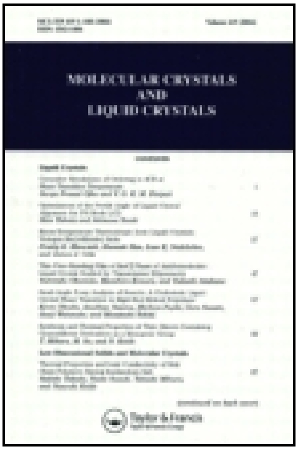

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Laser Flash Photolysis Study of the Primary Processes in the Photochromic Reaction of 1-acyloxy-2-methoxyanthraquinones

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Version of record first published: 24 Sep 2006.

To cite this article: N. P. Gritsan , A. Kellmann , F. Tfibel & L. S. Klimenko (1994): Laser Flash Photolysis Study of the Primary Processes in the Photochromic Reaction of 1-acyloxy-2-methoxyanthraquinones, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 246:1, 259-262

To link to this article: http://dx.doi.org/10.1080/10587259408037823

Mol. Cryst. Liq. Cryst. 1994, Vol. 246, pp. 259–262
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Printed in the United States of America

LASER FLASH PHOTOLYSIS STUDY OF THE PRIMARY PROCESSES IN THE PHOTOCHROMIC REACTION OF 1-ACYLOXY-2-METHOXYANTHRAQUINONES.

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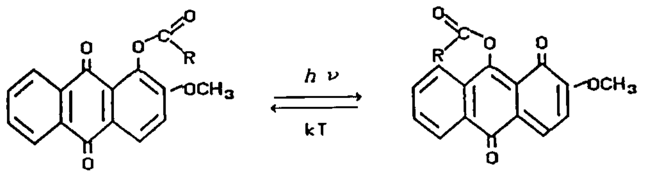
Abstract The nanosecond laser flash photolysis (time resolution 3 ns) has been used to study the primary processes in photochromic reaction of three O-acylic derivatives of 1-oxy-2-methoxyanthraquinone with methyl (I), ethoxyl (II) and diethylamino (III) in migrating acyl. The triplet-triplet absorption spectra of the reactive triplet states of quinones II and III were detected. The triplet and ground states absorption spectra of the photoproduct (ana-quinone) were observed ; the quantum yields of ana-quinone formation and the rate constants of all elementary steps were measured in toluene at room temperature. It was confirmed in the present work that photochemical migration of acyl groups is an adiabatic process occurring on the triplet potential energy surface.

INTRODUCTION

A new photochromic process, thermally reversible photochemical migration of acyl groups, has been discovered before for a series of 1-acyloxy-2-methoxy-anthraquinones[1,2]

Q



a-Q

with R : CH_3 (I), OC_2H_5 (II), $N(C_2H_5)_2$ (III)

The influence of temperature, solvent and migrant nature on the rate constant of thermal migration of the acyl group was previously studied[2]. The spectrum of the excited triplet state of the product was detected and a triplet adiabatic mechanism was proposed in the case of photochromic transformations of compound I, but the detailed study of the primary processes required a better time resolution[2].

The purpose of the present study was to investigate by nanosecond laser photolysis the primary photochemical step, migration of acyl group, and to study the influence of the acyl group nature on the rate constant of this process.

EXPERIMENTAL

The substituted anthraquinones investigated were synthesized and purified according to reference 2 and the solvents used were Merck Uvasol grade. Concentrations used were 2-5 x 10^{-5} M. The third harmonic (355 nm) of a pulsed YAG laser (Quantel YG 441 ; pulse width at half maximum 2 ns) was used as the excitation light source. The laser flash photolysis set-up and the details of the experimental technique was described in reference 3.

RESULTS AND DISCUSSION

Transient Species

Transient optical density (OD) changes obtained on laser excitation at 355 nm of deoxygenated toluene solutions of compound II at 297 K were monitored in the spectral region 300-800 nm, over a time range extending from a few nanoseconds to a few tens of microseconds after the laser pulse. The OD changes were found to be linearly dependent on the laser energy at low energies but to saturate at higher energies due to ground state depletion. The transient spectra obtained immediately after the end of the laser pulse (t = 0), at 50 ns and 5 μs after the pulse are shown in the figure. All kinetics are strictly first-order. Since the time phases 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, 1.1 μs, and 150 μs.

The longer lived transient spectrum is assigned to a photoproduct with a structure of ana-quinone (a-Q)[1,2]. Saturation of the solution with oxygen (9 x 10^{-3}M [O_2]) efficiently accelerated the decay of the microsecond transient and did not reduce the amount of ana-quinone formed. According to this result we assumed previously[2] that this spectrum is that of the triplet

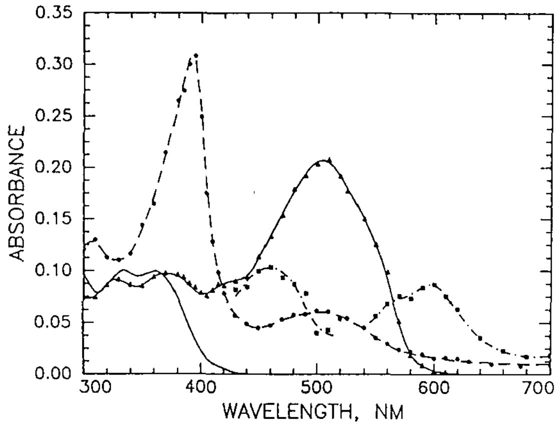


FIGURE Transient absorption spectra recorded upon laser excitation at 355 nm of compound II (2.5 x 10^{-5} M) in degassed toluene at 297 K: ■ , at the end of the laser pulse; ● , 50 ns and ▲ , 5 μs after the end of the pulse. Full line represents the absorption spectrum of anthraquinone II.

state of the ana-quinone. The high value obtained for the quenching rate constant k_q (2-3 x 10^9 $M^{-1}s^{-1}$) is indeed characteristic of triplet quenching by oxygen. It is reasonable to assume that the end-of-pulse absorption spectrum is due mainly to the triplet state of the anthraquinone. The following scheme is proposed from the experimental results :

$$\begin{tikzcd}
Q \arrow[r, "h\nu"] & {}^1(\,Q\,)^* \arrow[r] & {}^3(\,Q\,)^* \arrow[r, "k_1"] & {}^3(\,a\text{-}Q\,)^* \arrow[r, "k_2+k_Q\times{[O_2]}"] & a\text{-}Q \arrow[llll, bend left, "k_3"]
\end{tikzcd}$$

The behaviour of compounds I and III can be also described by this kinetic scheme.

Quantum Yields

The quantum yields of ana-quinone formation were determined in toluene at 297 K by comparing the a-Q concentration obtained upon excitation of solutions of compounds I, II and III with the concentration of the triplet of acridine used as a standard[4]. It was found that for compounds I and II the quantum yields are close to 1. The quantum yield of ana-quinone in the case of III is significantly smaller : ~5 × 10^{-2}.

CONCLUSION

In the three substituted anthraquinones the photochemical migration of acyl group takes place via triplet states. As shown in the table given below the nature of substituent in migrating acyl has an important effect not only on the rate constant of thermal migration[2], but also on the rate constant of the photochemical migration. Indeed substitution by electron-donor groups results in a significant decrease of the rate constants of both photochemical and thermal reactions.

TABLE Rate constants of the elementary reactions in toluene at room temperature

Comp.	R	k_1, s^{-1}	k_2, s^{-1}	k_Q, l/mol s	k_3, s^{-1}
I	CH_3	> 5×10^{8}	0.9×10^{6}	3.1×10^{9}	1.2×10^{6}
II	OC_2H_5	8.2×10^{7}	0.9×10^{6}	2.5×10^{9}	6.5×10^{3}
III	$N(C_2H_5)_2$	5.3×10^{5}	-	-	2.9^{2}

Acknowledgments

The authors are very grateful to Dr. L. Lindqvist for helpful discussions and to Ministere de la Recherche et de l'Espace for financial support for one of us (Dr. Nina Gritsan).

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