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# Laser Flash Photolysis Study of the Reaction Mechanism in the Photochromism of 1-(Acyloxy)-2-methoxyanthraquinones

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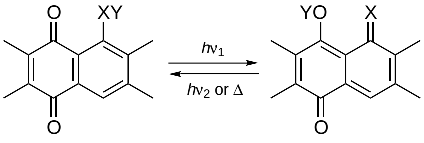
Nanosecond laser flash photolysis has been used to study the primary processes in the photochromic reaction of five *O*-acylic derivatives of 1-hydroxy-2-methoxyanthraquinone with methyl (I), tolyl (II), phenyl (III), ethoxyl (IV), and diethylamino (V) groups in the migrating acyl. The triplet−triplet absorption spectra of the reactive triplet states of quinones IV and V were detected, and the rate constants of the primary photochemical step were measured. The temperature dependence of the rate constants of acyl migration in the triplet states of quinones IV and V was studied, and the Arrhenius parameters were determined. The rate constants of thermal acyl migration and their Arrhenius parameters were measured for compounds I−V. It was found that migrant nature significantly influences the activation energy of both thermal and photochemical reactions of acyl migration. The activation energy of thermal migration increases from 37.9 ± 0.2 kJ/mol for compound I up to 66.5 ± 0.7 kJ/mol for compound V. The photochemical process is characterized by considerably lower values of the activation energy (15.9 ± 0.8 and 26.0 ± 1.7 kJ/mol for compounds IV and V, respectively). It was confirmed in the present work that photochemical migration of acyl groups is an adiabatic process occurring on the triplet potential energy surface.

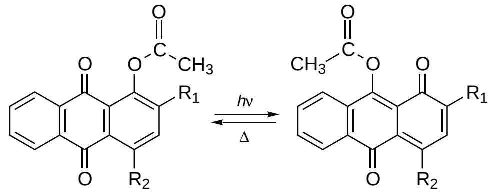
## 1. Introduction

Three types of photochromic processes are currently available to quinone derivatives. They are characterized by light-induced isomerization of the *p*-quinoid to the anaquinoid structure by photochemical migration of aryl, hydrogen, or acyl groups[1−7]



1, X = O, Y = Ph; 2, X = $CR_1R_2$, Y = H; 3, X = O, Y = C(O)R

The thermally reversible photochemical migration of acyl groups was discovered previously for a series of 1-acetoxyanthraquinones with donor substituents in the anthraquinone nucleus[5−7]



$R_1$ = $OCH_3$, $NHCOCH_3$, $N(CH_3)_2$, $R_2$ = H; $R_1$ = H, $R_2$ = $OCH_3$

The photochemical products have a structure of substituted 9-acetoxy-1,10-anthraquinones (ana-quinones, a-Q).

To account for the relationship between the reactivity of these compounds and their chemical structure, it was assumed that photochemical migration of the acetyl group occurs adiabatically.[5] Later,[6] the triplet state of the product (ana-quinone) was detected as a precursor of the ana-quinone ground state in the case of 1-acetoxy-2-methoxyanthraquinone (I). According to this result, a triplet adiabatic mechanism was proposed for the photochemical reaction of acyl group migration, but a detailed study of the primary processes required a better time resolution.[6]

The influence of temperature and solvent and migrant nature on the rate constant of thermal migration of the acyl group was previously studied.[6,7] It was found that donor substituents in the migrating acyl group significantly reduce the rate constant

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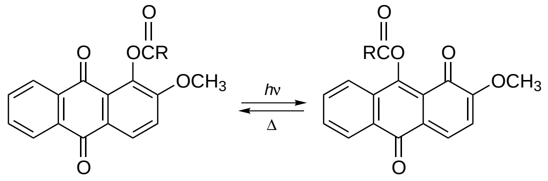
of the thermal migration. It is reasonable to expect, therefore, that donor substituents also reduce the rate constant of the photochemical migration. Therefore, the purpose of the present study was to investigate the primary photochemical step, migration of the acyl group, by nanosecond laser photolysis and to study the influence of the acyl group nature on the rate constant of this process. For this purpose, we used a series of *O*-acyl derivatives of 1-hydroxy-2-methoxyanthraquinone (I−V).



I, R = $CH_3$; II, R = $CH_2Ph$; III, R = Ph; IV, R = $OC_2H_5$; V, R = $N(C_2H_5)_2$

It was found, indeed, that donor substituents in the acyl significantly reduce the rate constant of the photochemical migration of the acyl group. The triplet−triplet absorption spectra of quinones IV and V were detected, and the rate constants of the primary photochemical step were measured. The triplet- and ground-state absorption spectra of the photoproduct (ana-quinone) were observed; the quantum yields of ana-quinone formation and the rate constants of elementary reactions were measured in toluene at room temperature for compounds I−V. It was confirmed in the present work that photochemical migration of acyl groups is an adiabatic process occurring on the triplet potential energy surface.

## 2. Experimental Details

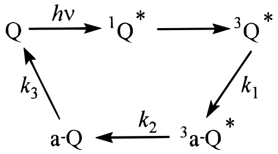
**2.1. Materials and Solutions.** *O*-Acyl derivatives (I−V) of 1-hydroxy-2-methoxyanthraquinone were obtained by acylation of 1-hydroxy-2-methoxyanthraquinone according to ref 6. The toluene used as the solvent was Merck Uvasol grade. The concentrations of the quinones used were $(2-5) \times 10^{-5}$ M. Sample solutions were contained in 1-cm × 1-cm silica cells and were deoxygenated by bubbling argon or oxygen saturated by bubbling oxygen.

**2.2. Laser Flash Photolysis.** The third harmonic (355 nm) of a pulsed YAG laser (Quantel YG 441; pulse width at half-maximum about 2 ns) was used as the excitation light source. Relative measurements of the laser energy were performed by focusing a small fraction of laser light on a pyroelectric joulemeter. Transient transmission changes were monitored at right angles to the laser beam using a xenon flash lamp (VQX 65N) as the probing light source. The detection system consisted of a monochromator (Jarrell-Ash Type 82-410; bandwidth 2 nm), a photomultiplier (HTV R928), and a digital oscilloscope (Tektronix 2440). The electric signal from the photomultiplier was fed into the oscilloscope through a field effect transistor probe (Tektronix P6021). The time resolution of the detection system was about 3 ns. The digital signals were analyzed using a microcomputer.

The sample solutions of compound V were changed after every laser pulse in order to avoid the effects due to the product. The photochemical transformations of quinones I−IV are highly reversible. Therefore, we could use the sample solutions of quinones I−IV for 10−15 laser pulses without any changes in the absorption spectra of the samples or in transient kinetics.

**2.3. Absorption and Fluorescence.** Conventional absorption and fluorescence measurements were performed using a Cary 210 spectrophotometer (Varian) and MPF-3 spectrofluorimeter (Perkin-Elmer), respectively.

**SCHEME 1**



**2.4. Quantum Yields.** The quantum yields of 2-methoxy-9-(acyloxy)-1,10-anthraquinone (a-Qs) formation were determined by comparing the a-Q concentrations obtained after laser excitation with that obtained by excitation at the same laser energy of a solution of acridine in benzene chosen as the standard. The triplet quantum yield of acridine is reported to be $0.73 \pm 0.07$.[8] In these experiments, less then 10% of the anthraquinones and acridine molecules were converted respectively into a-Qs and acridine triplet. The concentration of acridine triplet was monitored at its absorption maximum (442 nm) using a triplet extinction coefficient[8] $\epsilon = 2.7 \times 10^4$ $M^{-1}$ $cm^{-1}$. The a-Q concentration was monitored at the absorption maximum at 510 nm. The value of $\epsilon$ for the a-Q of compound I was estimated at 77 K from the data of low-temperature photolysis.[6] This value was found to be $1.1 \times 10^4$ $M^{-1}$ $cm^{-1}$ at the absorption maximum 526 nm. We used this value of $\epsilon$ for the a-Qs of all compounds under study (I−V) because substitution in the acyl group has only a minor effect on the spectra. We also estimated $\epsilon$ of the a-Q of compound IV from the analysis of the intensity dependence of a-Q absorption.

The quantum yield of compound V irreversible decomposition was determined from the decrease in optical density at the long-wavelength absorption maximum. The photoisomerization of 2-(dimethylamino)-3-chloro-1,4-naphthoquinone in benzene ($\varphi = 0.10 \pm 0.01$)[9] was used as an actinometric reaction.

**2.5. Quantum Chemical Calculations.** Experimental data were interpreted by quantum chemical calculations using the AM1[10] method based on the modified MNDO-85 program.[11] The conventional BFGS procedure[12] was used to optimize the geometry. The geometry and electronic structure of excited states were determined by the restricted Hartree−Fock technique in a “half-electron” approximation.[13]

## 3. Results and Discussion

**3.1. Reaction Scheme.** Solutions of $(2-5) \times 10^{-5}$ M 1-(acyloxy)anthraquinones (Q) I−V in toluene were studied by nanosecond laser photolysis in the temperature range 273−330 K in the presence and absence of oxygen. The results for compounds I−IV are consistent with the occurrence of the processes described in Scheme 1, where $^1Q^*$ represents the excited singlet state, $^3Q^*$ the lowest triplet state of the quinones, a-Q the ground state of the product with a structure of 9-(acyloxy)-1,10-anthraquinone (ana-quinone), and $^3$a-Q the lowest triplet state of the product. The arguments which have led to the proposal of this scheme are developed in the following sections. The scheme describing the peculiarity of compound V photolysis will be discussed in section 3.6.

**3.2. Spectra and Kinetics.** Transient optical density (OD) changes obtained by laser excitation at 355 nm of deoxygenated toluene solutions of compounds I−V at 297 K were monitored in the spectral region 300−800 nm, over a time range extending from a few nanoseconds to a few hundred microseconds after the laser pulse. The OD changes were found to be linearly dependent on the laser energy at low pulse energies but saturated at higher energies due to ground-state depletion (Figure 1). In our opinion, the linear relationship reflects the monophotonic character of the processes investigated.

The transient spectra obtained after laser excitation of compound IV (immediately after the end of the laser pulse, at

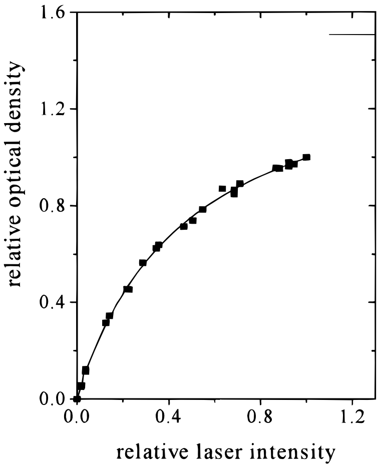


**Figure 1.** Dependence of a-Q (compound IV) absorption at the long-wavelength maximum (510 nm) on the laser intensity. Solid line: [3/3] Pade approximation of intensity dependence.

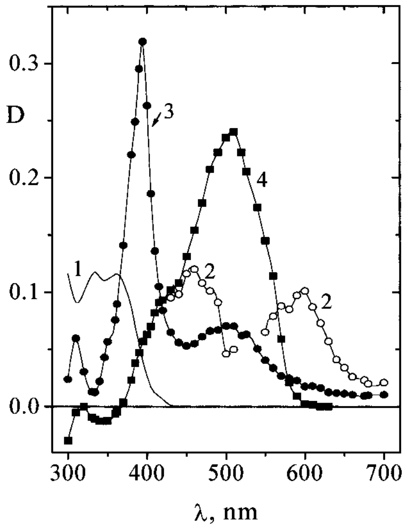


**Figure 2.** Absorption spectrum of quinone IV (1) and transient absorption spectra obtained upon excitation of compound IV ($2.9 \times 10^{-5}$ M) in degassed toluene at 295 K by a laser pulse at 355 nm: 2, spectrum detected immediately after the end of the laser pulse; 3, at 50 ns; 4, at 5 $\mu$s after the laser pulse.

50 ns and 5 $\mu$s after the pulse) are shown in Figure 2. Typical kinetic traces at selected wavelengths are shown in Figure 3. All kinetics are strictly first-order. Since the kinetic traces observed can be fitted at all wavelengths by three exponentials with the same time constants, these constants are assigned to the lifetimes of three transient species; their values are respectively 12 ns ($\tau_1$), 1.1 $\mu$s ($\tau_2$), and 150 $\mu$s ($\tau_3$).

The longer-lived transient spectrum with a maximum at 510 nm is assigned to a photoproduct with a structure of a-Q. This absorption spectrum is identical to that of the low-temperature (77 K) photoisomerization product.[6] Note that a similar spectrum had been detected for the a-Q of compound I in laser flash photolysis experiments at 195 K.[6] The precursor of a-Q with a lifetime of 1.1 $\mu$s has two absorption bands in the spectrum with maxima at 390 and 500 nm. The first short-lived intermediate has two absorption maxima at 460 and 600 nm.

Under our experimental conditions, it was impossible to achieve complete depletion of the ground state (Figure 1). Nevertheless, approximation of the OD dependence by the ratio of two polynomials (Pade approximation[14]) led to the limiting value of a-Q optical density in the case of complete depletion of the ground state. Figure 1 represents the [3/3] Pade approximation (the ratio of two third-order polynomials). Similar results were obtain for the [4/4] Pade approximation. Using the limiting values of optical density, the extinction coefficient of the a-Q of compound IV was estimated at the long-wavelength maximum ($\epsilon = 1.16 \times 10^4$ M$^{-1}$ cm$^{-1}$ at 510 nm). This value is practically coincident with the value of $\epsilon$ estimated for the a-Q of compound I at 77 K[6] ($\epsilon = 1.1 \times 10^4$ M$^{-1}$ cm$^{-1}$). This means that the [3/3] Pade approximation (Figure 1) gives a reasonable result. The absolute spectra of the intermediates (Figure 4a,b) were calculated from the difference spectra (Figure 2) combined with the kinetic results and using an estimated degree of depletion of the ground state. It should be noted that the extinction coefficients of compound IV triplet–triplet absorption are slightly underestimated (about 10–20%) due to its short lifetime ($\tau_1$ = 12 ns), comparable with the time resolution of the setup (about 3 ns).

**3.3. Oxygen Effect.** The concentration of molecular oxygen in the solution has no effect on the yield and lifetime of the long-lived intermediate a-Q. Saturation of the solution with oxygen ($9 \times 10^{-3}$ M)[15] efficiently accelerated the decay of its precursor and did not reduce the amount of a-Q formed. According to this result, the precursor of a-Q is its own excited state. This state is a triplet since its lifetime is rather long (1.1 $\mu$s in the absence of oxygen). Therefore, the spectrum with maxima at 390 and 500 nm can be attributed to the triplet–triplet spectrum of a-Q.

The kinetics of the disappearance of $^3$a-Q is exponential as noted before. The pseudo-first-order rate constant $k_2$ is dependent on the oxygen concentration in solution and can be described by (Figure 5).

$$k_2 = k_{20} + k_{2Q}[O_2] \qquad (1)$$

The quenching rate constant in the case of the $^3$a-Q of compound IV is equal to $(2.5 \pm 0.1) \times 10^9$ M$^{-1}$ cm$^{-1}$. The similar values of the quenching rate constant were obtained for the $^3$a-Qs of compounds I, II, and V (Table 1). These values are indeed characteristic of triplet quenching by oxygen.[16,17]

It is reasonable to assume that the end-of-pulse absorption spectrum is due mainly to the triplet state ($^3$Q) of anthraquinone IV. A very similar spectrum was detected immediately after the end of laser excitation of compound V (Figure 6). As in the case of compound IV, it was attributed to the triplet–triplet absorption spectrum of anthraquinone V. The lifetime of this triplet state ($\tau_1$) is equal to about 1 $\mu$s at room temperature in the absence of oxygen. Saturation of the solution with oxygen efficiently accelerated the decay of this intermediate (Figure 7) and reduced the yield of the following intermediates formed ($^3$a-Q and a-Q of compound V). The pseudo-first-order rate constant $k_1$ is linearly dependent on the oxygen concentration in solution (Figure 8). The quenching rate constant $k_{1Q}$ is equal to $(6.6 \pm 0.3) \times 10^8$ M$^{-1}$ cm$^{-1}$, which also lies within the range of typical values for triplet quenching by oxygen.[16,17] Since the lifetime of the $^3$Q of compound IV is very short (12 ns), saturation of the solution with oxygen has no effect on it.

**3.4. Quantum Yields.** The quantum yields of ana-quinone formation were determined in toluene at 297 K by comparing the a-Q concentrations obtained upon excitation of solutions of compounds I and III–V with the concentration of the triplet of acridine used as a standard (Table 2). It was found that for compounds I, III, and IV, the quantum yields are close to 1. The quantum yield of ana-quinone in the case of V is significantly smaller, ~0.1. The possible reasons for the lower quantum yield in the case of V will be analyzed below (section 3.6).

**3.5. Temperature Effect.** The effect of temperature on the kinetics was studied from 272 to 330 K. Temperature significantly influenced the rate constant of the thermal migration of

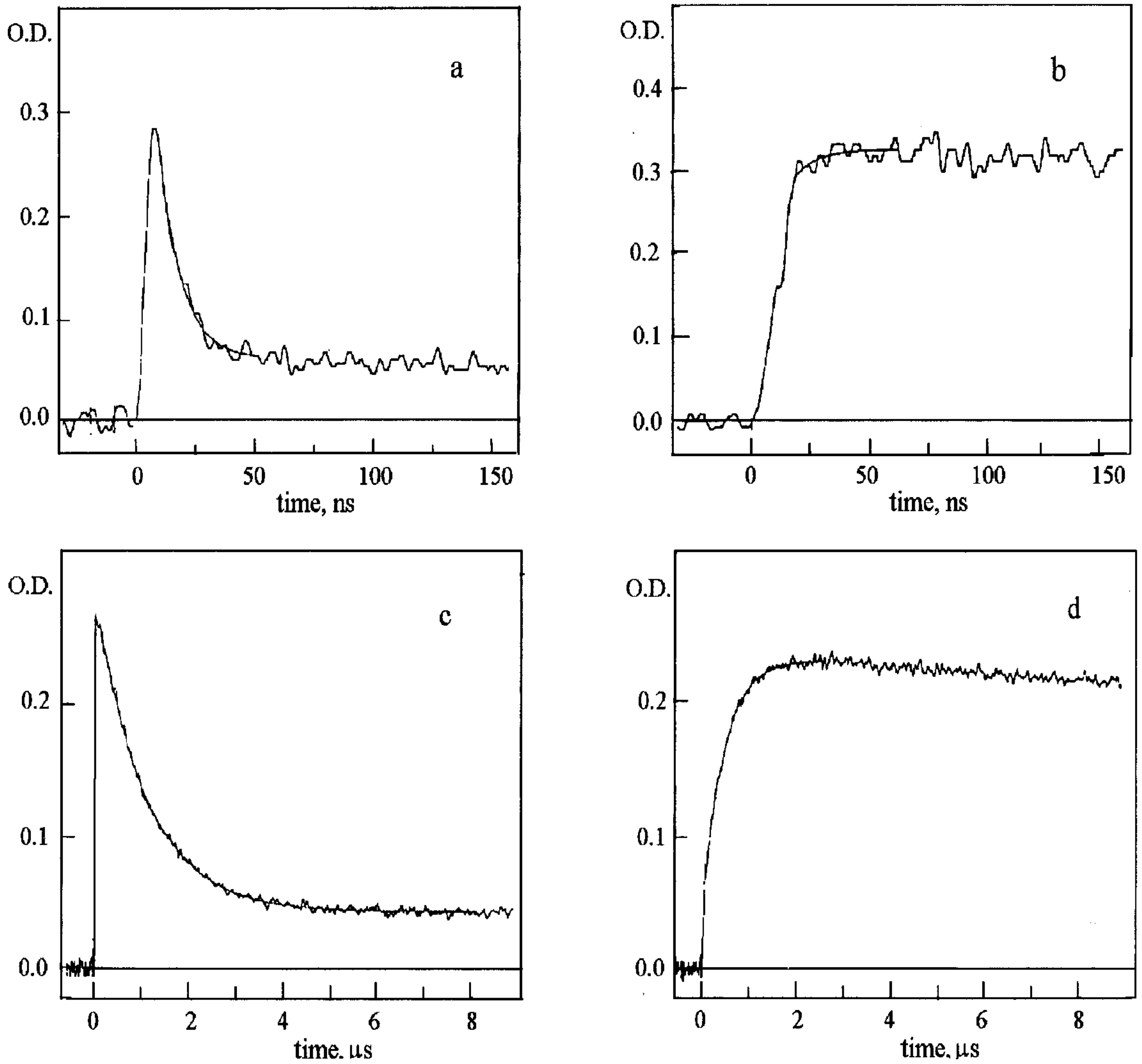


**Figure 3.** Kinetic traces showing the variation in optical density at different wavelengths ($\lambda$) on the excitation of anthraquinone IV ($2.9 \times 10^{-5}$ M) in degassed toluene at 295 K: (a) $\lambda = 600$ nm; (b, c) $\lambda = 390$ nm; (d) $\lambda = 510$ nm.

**TABLE 1: Values of the Lifetime ($\tau_2$) of the Triplet State of 9-(Acyloxy)-2-methoxy-1,10-anthraquinones in Toluene at Room Temperature in the Absence of Oxygen and the Rate Constants ($k_{2Q}$) of Their Quenching by Oxygen**

| compd | I | II | III | IV | V |
|---|---|---|---|---|---|
| R | $CH_3$ | $CH_2Ph$ | Ph | $OC_2H_5$ | $N(C_2H_5)_2$ |
| $\tau_2$, $\mu$s | 1.13 ± 0.08 | 1.18 ± 0.12 | 1.08 ± 0.05 | 1.15 ± 0.10 | 7.1 ± 0.9 |
| $10^{-9}k_{2Q}$, $M^{-1}$ $cm^{-1}$ | 3.11 ± 0.11 | 1.66 ± 0.10 |  | 2.5 ± 0.10 | 0.32 ± 0.02 |

the acyl group ($k_3$). Arrhenius plots were linear for all compounds under study. Arrhenius parameters are presented in Table 3. It is seen that the nature of the acyl group has only a minor effect on the preactivation factor. The large effect of the migrant nature on the rate constant of thermal migration is due to the variation of activation energy. Substitution of a methyl group by a diethylamino group results in an increase of activation energy from 38 to 66.5 kJ/mol and, therefore, in a decrease in the rate constant at room temperature of 6 orders of magnitude.

The triplet–triplet absorption of initial quinone ($^3$Q) and its decay were detected only in the case of compounds IV and V with donor substituents in the migrating acyl. In the case of compounds I–III, we were unable to detect their triplets due to the very high rate constant of acyl migration. The lifetime of the $^3$Q of compounds I–III should be substantially shorter than the time resolution of the detection system (about 3 ns). The lifetime of the $^3$Q of compound IV is short enough (12 ns at room temperature); nevertheless, its dependence on temperature was studied from 272 to 315 K. An Arrhenius treatment of the temperature dependence of $k_1$ for compound IV is shown in Figure 9. The activation parameters are listed in Table 3.

An Arrhenius treatment of the observed rate constant ($k_{obs}$) of the decay of the triplet state of quinone V is presented in Figure 10. The plot is clearly nonlinear. In this case, the rate constant of acyl migration is decreased significantly and the reactive triplet can also undergo intersystem crossing (ISC). The temperature dependence of $k_{obs}$ can be described as a sum of temperature-independent ($k_{isc}$) and temperature-dependent ($k_1$) terms (Figure 10, insert)

$$k_{obs} = k_{isc} + k_1 \tag{2}$$

$$k_{isc} = (4.3 \pm 0.4) \times 10^5\ s^{-1},\ k_1 = (2.1 \pm 1.1) \times 10^{10} \times \exp(-(3130 \pm 190)/T)\ s^{-1}$$

The rate constants of the decay of the product triplet excited states ($k_2$) are described for the a-Qs of compounds I–V by eq 1. The $k_{20}$ values are very slightly dependent on temperature for compounds I–IV. For instance, in the case of compound III, $k_{20}$ changes from $(8.0 \pm 0.2) \times 10^5$ to $(9.2 \pm 0.5) \times 10^5$ in

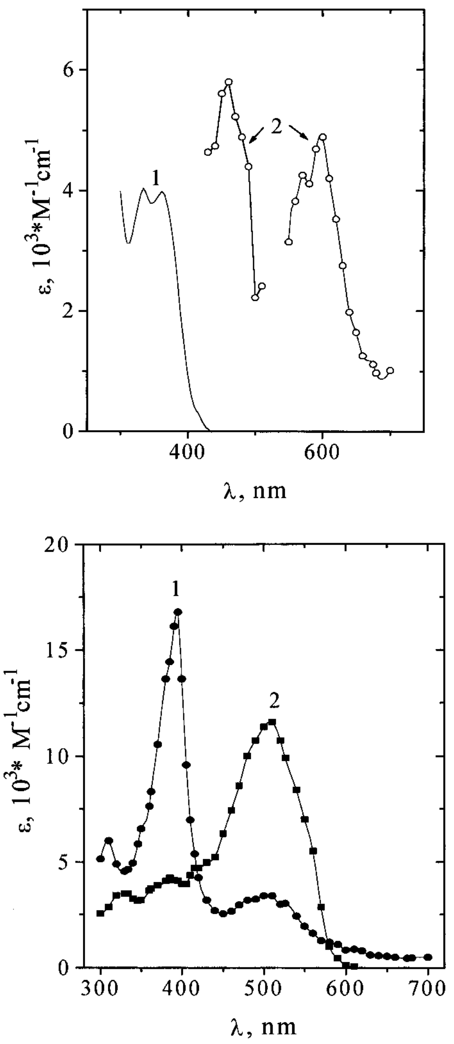


**Figure 4.** (a, top) Extinction coefficients ($\epsilon$) of anthraquinone IV (1) and its lowest triplet state (2). (b, bottom) Extinction coefficients ($\epsilon$) of the lowest triplet state of ana-quinone ($^3$a-Q) (1) and the ground state of ana-quinone (a-Q) (2) of compound IV.

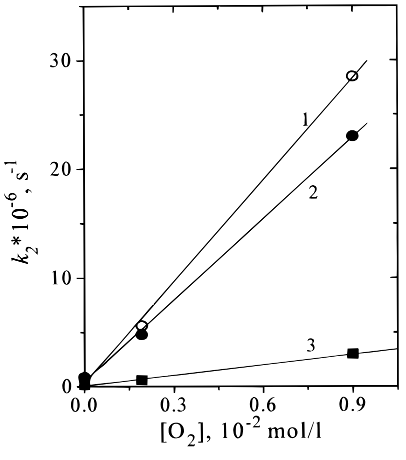


**Figure 5.** Dependence of the rate constant ($k_2$) of ana-quinone triplet state ($^3$a-Q) deactivation on the oxygen concentration: a-Q of compounds I (1), IV (2), and V (3).

the temperature range 275–330 K. These changes can be described in terms of an Arrhenius relationship in the following form

$$k_{20} = 10^{6.2\pm0.1}\exp\{-(200 \pm 50)/T\}$$

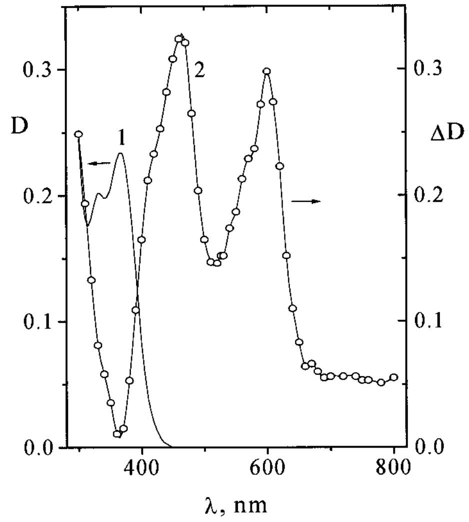


**Figure 6.** Absorption spectrum of quinone V (1) and transient absorption spectrum detected immediately after the end of the laser pulse (2) in toluene solution ($2.0 \times 10^{-5}$ M) at 295 K.

A similar dependence

$$k_{20} = 10^{6.44\pm0.07}\exp\{-(280 \pm 30)/T\}$$

was measured previously[6] for $^3$a-Q decay of compound I in the temperature range 160–300 K. The preexponential factor is low (about $10^6$) and typical of a spin-forbidden process. The activation energy of the interconversion is low (1.7–2.3 kJ/mol). It reflects the participation in the deactivation process of the vibrational mode with frequency 140–190 cm$^{-1}$. An analogous temperature dependence with a low activation energy (about 500 cm$^{-1}$) has been observed previously for the interconversion of the excited triplet states of the hydrocarbons.[18]

**3.6. Peculiarity of Anthraquinone V Photolysis.** At room temperature, $k_{\mathrm{obs}}$ for the triplet-state decay of compound V is equal to $(9.5 \pm 0.8) \times 10^5$ s$^{-1}$. Using this result and the estimated value of $k_{\mathrm{isc}}$, the quantum yield of formation of the product triplet state ($\Phi_T$) can be calculated to be $\Phi_T = 0.5 \pm 0.1$. This value is in good agreement with the estimation from the absorption of $^3$a-Q at 390 nm. If it is assumed that the extinction coefficients of triplet–triplet absorption do not depend on the substituent in the acyl group and $\Phi_T$ can be estimated as $0.5 \pm 0.1$.

As described in section 3.4, the presence of oxygen significantly influenced the lifetime of the triplet state of compound V (Figure 8). Figure 11 (plot 1) shows the Stern–Volmer plot for the quantum yield of the a-Q triplet state as a function of oxygen concentration. The slope of the curve ($K_Q = 680 \pm 30$ M$^{-1}$) is in good agreement with the value of $\tau_1 k_{1Q} = 690 \pm 70$ M$^{-1}$, extracted from the kinetic data (Figure 8).

It is seen from Table 2 that the quantum yields of a-Q formation are close to unity except for compound V. In the case of V, the quantum yield is significantly smaller (~0.1). But as we estimated before, the quantum yield of formation of the product triplet state is about 0.5. A possible explanation of this result is the occurrence of a side reaction in the $^3$a-Q of compound V. In agreement with this assumption, we observed a smaller effect of oxygen content on the yield of a-Q than on the yield of its precursor $^3$a-Q (Figure 11). This is due to the quenching by oxygen of the side reaction.

We have estimated the quantum yield of irreversible decomposition of compound V. In the absence of oxygen, it is high and equal to $0.25 \pm 0.05$. Saturation of the solution with oxygen results in a significant ($68 \pm 13$ times) decrease of the quantum yield of irreversible decomposition. This is consistent with the assumption that a side reaction occurs mainly in $^3$a-Q. Indeed,

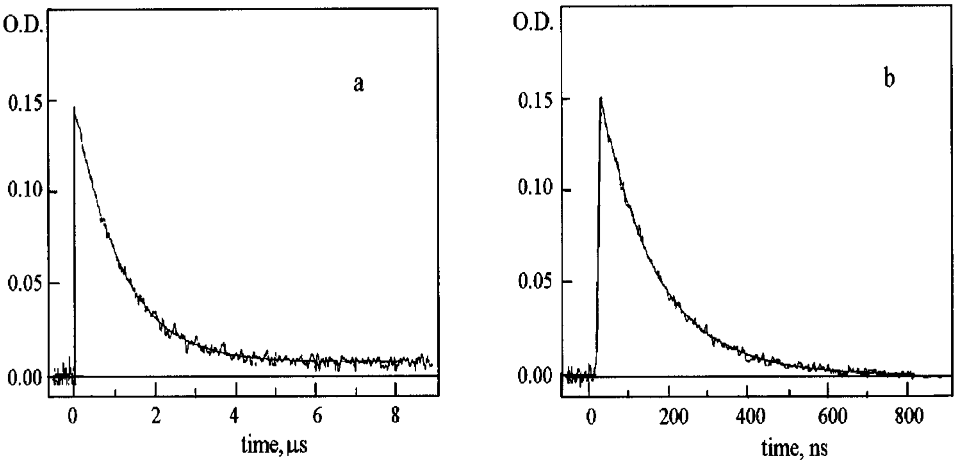


**Figure 7.** Kinetic traces showing the variation in optical density at 600 nm on excitation of anthraquinone V ($2.0 \times 10^{-5}$ M) at 295 K in degassed (a) and oxygen saturated (b) toluene.

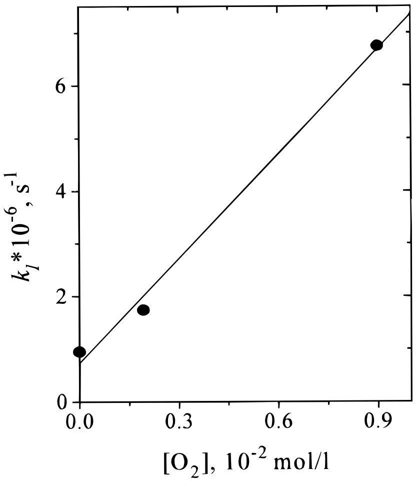


**Figure 8.** Dependence of the rate constant ($k_1$) of the quinone V triplet-state ($^3$Q) decay on the oxygen concentration.

**TABLE 2: Values of the Quantum Yields (Φ) of 9-(Acyloxy)-2-methoxy-1,10-anthraquinone Formation under Irradiation of 1-(Acyloxy)-2-methoxy-9,10-anthraquinones in Toluene at Room Temperature**

| compd | I | III | IV | V |
|---|---|---|---|---|
| Φ | 0.85 ± 0.17 | 0.92 ± 0.18 | 0.91 ± 0.18 | 0.10 ± 0.02 |

in this case, quenching by oxygen of both triplets ($^3$Q and $^3$a-Q) should lead to a very effective decrease of the quantum yield of the side reaction (60 ± 13 times).

As noted before, the rate constants of $^3$a-Q decay ($k_2$) are very slightly dependent on temperature in the case of compounds I−IV. It is in agreement with the fact that the main channel of decay is intersystem crossing to the ground state. This is not the case for compound V. An Arrhenius treatment of $k_2$ for compound V is shown in Figure 12. The plot is linear, and the temperature dependence can be fitted by

$$k_2 = 10^{8.3\pm0.3} \exp(-1820 \pm 160)/T)$$

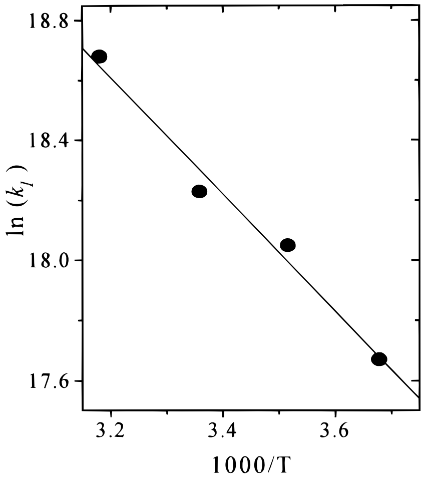


**Figure 9.** Arrhenius plot of the decay rate constant ($k_1$) of the quinone IV triplet state ($^3$Q).

The activation energy (15.1 ± 1.3 kJ/mol) is about 1 order of magnitude higher than in the case of compounds I−IV (1.7−2 kJ/mol). It is reasonable to assume that this activation energy is due to the side reaction.

One of the possible side reactions is the cleavage of the carbon−oxygen bond and formation of two radicals, one of them being an acyl radical. It is the well-known product of the photo-Fries rearrangement.[19] This photoprocess can be temperature activated.[19,20] But we did not isolate any product of rearrangement except 1-hydroxy-2-methoxy-9,10-anthraquinone. The chemical yield of 1-hydroxy-2-methoxy-9,10-anthraquinone upon irradiation of compound V in dry toluene in the presence of oxygen is equal to 88%. Further investigations are carried out in order to understand the nature of the side reaction.

Nevertheless, according to the data available, we propose Scheme 2 for the phototransformation of compound V.

**3.7. Quantum Chemical Calculations.** To interpret the experimental results and the influence of chemical structure on the rate constants of the elementary reactions (Scheme 1), we performed the quantum chemical calculation of the electronic

**TABLE 3: Values of the Rate Constants of Acyl Group Migration in the Excited Triplet State of *p*-Anthraquinones ($k_1$) and in the Ground State of Ana-anthraquinones ($k_3$, Measurement Accuracy ±10%) and Parameters of Their Arrhenius Plots**

| compd | R | $k_1$, $s^{-1}$ | log $A_1$, $s^{-1}$ | $E^1_{act}$, kJ/mol | $k_3$, $s^{-1}$ | log $A_3$, $s^{-1}$ | $E^3_{act}$, kJ/mol |
|---|---|---|---|---|---|---|---|
| I | $CH_3$ | | | | $1.2 \times 10^6$ | 11.8 ± 0.1 | 37.9 ± 0.2 |
| II | $CH_2Ph$ | | | | $1.6 \times 10^6$ | | |
| III | Ph | | | | $1.1 \times 10^5$ | 12.16 ± 0.13 | 40.5 ± 0.6 |
| IV | $OC_2H_5$ | $(8.2 \pm 1.0) \times 10^7$ | 10.7 ± 0.2 | 15.9 ± 0.8 | $6.5 \times 10^3$ | 12.33 ± 0.13 | 48.2 ± 0.8 |
| V | $N(C_2H_5)_2$ | $(5.2 \pm 0.5) \times 10^5$ | 10.3 ± 0.2 | 26.0 ± 1.7 | 2.9 | 12.20 ± 0.13 | 66.5 ± 0.7 |

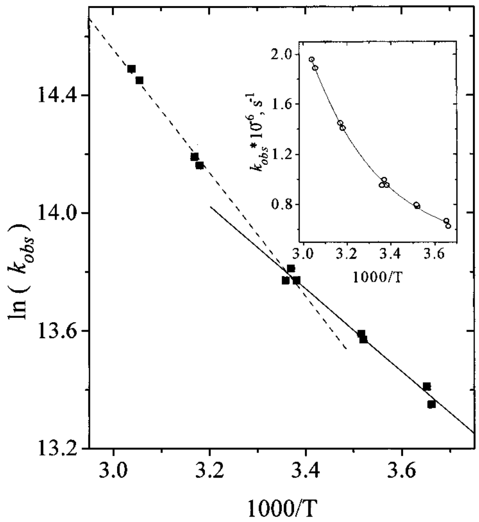


**Figure 10.** Arrhenius plot of the decay rate constant ($k_{obs}$) of the quinone V triplet state ($^3$Q) and fitting of $k_{obs}$ by exponential dependence, $k_{obs} = k_{isc} + A_1 \exp(-E/RT)$ (insert).

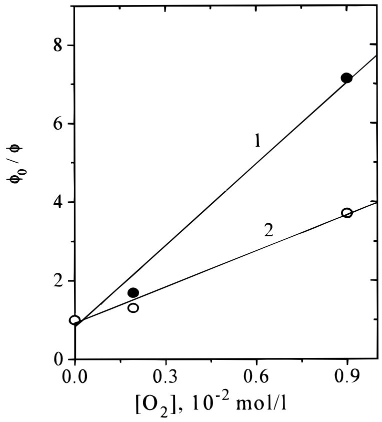


**Figure 11.** Stern–Volmer plots for the quantum yields of the a-Q triplet state (1) and the a-Q ground state (2) vs oxygen concentration under laser irradiation of anthraquinone V in toluene at 295 K.

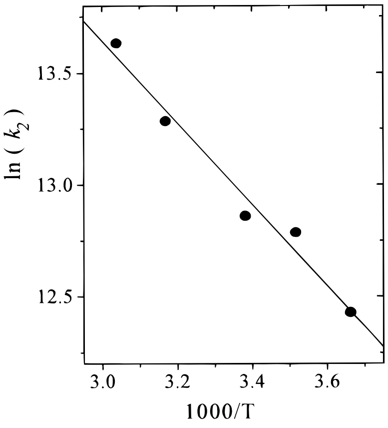


**Figure 12.** Arrhenius plot of the decay rate constant ($k_2$) of ana-quinone V triplet state ($^3$a-Q).

structure and geometry of anthraquinones I–V, their a-Q forms, and the lowest triplet states of Q and a-Q of I–V. Figure 13 presents the predicted relative energies of the ground and lowest triplet states of quinone IV and its ana-quinone form. The patterns for the other compounds under study are very similar. The energy difference between the ground states of a-Q and Q (reaction enthalpy for thermal acyl group migration) depends very slightly on the nature of the substituent in the acyl group (−62.0 and −69.6 kJ/mol for compounds I and V, respectively). It was noted before that the experimental absorption spectra of quinones I–V and all the transients are practically independent of the nature of the acyl group. According to this fact, calculated positions of the triplet states of Q and a-Q are also very slightly dependent on the substituent in the acyl group. Therefore, the reaction enthalpy for acyl group migration in the excited triplet state is practically independent of substituent in the migrant (−66.6, −69.6, and 63.3 kJ/mol for compounds I, IV, and V, respectively). Consequently, in this case, the influence of the acyl substituent on the reaction rate constant does not correlate with the thermodynamics of the process.

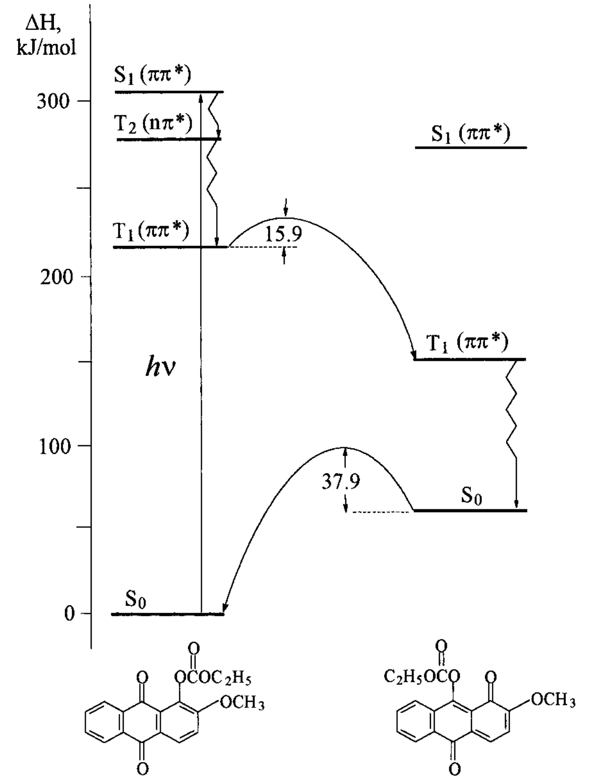
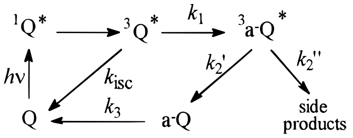


**Figure 13.** Energy correlation diagram for the process of thermally reversible photochemical acyl group migration. The formation enthalpies of quinone IV, ana-quinone of IV, and their lowest triplet states were calculated using the AM1 method. The energies of excited singlet states were estimated from experimental absorption spectra of quinone and ana-quinone. The position of the second triplet state (T$_2$, nπ* type) of quinone IV was estimated from the experimental data for 9,10-anthraquinone.[23] The energies of the transition states for the thermal and photochemical reactions were calculated from experimental activation energies.

## SCHEME 2



In a previous work,[6] it was assumed that the influence of substituents on the rate constant of thermal acyl migration is due to the change of the charge on the carbon atom of the migrating COR group: a higher rate of migration is observed for a larger positive charge. Our calculation showed that a significant positive charge is localized on a carbon atom of the carbonyl group (about 0.4), and accordingly, a large negative charge is localized on the quinone oxygen (about −0.4). However, for compounds with donor substituent (a-Qs of IV and V), our calculations gave an even bigger positive charge (0.41) then for the a-Q of I (0.34). Therefore, the results of the AM1 calculations do not confirm the assumption of our earlier study.[6]

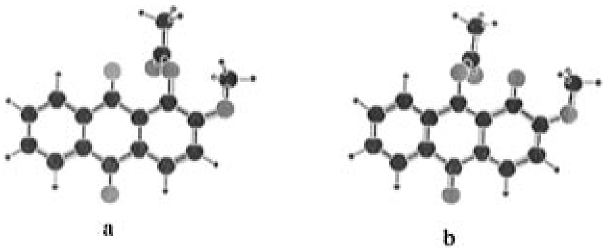


**Figure 14.** Computer-generated drawing of 1-acetoxy-2-methoxy-9,10-antraquinone (a) and 9-acetoxy-2-methoxy-1,10-antraquinone (b). Geometry was optimized by the AM1 method.

It is seen from Figure 14 that the acetoxy group of quinone I lies in the plane practically perpendicular to the plane of the anthraquinone rings. The angle between these planes is even less than 90° and equals 74° for the a-Q of I and 79° for the a-Q of V. This angle is also smaller in the triplet states and equals 70° and 72° for compounds I and V, respectively. It is clear that the reaction coordinate has to be mainly a combination of stretching and bending OC modes. According to the results of the calculations, the difference in nuclear configuration of the initial and final states will be smaller in the case of compound I than compounds IV and V. Moreover, this difference is smaller in the excited triplet states than in the ground states. Let us assume that the potential energy dependence on the reaction coordinate is harmonic with a frequency slightly dependent on the substituent in the acyl group. In this case, the barrier height (or activation energy) will depend both on the enthalpy of reaction and on the difference in nuclear configuration of the initial and final states. It is seen that in our case (thermal and photochemical acyl migration), a higher rate of migration is observed for the smaller difference in nuclear configuration.

As we can see from the experimental data, the photochemical acyl migration reaction occurs completely on the triplet potential energy surface. We think that the absence of photoreaction in the excited singlet state of compounds I−V is due mainly to the short lifetime of this state. We failed to detect the luminescence of compounds I−V, which means that the quantum yield of fluorescence is smaller than $10^{-3}$. Using these data and a rough estimate of the radiative lifetime (∼25 ns), we can deduce that the lifetime of the singlet excited state is significantly smaller than 25 ps. It is known that the rate constant of intersystem crossing between excited states of different symmetry ($\pi\pi^*$ and $n\pi^*$ states) can be very high ($\sim 10^{10}-10^{11}$ s$^{-1}$).[21] This situation is realized in our case (Figure 13), and it is the reason for the very short lifetime of the singlet excited $\pi\pi^*$ state. It should be noticed that the growth lifetime of the reactive triplet state of quinone IV from a precursor has been estimated to be about 70 ps.[22] This is longer than our estimation for the lifetime of the singlet excited state and may be equal to the lifetime of the intermediate triplet state $T_2$ of $n\pi^*$ type.

## 4. Conclusions

In the *O*-acylic derivatives of 1-hydroxy-2-methoxyanthraquinone (I−V), photochemical migration of the acyl group takes place via the triplet excited state. It was confirmed in the present work that photochemical migration of acyl groups is an adiabatic process occurring on the triplet potential energy surface. The absence of photoreaction in the excited singlet state of compounds I−V is due mainly to the short lifetime of this state. The process of acyl migration in the triplet excited state of quinones is termally activated, but the activation energy is low (15.9 ± 0.8 and 26.0 ± 1.7 kJ/mol for compounds IV and V, respectively). Activation energies for the thermal migration of acyl groups are significantly higher. It can be due to a bigger difference in nuclear configurations for the migration in the ground state than in the excited triplet state.

The migrant nature significantly influences the activation energy of both thermal and photochemical reactions of acyl migration. The activation energy of thermal migration increases from 37.9 ± 0.2 kJ/mol for compound I up to 66.5 ± 0.7 kJ/mol for compound V with donor diethylamino substituent in the migrating acyl. The activation energy of the photochemical process changes from 15.9 ± 0.8 (compounds IV) to 26.0 ± 1.7 kJ/mol for compound V. The influence of the nature of the migratory group on the activation energy can also be due to the magnitude of the change in the nuclear configurations of the initial and final states of the reaction of acyl migration. The preexponential factors are practically independent of the migrant nature and are equal to $10^{10}-10^{11}$ s$^{-1}$ for the photochemical process and about $10^{12}$ s$^{-1}$ for the thermal migration.

The quantum yields of photochemical migration of the acyl group in quinones I−IV are close to unity. Such values are consistent with the adiabatic nature of the process. The very low quantum yield (∼0.1) of ana-quinone formation and the high quantum yield of irreversible photodecomposition in the case of compound V are connected with the appearance of an effective side reaction in the excited triplet state of ana-quinone. The origin of this side reaction will be the subject of further study.

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