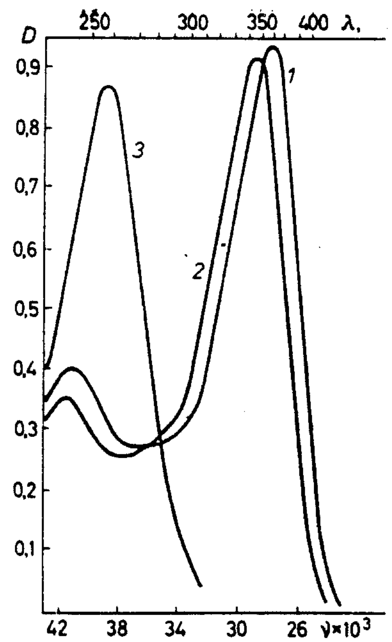


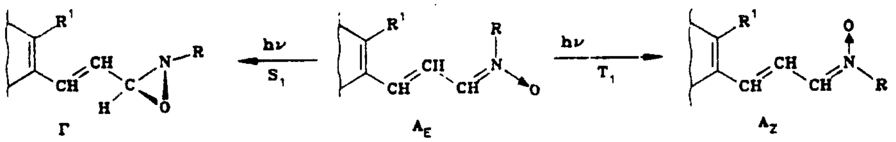
Fig. 1. Electronic absorption spectra of aldonitrone IV (isopentane, 293 K, c = $3 \cdot 10^{-5}$ mole/liter): 1) before irradiation; 2) after irradiation at the absorption band of the sensitizer (iodine–eosine, λ_{obs} 546 nm); 3) after 120-sec irradiation of the starting solution (λ_{obs} 365 nm).

the starting nitrone (λ 320-390 nm). The photoreaction is not sensitized by triplet-energy donors, and its quantum efficiency does not depend on the temperature or the structure of the aldehyde fragment, but decreases markedly when a bromine atom is included in the N-aryl radical (III) or when replacement of the latter by an N-alkyl radical occurs (compare I and II). [Quantum yields of the nitrone–oxaziridine photorearrangement (in DMSO, 293 K), Φ: 0.04 (I), 0.40 (II), 0.01 (III), 0.48 (IV), 0.43 (X), 0.41 (XI).] In the first case, as is well known, the rate of the intercombination conversion ($S_1 \sim\rightarrow T_1$) increases substantially, while in the second case there is the possibility of the development of a low-lying $n_0\pi^*_{N\cdots O}$ state, which is due to the rapid internal conversion ($S_{1\pi\pi^*} \sim\rightarrow S_{n\pi^*}$). Consequently, processes that compete effectively with the photoreaction are realized in both cases.

Thus, according to the data presented, the $A_E \rightarrow D$ photoreaction proceeds diabatically without an energy of activation in the S^*_1 state.

On the other hand, the photoexcitation of the starting nitrone molecule via triplet-triplet sensitization (whereas also in the case of direct photoexcitation in the case of III) leads to a short-wave (6000-7000 cm^{-1}) shift of the absorption band (Fig. 1). The photoinitiated changes in the spectra in this way, are characteristic for a reaction involving photo trans-cis isomerization relative to the C=N bond ($A_E \rightarrow A_Z$), which takes place exclusively through the triplet state [3].

Thus, alternative structural mechanisms of the photoreactions are associated with the different multiplicities of the photoactive states in aldonitrone vinylogs that do not contain an o-hydroxy group, just as in the case of the previously investigated nitrones [3]:



In contrast to the above-described molecules, the irreversible formation of structure D is generally not observed in solutions of aldonitrone molecules that contain an o-hydroxy group in the aryl ring (V-IX, XII-XIV), and photoinitiated reversible changes occur in the electronic absorption spectra upon irradiation in the long-wave absorption band of starting form A.

The changes are associated with a decrease in the intensity of this band and the formation of new bands (Fig. 2): a structured short-wave band ($\lambda_{1max} \sim 365$ nm) and two structureless long-wave bands ($\lambda_{2max} \sim 400$ nm, $\lambda_{3max} \sim 560$ nm). It has been previously shown [1] that the λ_1, λ_2, and λ_3 bands should be ascribed to a chromene structure (C), as well as cis-(B_Z) and

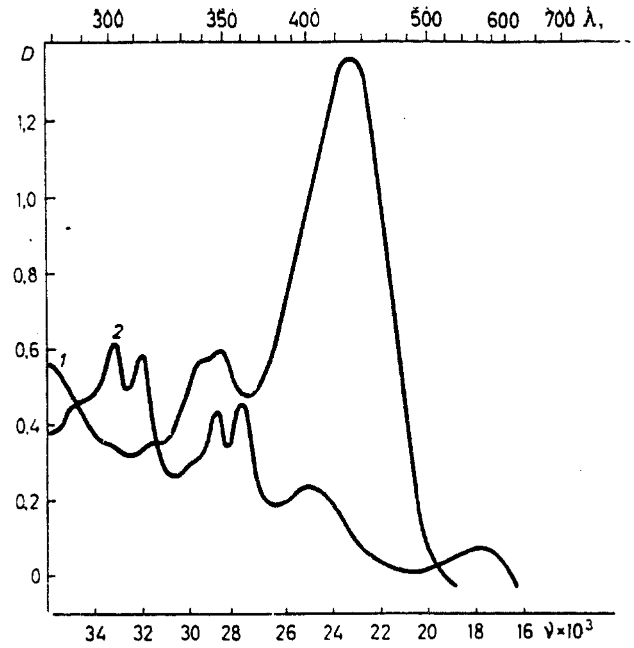


Fig. 2. Photoinduced changes in the absorption spectrum of aldonitrone XIV [isopentane–isopropyl alcohol (4:1), 77 K, c = 4.2·10^{-5} mole/liter]: 1) before irradiation; 2) after irradiation for 180 sec (λ_{irr} 365 nm).

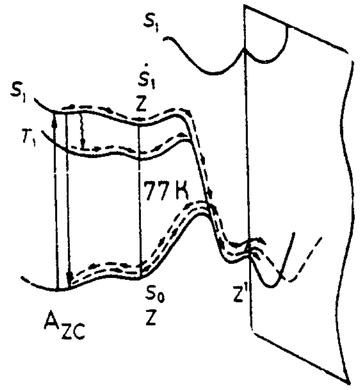
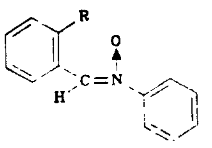


Fig. 3. Energic diagram of the photochemical and thermal transformations in molecules of o-hydroxyaldonitrone vinylogs (the letter designations correspond to those presented in the structural scheme).

trans-(B_E) isomeric quinoid structures, respectively. It is apparent that a necessary condition for the formation of these structures is the realization, as the primary process, of intramolecular (O → O) proton phototransfer, which usually takes place adiabatically as a consequence of the existence of an intramolecular hydrogen bond (IMHB) (O–H···O). One should therefore assume that the starting form has cisoid structure A_{ZC}, which is stabilized by an IMHB.

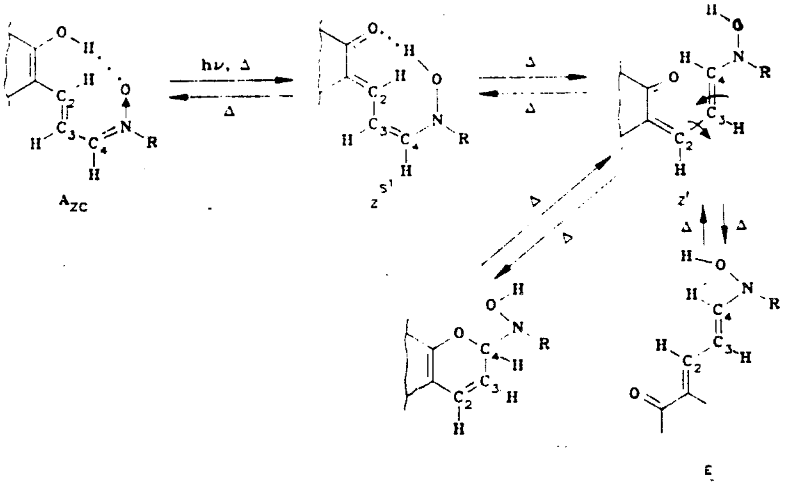
The presence of a characteristic band in the IR absorption spectra ($\nu \approx 3100\ \mathrm{cm}^{-1}$) [4], a structured long-wave band in the UV absorption spectra [5], and the absence of the characteristic (for nitrone molecules) of photoreactions involving the formation of an oxaziridine ring ($A_E \rightarrow D$) and E → Z isomerization indicates the existence of this sort of structure with an IMHB. As demonstrated by the results of our comparative investigation of simple model structures XV and XVI, the formation of an IMHB actually should lead to a pronounced decrease in the effectiveness of the nitrone–oxaziridine photoreaction [Φ:0.22 (XV), 0.03 (XVI)] and the manifestation of fluorescence with an anomalous Stokesian shift (ASS) that is characteristic for the structure formed as a result of adiabatic proton transfer in the S_1 state:



XV $R=OCH_3$;
XVI $R=OH$

Consequently, the manifestation by the investigated aldonitrones with an o-OH group (V-IX, XII-XIV) of a long-wave fluorescence band with a large Stokesian shift ($\Delta\nu > 6$ t-cm^{-1}), which is particularly intense in frozen solutions (77 K), constitutes direct evidence for the existence in the first stage of the photoreaction of an adiabatic process involving intramolecular proton transfer with the formation of the $B_Z^{S_1}$ structure (Fig. 3).

The peculiarities of the energetics and structural mechanism of the subsequent steps in the photoreaction were investigated by studying the dependence of the quantum yield of the photoreaction on the concentrations of the triplet energy donors and acceptors, as well as on the temperature of the solution.



The absence of an appreciable effect of quenchers of the triplet states on the kinetics of formation of the chromene (C) constitutes evidence that this reaction proceeds primarily through the S_1 state. At the same time, it is realized with appreciable efficiency also in the triplet state that is populated by means of a triplet energy donor. The activity of the T_1 state is also one of the reasons for the increase in the efficiency of the photoreaction when a heavy atom (Br) is included in the nitrone molecule (compare VI and IX and VII and VIII in Table 1).

The high reactivities of both lowest excited states that differ in multiplicity is characteristic for photo-trans-cis isomerization relative to the C=C bonds [6]. In fact, in the case under consideration the formation of the B_Z structure as a result of diabatic trans-cis-photoisomerization relative to the $C_{(1)}=C_{(2)}$ bond ($B_Z^{S_1} \rightarrow B_Z^{S_0}$) is a necessary step in the process involving the formation of cyclic chromene structure C. The energy of activation of the formation of structure C has a value on the

TABLE 1. Quantum Yields (Φ), Energies of Activation ($E_{h\nu}$) of the Photoreactions, Relative Fluorescence Quantum Yields (Φ_{fl}), and Energies of Activation of the Reverse Dark Processes (E_Δ) of o-Hydroxyaldonitrones

	Φ	Φ *	$E_{h\nu}$,	E_Δ,		Φ	Φ *	$E_{h\nu}$,	E_Δ,
V	0,42	0,25	0,57	17,4	IX	0,50	0,20	0,31	7,8
VI	0,45	0,25	0,37	13,8	XII	0,11	1	0,74	9,9
VII	0,37	0,30	0,63	8,7	XIII	0,20	0,45	0,98	7,5
VIII	0,56	0,20	0,30	8,9	XIV	0,29	0,35	0,84	5,1

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*The fluorescence quantum yields relative to XII are presented.

order of 10^{-1} kcal/mole (Table 1), which is characteristic for structural transformations that compete with processes involving deactivation of the S_1 state. This is expressed, in particular, in the antibatic dependence of the quantum yields of the photoreaction and fluorescence (with a large Stokesian shift), which is ascribable to the $B_Z^{S_1}$ structure, on the structural factors (Table 1). Thus the potential barrier that determines the rate of the photoreaction is located on the potential energy surface (PES) of the S_1 state at the coordinate of the diabatic stage of the reaction involving trans-cis isomerization relative to the $C_{(1)}=C_{(2)}$ bond ($B_Z^{S_1} \rightarrow B_Z$). All of the subsequent stages in the photoinitiated reaction take place in the ground state (Fig. 3); the $B_Z \rightarrow C$ cyclization process competes with the reaction involving s-trans-cis isomerization relative to the $C_{(2)}=C_{(3)}$ bond ($B_Z \rightarrow B_E$). In evaluating the energy of activation of the reverse dark process $C \xrightarrow{\Delta} A_{ZC}$, which is associated with the establishment of the starting (before irradiation) equilibrium of the isomeric structures we obtain values that are close to the values that are characteristic for processes involving thermal isomerization relative to the C=C bonds (10-20 kcal/mole) (Table 1).

From the point of view of the proposed structural-energic scheme the effect of the molecular structure on the efficiency of the photoreaction should be due primarily to a dependence on the structure of two factors, viz., the potential barrier of the diabatic $B_Z^{S_1} \rightarrow B_Z$ step and the efficiency of the processes involving deactivation of the S_1 state in the $B_Z^{S_1}$ structure (Table 1).

Thus, stabilization of the $B_Z^{S_1}$ structure by annelation of the aldehyde fragment (compare V and XII and VI and XIV) or by introduction of an N-alkyl substituent in place of an N-aryl substituent (for example, compare V and VI and VII) increases the energy of activation, thereby decreasing the efficiency of the photoreaction and increasing the fluorescence quantum yield.

The second factor is responsible for the observed absence of a strict correlation between the activation barrier and the efficiency of the photoreaction in the V-IX series, particularly XII and XIV. This may be associated (as for nitrones I-IV) with an increase in the efficiency of the intercombination (when a Br atom is introduced) or internal (when an N-phenyl radical is replaced by an N-alkyl radical) conversions, which substantially increase the rate of the nonemissive deactivation of the S_1 state, which competes with the photoreaction.

EXPERIMENTAL

The electronic absorption spectra were recorded with UV-vis and Specord M-40 spectrophotometers with an apparatus for a smooth change in the sample temperature. The fluorescene and fluorescence-excitation spectra (at 77-293 K) were recorded with a Fotolyum apparatus. The quantum yields of the photoreactions were calculated by the method in [7] using a ferrioxalate actinometer.

The conventional energies of activation of the photoreactions were calculated from the temperature dependence of the quantum yields (T 150-290 K), which were determined from the slopes of the kinetic curves at the start of the photoreactions. The sensitization and inhibition of the photoreactions using triplet-energy donors and acceptors were carried out in DMSO at T 293 K. Serving as a sensitizer, iodine–eosin (E_T = 174 kJ/mole, $\varphi_{SI} \approx 1.0$ [8], λ_{max}^{abs} 532 nm [9], c = 10^{-7}-10^{-5} mole/liter), satisfied the optimal conditions of sensitization of the photoreaction. 9-Anthraldehyde (E_T = 167 kJ/mole [10]), perylene, naphthacene, and oxygen (E_T = 150, 121, and 96 kJ/mole, respectively [8]; c = 10^{-6}-10^{-4} mole/liter) were used as quenchers of the triplet levels. The amount of dissolved oxygen was varied by bubbling argon through the solution and was monitored by a polarographic method.

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