EFFECT OF TEMPERATURE, MEDIUM, AND NATURE OF SUBSTITUENTS ON THE THERMAL STAGE IN THE PHOTOCHROMIC TRANSFORMATIONS OF 1-METHYLANTHRAQUINONE DERIVATIVES

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UDC 514.12.036:541.12.038:541.14:547.673

In [1] it was shown that the initial stage in the photolysis of 1-methylanthraquinone (I) is removal of a hydrogen atom from the methyl group and its transfer to the quinonoid oxygen atom. The obtained 9-hydroxy-1,10-anthraquinone-1-methide (Ia) is unstable at room temperature; the initial structure is reestablished under dark conditions. The rate of the dark stage depends on the solvent, the temperature, and the nature of the substituents introduced into the initial compound. The aim of the present work was to investigate the effect of the above-mentioned factors on the kinetics of the dark stage in the photochromic transformations of 1-methylanthraquinone in detail.

EXPERIMENTAL

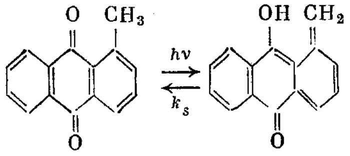
The kinetic curves for the transformation of the products from photolysis of (I) and its derivatives were recorded by the flash photolysis method. The apparatus was described in [1]. The absorption of the unstable products was recorded at 560 or 500 nm (in the case of 1-hydroxy-4-methylanthraquinone). The cuvette containing the sample was thermostated with an accuracy of 0.1°C by means of a U-8 thermostat in the range of 40-95°C.

Solvents of chemical purity or very special purity were used without additional purification. Argon was bubbled into the solution for 15-20 min in order to remove oxygen.

The calculations of the distribution of π-electron densities and determination of the energy characteristics of the substituted anthraquinones and their photolysis products were realized by the PPP method in the "variable β" approximation [2-4].

DISCUSSION OF RESULTS

According to [1], the cycle of photochromic transformations in 1-methylanthraquinone is described by the following scheme:



(I) (Ia)

The kinetic curves for the transformations of the products from photolysis of the 1-methylanthraquinone derivatives into the initial compounds in oxygen-free solutions obey a first-order law under all the experimental conditions (at various temperatures, in various solvents, and for all substituents). Consequently, the dark stage of the photochromic cycle can be described by a first-order rate constant k_s.

As seen from Table 1, with the exception of 1-hydroxy-4-methylanthraquinone which requires special treatment, the variations in k_s are small. It is, however, possible to trace the reason giving rise to these variations. The effect of the substituents is due to a change in the π-electron density at the carbon atom of the methide group. The introduction

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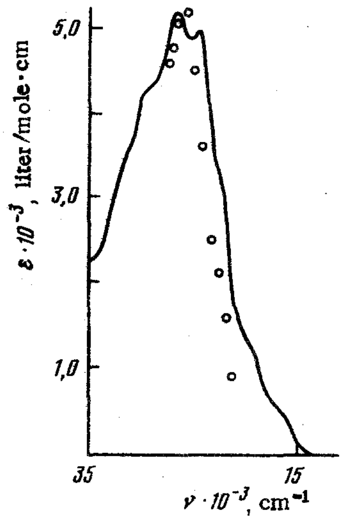


Fig. 1

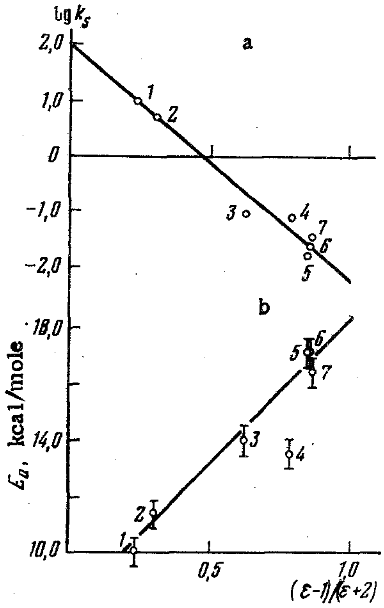


Fig. 2

Fig. 1. The experimental spectra of the product from photolysis of 1-hydroxy-4-methylanthraquinone at 77°K and at room temperature (points).

Fig. 2. The dependence of log k_s (298°K) (a) and of the activation energy (b) of the dark stage in the photochromic transformations of 1-hydroxy-4-methylanthraquinone on a function of the dielectric constant: 1) heptane; 2) benzene; 3) ethyl acetate; 4) pyridine; 5) isopropyl alcohol; 6) isobutyl alcohol; 7) acetone.

of the cyclohexyl substituent, which has a positive inductive I_π effect, gives rise to an increase in the π-electron density at the carbon atom of the methide group. This leads to a gain in the energy of electrostatic interaction between the proton of the hydroxy group and this carbon atom and, as a result, to an increase in the rate constant k_s. On the other hand, according to the calculations, in the methoxy derivative (III) the electron density at the carbon atom of the methide group decreases, and the k_s constant decreases. A correlation between the k_s constants and the π-electron densities is also observed for other substituents (Table 1).

The introduction of a hydroxy group leads to a decrease of 10^6 times in k_s, and this cannot be explained from the standpoint of the ideas set out above about the effect of substituents on the k_s constant, for the effect of hydroxy and methoxy groups should be approximately the same.

TABLE 1. The Dependence of the Rate Constant k_s of the Dark Stage in the Photochromic Transformations of 1-Methylanthraquinone Derivatives on the Charge at the Carbon Atom of the Methide Group [$q_C(CH_2)$] (290°K, isopropanol)

Compound	Substituent	k_s, sec^{-1}	$q_C(CH_2)$
(I)	Without substituent	$6{,}00\cdot10^3$	$-0{,}051\equiv\delta_0$
(II)	3-(1-Cyclohexenyl)	$8{,}35\cdot10^3$	$-0{,}052$
(III)	4-Methoxy	$4{,}55\cdot10^3$	$-0{,}045$
(IV)	3-Cyclohexyl	$1{,}15\cdot10^4$	$\delta<\delta_0$
(V)	3-(2-Nitro-1-cyclohexenyl	$3{,}80\cdot10^3$	$\delta>\delta_0$
(VI)	4-Cl	$1{,}05\cdot10^4$	
(VII)	4-Hydroxy	$7{,}60\cdot10^{-3}$	$-0{,}045$

TABLE 2. The Activation Energies and Preexponential Factors of the Rate Constants for the Dark Stage k_S in the Photochromic Transformations of 1-Methylanthraquinone Derivatives

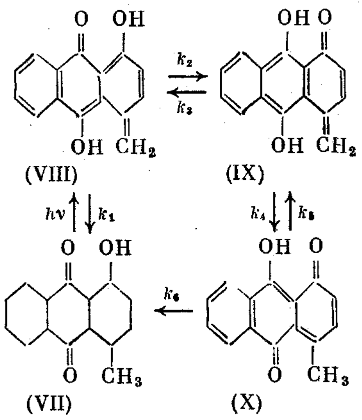
Compound	Substituent	Solvent	k_0, sec^{-1}	E_a, kcal/mole	k_s (298K), sec^{-1}
(I)	Without substituent	Isopropyl alcohol	$7{,}2 \cdot 10^{11}$	$10{,}0 \pm 0{,}25$	$1{,}55 \cdot 10^4$
(II)	Methoxy	"	$2{,}5 \cdot 10^{11}$	$10{,}3 \pm 0{,}25$	$8{,}00 \cdot 10^3$
(VIII)	Hydroxy	"	$5{,}1 \cdot 10^{10}$	$17{,}1 \pm 0{,}5$	$1{,}80 \cdot 10^{-2}$
		Isobutyl alcohol	$7{,}4 \cdot 10^{10}$	$17{,}1 \pm 0{,}5$	$2{,}50 \cdot 10^{-2}$
		Acetone	$3{,}7 \cdot 10^{10}$	$16{,}4 \pm 0{,}5$	$3{,}70 \cdot 10^{-2}$
		Pyridine	$6{,}2 \cdot 10^8$	$13{,}5 \pm 0{,}5$	$8{,}60 \cdot 10^{-2}$
		Ethyl acetate	$1{,}6 \cdot 10^9$	$14{,}0 \pm 0{,}5$	$9{,}80 \cdot 10^{-2}$
		Benzene	$9{,}6 \cdot 10^8$	$11{,}4 \pm 0{,}5$	$5{,}45$
		Heptane	$2{,}9 \cdot 10^8$	$10{,}1 \pm 0{,}5$	$1{,}05 \cdot 10$

In the case of compound (VII), in addition to the initial stage of the transfer of a hydrogen atom from the CH_3 group, leading to the formation of 4,9-dihydroxy-1,10-anthraquinone-1-methide (VIII), the photolysis mechanism also includes a dark stage of the transfer of the hydrogen atom of the hydroxy group in a hydrogen bond. The final product from such a transformation is 9,10-dihydroxy-1,4-anthraquinone-1-methide (IX). The higher stability of compound (IX) compared with (VIII) may be the reason for the anomalously low value of k_S.

It must be supposed that the formation of (IX) also occurs even at 77°K, since the spectrum of the products from the photolysis of compound (VII) at 20°C (Fig. 1) is close to the spectrum of the product from photolysis at 77°K.

The proposed mechanism is favored by an analysis of the experimental and calculated absorption spectra for the products from photolysis of compounds (I-VII). The spectrum of the products from photolysis of (VII) differs from the similar spectra of the products from photolysis of compounds (I-VI) and agrees better with the calculated spectrum of structure (IX) than of (VIII). In addition, from quantum-chemical calculations it follows that the structure (IX) is highly favorable energetically compared with structure (VIII). Thus, in combination these data indicate that (IX) is formed during the photolysis of compound (VII).

A fundamentally possible scheme for the photochromic transformations in compound (VII) at ∿20°C is given below:



The initial photochemical stage is the formation of 4,9-dihydroxy-1,10-anthraquinone-1-methide (VIII), which isomerizes to 9,10-dihydroxy-1,4-anthraquinone-1-methide (IX). The reverse thermal transition from (IX) to (VII) may be realized in two ways.

The temperature dependence of the rate constant for the dark stage k_S was investigated for compounds (I) and (III) in isopropyl alcohol and for (VII) in a large number of solvents with various characteristics. In all cases the variation of the rate constants k_S in the experimental temperature range fits well into the Arrhenius curve. As seen from Table 2, a compensation effect is observed for compound (VII) in the series of solvents, leading to the result that the rate constant only changes by three orders of magnitude with change in the activation energy by 7 kcal/mole in the transition from hexane to isopropanol. The effect of the solvent on the rate constant may be due to nonspecific electrostatic interaction and also to the formation of a hydrogen bond. In order to determine the character of the effect of the medium on the rate of the dark stage we used a series of solvents with various dielectric constants ε and various proton-accepting abilities. The effect of ε on the reaction rate is described within the scope of transition state theory [5]:

$$\lg k_s = \lg k_g - (\varepsilon_S^{\neq} - \varepsilon_{sr})/2{,}3\,RT$$

where $\varepsilon_S^{\neq}$ is the free energy of solvation of the transition state, and ε_{sr} is the free energy of solvation of the reagent. The values of $\varepsilon_S^{\neq}$ and ε_{sr} can be calculated by means of the Onsager—Böttcher model [6]:

$$\varepsilon_S = \varepsilon_L + \varepsilon_D - {}^1/_2\, f\vec{\mu}\,(1 - f\alpha)^{-1}\,\vec{\mu}$$

where ε_L is the energy of formation of a cavity; ε_D is the energy of dispersion interactions; $\vec{\mu}$ is the dipole moment; α is the polarizability; $f = 2/a^3(\varepsilon - 1)/(2\varepsilon + 1)$; a is the dimension of the Onsager sphere. The variation of ε_L and ε_D during the reaction can be disregarded. The main contribution then comes from interactions of the orientation—induction type. If it is supposed that $\alpha = a^3/2$ [7]

$$\varepsilon_S^{\neq} - \varepsilon_{sr} = -1/a^3\,\frac{\varepsilon - 1}{\varepsilon + 2}\,\{(\mu^{\neq})^2 - (\mu_r)^2\}$$

Thus, if nonspecific interactions have a predominating effect on the rate constant k_S, a linear relation can be expected between log k_S and the parameter $(\varepsilon - 1)/(\varepsilon + 2)$. An appreciable deviation from this relationship must be expected if the medium has a significant nonspecific effect (e.g., with the formation of strong hydrogen bonds).

An experimental investigation into the effect of the medium on the dark stage was undertaken for the products from the photolysis of compound (VII), since it was in this case possible to study the reaction over a wide range of ε values and temperature. A special feature of the system is the possibility of reaction along two channels through two stages (see the scheme). Experimental investigation of the reaction in various media showed that there is a satisfactory linear correlation between log k_S (298°K) and $f(\varepsilon) = (\varepsilon - 1)/(\varepsilon + 2)$ (Fig. 2). There is an analogous correlation between E_a and $f(\varepsilon)$. It should be noted that anomalously small values for the rate constant are not observed even when the reaction is carried out in a solution of a strong proton acceptor (pyridine). This fact and also the presence of a satisfactory linear correlation favors the suggestion that the nonspecific effect of the solvent on the process rate makes a predominating contribution.

It seemed of interest to discuss the mechanism of the investigated dark reaction in the product from the photolysis of compound (VII). As already mentioned, the transformation from (IX) to (VII) can be realized in two ways. In this case the effective rate constant is given by:

$$k_{\text{eff}} = k_1k_3/(k_1 + k_2) + k_6k_4/(k_5 + k_6)$$

The main contribution to k_{eff} evidently comes from a process occurring according to the scheme (IX)$\rightleftharpoons$(VIII)$\rightarrow$(VII). In order to substantiate this suggestion we will examine the transformation of compound (IX) in greater detail. The energies of the π bonds in structures (VII-X) were calculated by quantum-chemical methods. In the calculation of the energies of the σ bonds the following assumptions were made: a) the energies of the σ bonds in (VIII) and (IX) are equal; b) the energies of the σ bonds in (VII) and (X) are also equal and are 8 kcal/mole higher than the energies of the σ bonds in compounds (VIII) and (IX). This value corresponds to the difference between the experimental energies of the O—H and C—H bonds in phenol and methylnaphthalene [8, 9]. If only the energies of the bonds are taken into account, this leads to the conclusion that the two channels for the transformations from (IX) to (VII) are equivalent in energy. However, allowance for the energies of the σ bonds shows that the transition from the state (IX) to (VII) through (X) requires a higher activation energy compared with the channel described by the scheme (IX)$\rightleftharpoons$(VIII)$\rightarrow$(VII). Thus, the dark stage probably goes through state (VIII). Within the scope of this supposition $k_{\text{eff}} = k_1k_3/(k_1 + k_2)$. At 77°K, $k_2 \gg k_1$, since the process (VIII)$\rightarrow$(IX) occurs, whereas the process analogous with (VIII)$\rightarrow$(VII) does not occur for compounds (I-VI). Evidently, $k_2 \gg k_1$ also at normal temperatures. In this case $k_{\text{eff}} = k_1k_3/k_2$. If it is assumed that the k_1 value is equal to k_S for compound (III), it is possible to determine the constant of the equilibrium (VIII)$\rightleftharpoons$(IX). As follows from Table 2, $k_3/k_2 = 0.2\cdot\exp[-(6800 \pm 750)/RT]$. The ΔH value of 6.8 kcal/mole obtained from experiment agrees well with the difference of 6.04 kcal/mole in the energies of the π bonds of (VIII) and (IX), calculated by the quantum-chemical method. Such agreement confirms the validity of the assumption made about the mechanism of the transformations from compound (IX) to the initial compound (VII).

CONCLUSIONS

1. The effect of substituents on the rate constant and activation energy of the dark stage in the photochromic transformations of 1-methylanthraquinone derivatives was studied. It was found that there is a correlation between the π-electron density at the carbon atom of the methide group and the rate constant.

2. A quantum-chemical calculation of the rate constant for the dark stage of the process was made on the basis of the proposed mechanism for the photochromic transformations of 1-hydroxy-4-methylanthraquinone. The calculated rate constant agrees satisfactorily with the experimental value.

3. The effect of the nature of the solvents on the rate constant and on the activation energy of the dark stage in the photochromic transformations of 1-hydroxy-4-methylanthraquinone was studied. The nonspecific effect of the solvent on the process rate predominates.

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