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ARTICLE *in* THEORETICAL AND EXPERIMENTAL CHEMISTRY · JULY 1984

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MECHANISM OF THE PHOTOCHEMICAL MIGRATION OF THE ACETYL
GROUP IN PERIACETOXY DERIVATIVES OF 1,4- and 9,10-ANTHRAQUINONE

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UDC 541.143+547.673

Among the photochemical processes associated with the migration of individual groups, the reactions of phototransfer of a proton [1] or hydrogen atom [2, 3] have been studied in the greatest detail. Extremely little is known about processes of photochemical migration of heavy atomic groups. The phototransfer of an aryl group in the series of derivatives 1-aryloxy-9,10-anthraquinone has been investigated in the greatest detail [4-6].

Several cases of reversible phototransfer of an acetyl group of the type of $N \xrightleftharpoons[kT]{hv} O$ or

$O \xrightleftharpoons[kT]{hv} N$ are also known for certain heterocyclic compounds [7]. Irreversible migration of an acetyl group occurs in the photochemical reaction of Fries [8]. Recently [9] we were the first to establish a thermally reversible phototransfer of an acetyl group of the type of

$O \xrightleftharpoons[kT]{hv} O$ on the example of derivatives of periacetoxy-9,10- and 1,4-anthraquinones. The present work is devoted to an elucidation of the detailed mechanism of the photochemical and thermal migration of an acetyl group in a series of periacetoxy derivatives of 1,4- and 9,10-anthraquinone.

EXPERIMENTAL

Photolysis was investigated at the temperature of liquid nitrogen or argon by the method of low-temperature spectrophotometry according to the procedure of [2]. Products unstable at room temperature were recorded by the method of pulsed photolysis on a setup working in two systems: with electrical energy of the flash 100 J, duration 2 μ sec, and 1000 J, with duration 15 μ sec. The quantum yields of the formation of unstable compounds were estimated on a pulse photolysis setup. The reversible reaction of photoenolization of 1-methylantraquinone with quantum yield 0.8 ± 0.2 was used as the actinometric reaction [2]. The portion 280-330 nm was isolated from the spectrum of the pulse lamp by a combination of a UFS-2 glass filter and a liquid filter of a saturated aqueous solution of $NiCl_2$.

Quantum-chemical calculations of the absorption spectra were performed by the PPP method in the "variable β " approximation [10, 11]. To calculate the properties of the molecules in the ground state we used the PPP method with Dewar parametrization [12, 13]. The bond length and two-center integrals for neighboring atoms were varied at each step of the iteration process. The calculation algorithm was described in [14]. The method of correlation diagrams was used for the interpretation of the experimental results [15].

RESULTS

Recently [9] we found that in low-temperature photolysis of certain methoxy- and amino-derivatives of 1-acetoxy-9,10-anthraquinone, as well as 9-acetoxy-1,4-anthraquinone, containing no substituents, products are formed, in the absorption spectra of which a substantial (110-220 nm) bathochromic shift of the long-wave maximum is observed in comparison with the spectrum of the initial compounds. In this work we investigated compounds I-XII, the absorption spectra of which are cited in Table 1. As an example, Fig. 1 presents the change in the

Institute of Chemical Kinetics and Combustion, Siberian Branch, Academy of Sciences of the USSR. Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Novosibirsk. Translated from *Teoreticheskaya i Eksperimental'naya Khimiya*, Vol. 19, No. 4, pp. 455-462, July-August, 1983. Original article submitted October 18, 1982.

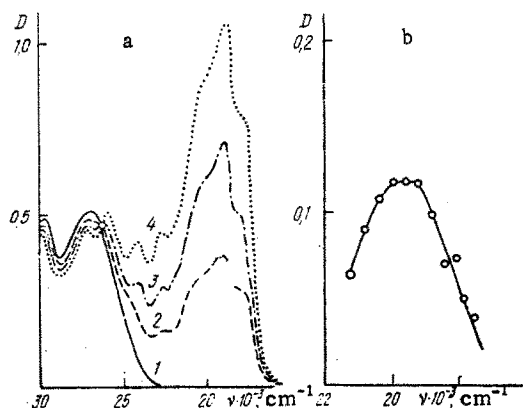


Fig. 1. a) Optical absorption spectrum of 1-acetoxy-2-methoxy-9,10-anthraquinone (1) in ethanol at 77°K and its change under irradiation by a DRSh-500 lamp through UFS-2 filter for: 2) 3 sec; 3) 12 sec; 4) 10 min ($C = 5.3 \cdot 10^{-4}$ M, $l = 0.15$ cm), b) absorption spectrum of an unstable product in the case of pulse excitation of 1-acetoxy-2-methoxy-9,10-anthraquinone in toluene at room temperature ($C = 10^{-4}$ M).

absorption spectrum of 1-acetoxy-2-methoxy-9,10-anthraquinone (II) in ethanol at 77°K in the course of irradiation. In the absorption spectrum of the product an intense long-wave band with $\lambda_{\max} = 19,000 \text{ cm}^{-1}$ (526 nm) appears. Analogous spectra changes also occur in the low-temperature irradiation of 1-acetoxy-4-methoxy- and 1-acetoxy-2-dimethylamino-9,10-anthraquinones (IV, V). Such spectra changes are characteristic of photoprocesses with the formation of 1,10-anthraquinone (ana-quinone) derivatives as the photoinduced form; moreover, the absorption spectra of the photoproducts (IIa, IVa, Va) are similar to the spectra of the corresponding derivatives of 9-aryloxy-1,10-anthraquinone [5, 6] (Table 1). During the thawing of

TABLE 1. Experimental and Calculated Values of the Maxima of the Long-Wave Bands in the Absorption Spectra of Derivatives of 1-Acetoxy-9,10-anthraquinone (I-XI), 9-Acetoxy-1,4-anthraquinone (XII), Products of Their Photolysis at 77°K, and Photoinduced Forms of Derivatives of 1-Phenoxy-9,10-anthraquinone

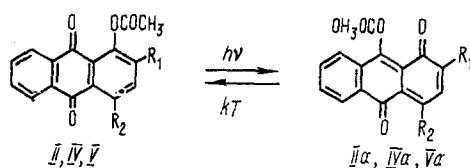
No.	Substituent	Initial compound		Photoinduced form		ΔE_{theor} , kJ/mole	$\lambda_{\text{exp}}^{\text{max}}$, nm (for photoinduced forms of derivatives of 1-phenoxy-9,10-anthraquinone)
		$\lambda_{\text{exp}}^{\text{max}}$, nm ($\log \epsilon$) [*]	$\lambda_{\text{exp}}^{\text{theor}}$, nm	$\lambda_{\text{exp}}^{\text{max}}$, nm	ϵ , liters/mole-cm		
I	—	330 (3.77)	335	—	—	74.2	480
II	2-OCH ₃	374 (3.80)	345	526	$1.1 \cdot 10^4$	72.5	506
III	2-OCOCH ₃	331 (3.78)	339	—	—	65.4	483
IV	2-N(CH ₃) ₂	463 (3.70)	356	683	—	71.0	641
V	4-OCH ₃	402 (3.78)	411	510	$0.95 \cdot 10^4$	72.9	490
VI	4-OCOCH ₃	340 (3.77)	350	—	—	—	—
VII	4-NHC ₆ H ₁₁	527 (3.90)	—	—	—	71.3	621
VIII	5-OH	340 (3.77)	350	—	—	73.8	477
IX	5-OCOCH ₃	342 (3.76)	351	—	—	74.6	—
X	8-OH	340 (3.72)	350	—	—	—	—
XI	8-OCOCH ₃	338 (3.78)	—	—	—	—	—
XII	—	410 (3.72)	400	468	$1.0 \cdot 10^4$	21.5	—

* ϵ is the coefficient of extinction at the maximum; ΔE_{theor} is the theoretical estimate of the energy difference of the ground states of the initial compounds I-XII and products of photochemical migration of the acetyl group Ia-XIIa.

TABLE 2. Values of the Rate of Constants of the Dark Migration of an Acetyl Group and Quantum Yields of Photolysis in Benzene at 285°K

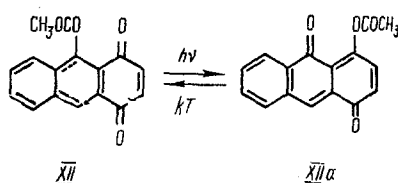
Compound	K, sec^{-1}		φ
	benzene	isopropanol	
II	$2.5 \cdot 10^5$	$2.9 \cdot 10^5$	≈ 0.3
IV	$6.2 \cdot 10^4$	$9.1 \cdot 10^4$	—
V	—	$3.1 \cdot 10^5$	≈ 0.4
XII	$3.1 \cdot 10^3$	$5.0 \cdot 10^3$	1.0 ± 0.2

the samples irradiated at 77°K, the initial compounds II, IV, and V are formed, respectively. The action of light with $\lambda \geq 400$ nm does not produce any changes in the spectrum of the photoinduced form (compounds IIa, IVa, Va). Consequently, the process discussed can be described by the scheme:



(II, IIa — $R_1 = \text{OCH}_3$, $R_2 = \text{H}$; IV, IVa — $R_1 = \text{N}(\text{CH}_3)_2$, $R_2 = \text{H}$; V, Va — $R_1 = \text{H}$, $R_2 = \text{OCH}_3$). The detected transfer of an acetyl group, including photo and dark processes, is entirely reversible, can be multiply repeated, and therefore represents a new photochrome conversion.

In addition to compounds II, IV, and V, we subjected unsubstituted 1-acetoxy-9,10-anthraquinone (I) and a number of its derivatives with substituents in the 2,4,5, and 8-positions (compounds III, VI-XI; Table 1) to prolonged irradiation at 77°K. Not one of these compounds isomerizes during prolonged irradiation with light of a DRSh-500 lamp. At the same time, in the irradiation of 9-acetoxy-1,4-anthraquinone (XII), compound (XIIa), possessing the absorption spectrum characteristic of 1,10-anthraquinone derivatives, is formed (Fig. 2). Reversion to the initial compound XII also occurs only when the matrix is heated:



From Fig. 2 it can be seen that in the course of irradiation of compound XII, certain characteristic bands in its UV spectrum disappear (for example, $\nu_{\text{max}} 42,500 \text{ cm}^{-1}$, 3400 cm^{-1}). Consequently, the process occurs to profound degrees of conversion, which permits an estimation of the coefficients of extinction of XIIa with satisfactory accuracy. An analogous disappearance of the characteristic bands occurs in the photolysis of compounds II and V. Estimates of the coefficients of extinction at the maxima of the long-wave bands in the spectra of compounds IIa, Va, and XIIa are cited in Table 1.

In the case of pulse excitation of compounds possessing a photoinduced form at 77°K (II, IV, V, and XII), the formation of unstable products with absorption spectra identical with the spectra of the corresponding low-temperature products was recorded (Figs. 1b, 2c). The formation of these products was detected in solvents of various kinds, for example, in alcohols and benzene. The kinetic curves of the drop in the absorption of the intermediate products are described by an exponential time dependence. The first-order constants, obtained from the experimental data, are cited in Table 2. The values of the constants do not depend on the oxygen content in solution, within the limits of the experimental accuracy ($\sim 10\%$), and they depend weakly on the polarity of the medium (Table 2). In the case of stationary irradiation of the compounds under consideration (with the exception of IV), irreversible destruction occurs slowly.

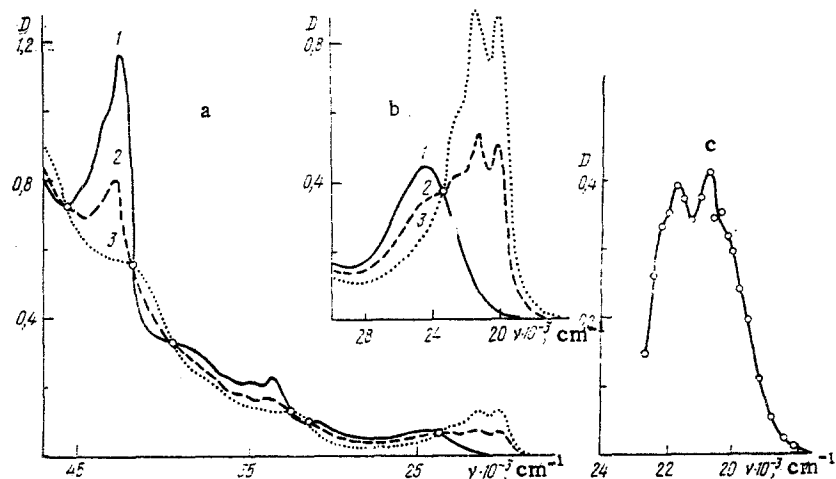


Fig. 2. Absorption spectrum of 9-acetoxy-1,4-anthraquinone in ethanol at 77°K (1) and its change in the course of irradiation with a DRSh-500 lamp through a UFS-2 filter for: 2) 3 sec; 3) 6 min; a) $C = 9 \cdot 10^{-3}$ M, $l = 0.15$ cm; b) $C = 5.5 \cdot 10^{-4}$ M, $l = 0.15$ cm; c) absorption spectrum of an unstable product in pulse excitation of 9-acetoxy-1,4-anthraquinone in benzene at room temperature ($C = 10^{-4}$ M).

In the case of stationary irradiation of compound I in alcohols at room temperature in the absence of oxygen, a compound with the spectrum characteristic of 9,10-anthrahydroquinone and its derivatives [16] is formed with a high quantum yield. In pulse excitation of compound I, as well as compounds III, VI-XII, which do not possess a photoinduced form at 77°K, the formation of unstable products absorbing in the visible region of the spectrum was not recorded in benzene at room temperature. In the case of pulse excitation of I in isopropanol, an intermediate product with spectrum similar to the spectrum of the anthrasemiquinone radical [17] was recorded. The characteristic time of conversion of this product depends on the oxygen concentration and is equal to 125 μ sec at the normal content of O_2 and 750 μ sec after bubbling of Ar through the solution. Consequently, in the photolysis of 1-acetoxy-9,10-anthraquinone in alcohols, the reaction of stripping of a hydrogen atom from the solvent typical of 9,10-anthraquinone and some of its derivatives [16, 17] occurs.

Thus, in the case of irradiation of 9-acetoxy-1,4-anthraquinone and 2-methoxy-2-dimethylamino-, 4-methoxy-derivatives of 1-acetoxy-9,10-anthraquinone, a thermally reversible phototransfer of an acetyl group is observed. Analogous photoconversions of 1-acetoxy-9,10-anthraquinone and some of its derivatives (2-, 4-, 5-, and 8-acetoxy-, 5-, and 8-hydroxy-, and 4-cyclohexylamino-) were not recorded.

DISCUSSION OF THE EXPERIMENTAL RESULTS

The main purpose of this work was to establish the mechanism of the photochemical conversions of the investigated acetoxy derivatives of para-anthraquinones and to explain the dependence of the photochemical behavior on the chemical structure. However, a preliminary interpretation of the spectrum, as well as a determination of the nature and position of the lower excited states of these compounds, were necessary. In the interpretation of the experimental data, we used the results of quantum-chemical calculations. Table 1, for example, cites the calculated values of the positions of the maxima of the long-wave bands of the $\pi\pi^*$ -type (for $la_{\pi\pi^*}$ -type), on the assumption that the fragment $-O-C=O$ lies in the plane of the rings and participates in conjugation with them. The results of the calculation are in good agreement with the experiment in all cases, with the exception of II and IV. For compounds II and IV the discrepancy is evidently due to steric hindrances, which disrupt the coplanar structure of the $-O-C=O$ fragment. The substituents in these compounds are in the neighboring 1- and 2-positions. Let us note that the calculation renders all the peculiarities of the influence of the acetoxy group. For example, the introduction of an acetoxy group into the anthraquinone molecule has practically no effect on the spectrum of 9,10-anthraquinone. In the spectrum of 1-hydroxy- and 1-methoxy-9,10-anthraquinone (λ_{max} 415 and 397 nm, respective-

TABLE 3. Theoretical Estimates of the Position of the Excited Singlet State of the $n\pi^*$ Type (O-O Transition) of Compounds I-XII

Compound	$\frac{E_{n\pi^*}}{hc} \cdot 10^{-3}, \text{cm}^{-1}$		Compound	$\frac{E_{n\pi^*}}{hc} \cdot 10^{-3}, \text{cm}^{-1}$	
	starting material	photoinduced form		starting material	photoinduced form
I	23,5	22,5	VII	23,7	22,8
II†	23,9	22,6	VIII	23,6	22,5
III	23,6	22,2	IX	23,3	22,2
IV	23,8	22,7	X	23,6	—
V	23,6	22,6	XI	23,3	—
VI	23,3	—	XII	23,2	22,4

†In 1-acetoxy-2-methoxy-9,10-anthraquinone the states $^1\lambda_{\pi\pi^*}$ and $^1n\pi^*$, according to the estimates, are very close in energy ($\Delta E \approx 100 \text{ cm}^{-1}$).

ly), the introduction of an acetoxy group causes a change that depends greatly on its position relative to the hydroxy (methoxy) group (V, VIII, X).

A construction of the diagrams of the energy levels of the investigated compounds (Figs. 3-6) was performed as follows. 1. The position of the $^1\pi\pi^*$ ($^1\lambda_{\pi\pi^*}$) levels was estimated from the absorption spectra, assuming that the O-O band lies approximately 2800 cm^{-1} below the maximum in the absorption spectrum. This value is typical of 9,10-anthraquinone and some of its derivatives [18]. 2. The energy of the $^1n\pi^*$ state ($E_{n\pi^*}$) for 9,10-anthraquinone is defined by using the experimental value of $E_{n\pi^*}$ for 9,10-anthraquinone, equal to $23,800 \text{ cm}^{-1}$ [18], and the linear correlation ratio between the energy of the $n\pi^*$ level and the calculated value of the energy of the first excited orbital of the π^* type [19] (theoretical estimates of $E_{n\pi^*}$ for a number of anthraquinone derivatives are cited in Table 3). 3. Singlet-triplet splitting between states of the $n\pi^*$ type was assumed equal to $\sim 2000 \text{ cm}^{-1}$ [18]. 4. In the construction of the energy diagrams for hypothetical products (Ia, IIIa, VIa-XIa), the experimental absorption spectra of the corresponding derivatives of 9-phenoxy-1,10-anthraquinone were used [5, 6] (Table 1). 5. The energy difference of the ground states of the starting materials and reaction products was calculated quantum chemically.

From the energy diagrams constructed in this way, it follows that in compounds that isomerize under the action of light to the corresponding anthraquinones, the lower excited states are the states of the $\pi\pi^*$ (XII) or $\lambda_{\pi\pi^*}$ (II, IV, V) type (see for example, Fig. 3). For the remaining compounds investigated (with the exception of VII) evidently states of the $\pi\pi^*$ type are the lower excited states. From Table 1 it follows that the position of the long-wave band of the $\pi\pi^*$ type in these compounds is close to the value for 9,10-anthraquinone (330 nm). Therefore we should expect that the structure of the levels in these compounds and in 9,10-anthraquinone is the same (Fig. 4).

The observed relationship of the reactivity to the type of the lower excited state can be explained using the method of correlation diagrams [15] (see Figs. 3-6). The states of the initial compound and photoproduct with the same number of σ - and π -electrons are correlated with one another. Such an approach is analogous to the concepts of Woodward and Hoffman on the conservation of orbital symmetry in the course of the reaction [20]. The only element of symmetry preserved in the course of the migration of the acetyl group is the plane of the aromatic rings. The wave functions of the σ -electron are symmetrical with respect to this plane, while those of the π -electrons are antisymmetrical. Therefore, in the course of migration of the acetyl group the excited state of the $\pi\pi^*$ ($\lambda_{\pi\pi^*}$) type of the initial compound is correlated with the excited state of the $\pi\pi^*$ ($\lambda_{\pi\pi^*}$) type of the reaction product. In this case the zwitterion state Z [15], which is realized in the case of migration of an acetyl group in the cationic form, is transitional. The possibility of migration of an acetyl group in the form of a cation is confirmed by the results of a calculation of the distribution of electron density on the reaction site. From the calculation it follows that a positive charge of +0.32 is localized on the carbon atom of the acetyl group in the initial state, while a negative charge of -0.5 is localized on the quinoid oxygen. The possibility of an adiabatic photochemical migration of an acetyl group in compounds XII and V is illustrated by the correlation diagrams cited in Figs. 3 and 5. It can be seen that the lower excited state of the reaction product of the $\pi\pi^*$ type lies lower in energy than the reaction state of the initial compound. Let us note that the photochemical reactions of proton transport along a hydrogen

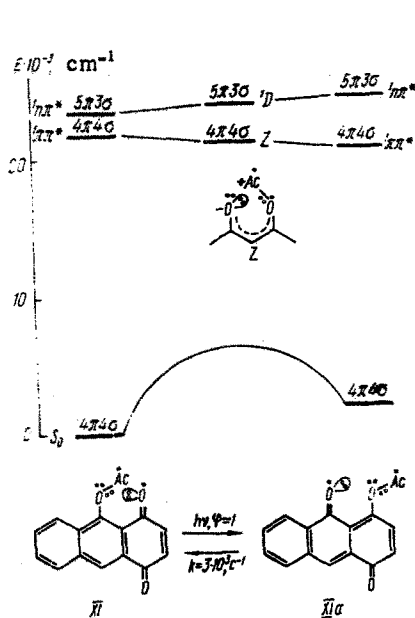


Fig. 3

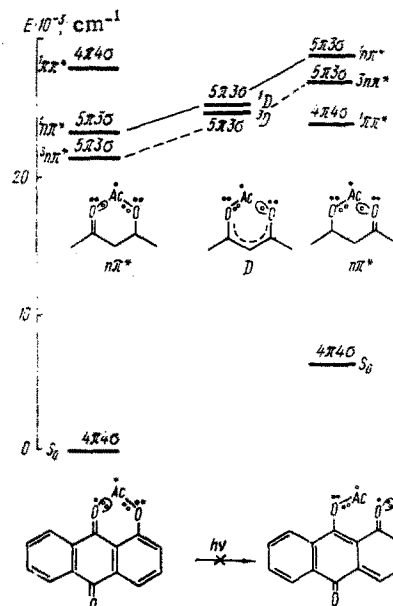


Fig. 4

Fig. 3. Correlation diagram for the process of photochemical migration of an acetyl group in 9-acetoxy-1,4-anthraquinone (electrons of the π (●) and σ (○) types, localized on the reaction site).

Fig. 4. Correlation diagram for the hypothetical process of migration of an acetyl group in 1-acetoxy-9,10-anthraquinone (electrons of the π (●) and σ (○) types, localized on the reaction site).

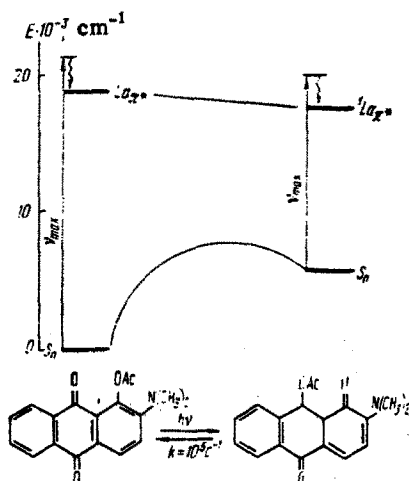


Fig. 5

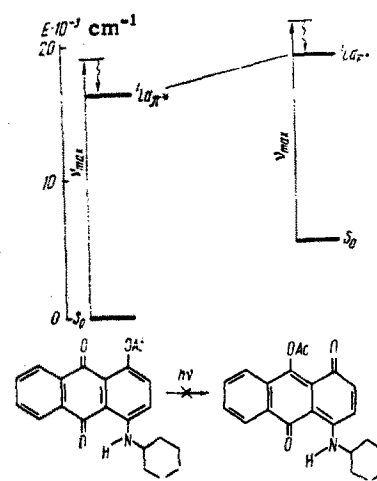


Fig. 6

Fig. 5. Correlation energy diagram for an adiabatic photochemical process of migration of an acetyl group in 1-acetoxy-2-dimethylamino-9,10-anthraquinone.

Fig. 6. Correlation diagram for a hypothetical process of photochemical migration of an acetyl group in 1-acetoxy-4-cyclohexylamino-9,10-anthraquinone.

bond should be described by a similar diagram. Actually, these processes usually occur from a single excited state of the $\pi\pi^*$ type, with preservation of the excitation [1].

If the reaction state in the photochemical migration of an acetyl group were a state of

the $n\pi^*$ type, it would be correlated with an excited state of the reaction product also of the $n\pi^*$ type. However, from Fig. 4 it can be seen that the state of the $n\pi^*$ type of the hypothetical product of the photochemical reaction of 1-acetoxy-9,10-anthraquinone lies higher in energy than in the original compound. Consequently, in this case an adiabatic process is impossible. The probability of a nonadiabatic channel of the reaction, however, is low. For the same reason, the remaining (with the exception of VII) investigated derivatives of 1-acetoxy-9,10-anthraquinone also do not isomerize. In 1-acetoxy-4-cyclohexylamino-9,10-anthraquinone (VII), the lower excited state is a state of the $\lambda a_{\pi\pi^*}$ type. However, in this case (Fig. 6) the excited state of the reaction product correlated with it lies higher in energy, and an adiabatic process is energetically prohibited.

Let us note that we did not establish multiplicity of the reaction state. Only the positions of the singlet excited states of the $\pi\pi^*$ type are cited on the correlation diagrams (Figs. 3-6). However, it is known that the singlet-triplet splitting of states of the $\pi\pi^*$ (or $\lambda a_{\pi\pi^*}$) types in anthraquinone derivatives are close and come to an average of 6000 cm^{-1} [21]. It can be assumed that the relative position of the triplet states for the investigated compounds did not differ from the relative positions of the singlet states cited above (see, for example, Figs. 4-6).

Thus, in the periacetoxy derivatives of 1,4- and 9,10-anthraquinones that we investigated, three situations are realized, differing in the type of excited reaction state and relative position of the levels of the initial compound and the product of its photochemical reaction.

1. The lower excited state of the $\pi\pi^*$ ($\lambda a_{\pi\pi^*}$) type is correlated with the state of the reaction product, which lies at a lower energy. In this case an adiabatic photochemical migration of an acetyl group occurs with a high quantum yield (Table 2).
2. A state of the $\lambda a_{\pi\pi^*}$ type, correlated with a state of the reaction product lying higher in energy, is also the lower excited state.
3. The absorption spectra of acetoxy derivatives of 9,10-anthraquinone differ slightly from the spectrum of unsubstituted 9,10-anthraquinone. The lower excited state in this case is evidently a state of $n\pi^*$ type, which is correlated with a state of the same nature, lying higher in energy, as a result of which photochemical migration of the acetyl group does not occur. At room temperature 9,10-acetoxy derivatives of 9,10-anthraquinone are capable of a photochemical reaction of stripping of a hydrogen atom from the solvents, which usually occurs in a state of the $n\pi^*$ type.

The authors would like to express their gratitude to N. M. Bazhin and E. P. Fokin for their useful discussions.

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MODEL OF REACTIONS OF COMPLEX FORMATION BY METAL SALTS WITH ELECTRICALLY NEUTRAL LIGANDS GRAFTED TO A SURFACE

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UDC 541.49:541.183

Complex formation by metal ions with donor atoms on the surface of a solid or a polymeric matrix is obviously a phenomenon encountered just as widely in nature as complex formation in solutions. In connection with the synthesis of new modified supports (porous and non-porous) containing grafted ligands of various types, knowledge of the relationships governing complex formation on surfaces takes on great practical importance, for example in the concentration and separation of metal ions, the synthesis and application of grafted (heterogenized) metal-complex catalysts, and many other fields.

Thus far, attempts at quantitative description of the equilibria of complex formation on the surface of a support when metal salts are sorbed from solution have been based on use of the law of mass action in its conventional form, describing the equilibria of complex formation in solution [1, 2]:



$$\beta_n = [MR_n]/[M][R]^n, \quad (2)$$

where $[M]$ is the equilibrium concentration of the metal ion in solution, in units of moles/dm³; $[R]$ and $[MR_n]$ are the respective concentrations of the grafted ligand and the grafted complex, expressed in this case in the same units of moles/dm³ and referred to the total volume of the suspension.* The charges on M , R , and MR_n have been omitted in Eqs. (1) and

*Since the volume of the support usually makes up a very small fraction of the total volume of the suspension, the volume of the solution is often taken as total volume of the suspension.

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