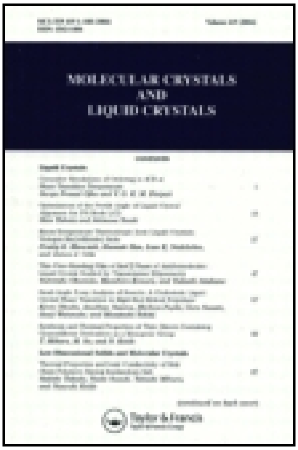

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Photochromism of Quinoid Compounds

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PHOTOCHROMISM OF QUINOID COMPOUNDS.

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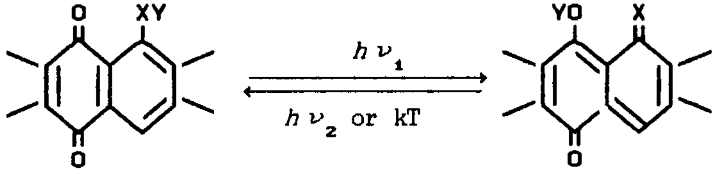
Abstract The paper presents the results of studies on the photochromic transformation mechanisms for three classes of quinone derivatives. Photoisomerization of the para-quinone to the ana-quinone due to photochemical migration of hydrogen, aryl, or acyl groups is common to these processes. The mechanism of photochromic transformations of 1-alkyl- and 1-acyloxyanthraquinones has been investigated in detail. The primary photochemical steps of these processes - the migrations of hydrogen or an acyl group - are adiabatic photochemical reactions at the triplet potential energy surface. Variation of substituents in the anthraquinone ring, in the alkyl group of 1-alkylanthraquinones, and particularly in the acyl group of 1-acyloxyanthraquinones makes it possible to change (from several microseconds to seconds) the lifetimes of coloured photoinduced products at room temperature.

INTRODUCTION

Three types of photochromic transformation are currently available to quinone derivatives. They are characterized by light-induced isomerization of the para-quinoid to the ana-quinoid structure due to the photochemical migration of hydrogen[1,2], acyl[3] or aryl[4] groups

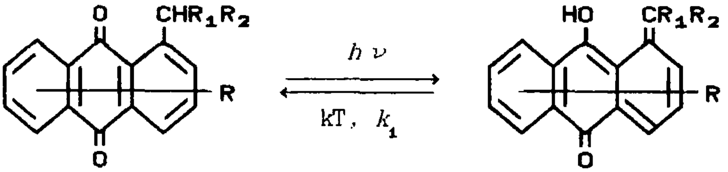


1) $X{=}CR_1R_2$, $Y{=}H$; 2) $X{=}O$, $Y{=}COR$; 3) $X{=}O$, $Y{=}Ar$.

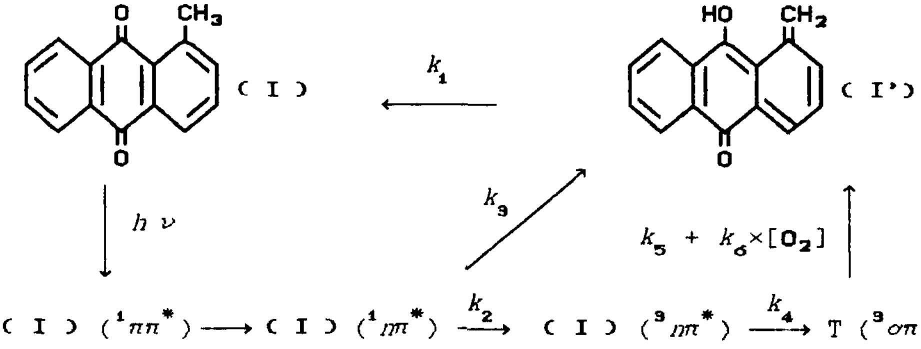
As seen from the above scheme, structural changes caused by the photochemical migration of hydrogen, acyl and aryl groups are similar. However, despite the similar structural changes, these processes turned out to differ in the nature of the photoreactive state and in the details of the mechanism of the photochromic transformation. Details of each type (mainly 1 and 2) photochromic processes will be discussed.

PHOTOCHROMISM OF α-ALKYLANTHRAQUINONE

Thermally reversible photoenolization of methyl derivatives of para-quinones was first discovered for 5-methyl-1,4-naphthaquinone[1] and for 1-methylanthraquinone[2] (I) and series of derivatives with substituents in the anthraquinone ring and methylene group



Migration of the H (or D) atom in the singlet $n\pi^*$ state of 1-methylantraquinone (I) results in formation of the quinone-methide I' in the ground state. If the H (or D) atom migrates in the $^3n\pi^*$ state, the primary product is the triplet-excited quinone-methide (T). Therefore migration of hydrogem atom is adiabatic photochemical reaction at the triplet potential energy surface. The photoenolization process of I and its deutero analogue I-d_6 can be presented in the following rather complex scheme[5]:



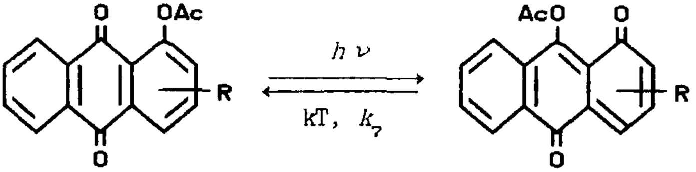
$$(\mathrm{I})\ (^1\pi\pi^*) \longrightarrow (\mathrm{I})\ (^1n\pi^*) \xrightarrow{k_2} (\mathrm{I})\ (^3n\pi^*) \xrightarrow{k_4} \mathrm{T}\ (^3\sigma\pi)$$

Substituents in the anthraquinone ring and in the methylene group have a significant influence on the rate constant of the thermal migration of hydrogen (k_1). It has been found that this effect is related to a change in π-electron density at the carbon atom of the methylene group:

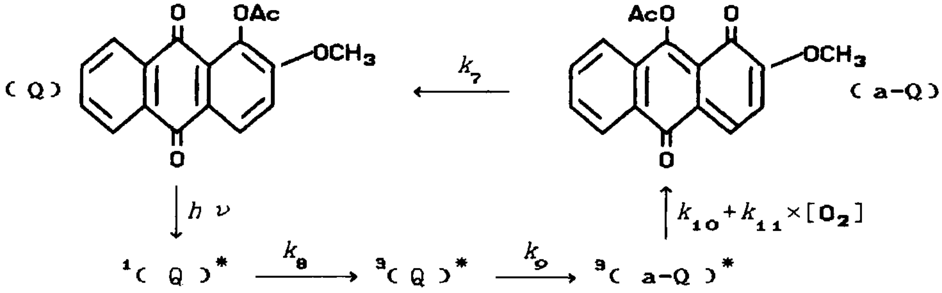
k_1 increases with increasing π-electron density and decreases with decreasing π-electron density. The value of k_1 is also strongly affected by the temperature and nature of the solvent. An increase in polarity and, particularly, in the proton-donor ability of the solvent decreases k_1 by several orders of magnitude.

PHOTOCHROMISM OF α-ACYLOXYANTHRAQUINONE

In 1983, we discovered a new class of photochromic anthraquinone - some substituted 1-acetoxyanthraquinones[3]



The data available confirm the assumption that intramolecular photochemical migration of acyl group is adiabatic reaction at the triplet potential energy surface[6]

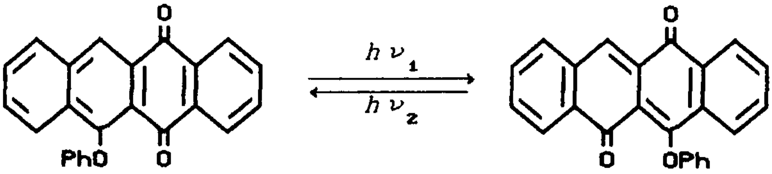


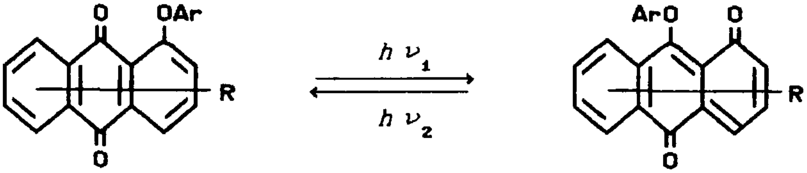
A series of O-acyl derivatives of 1-hydroxy-2-methoxyanthraquinone has been synthesized and investigated in order to control the rate constants of the thermal and photochemical migration of acyl group. It has been found that introduction of donor substituents into the migrating acyl results in a strong decrease in both the thermal and photochemical migration rate constants (k_7, k_9).

PHOTOCHROMISM OF α-ARYLOXYANTHRAQUINONES

Photochromism was first observed for quinones by Yu. E. Gerasimenko and

N. T. Poteleschenko in 1971[4]. On exposure to light, 1-phenoxyantraquinone and 6-phenoxy-5,12-naphthacenequinone have proved to change colour both in solution and in the crystalline state[4]. The photoinduced product disappears on irradiation by visible light, and the spectrum of the initial para-quinone is completely recovered





A substantial disadvantage of photochromic materials based on 1-phenoxyanthraquinone and its derivatives is the limited number of cycles of recording and erasure due to destruction of the photoisomer by the attack of traces of water. The degradative processes are determined by the unusually high reactivity of ana-quinones towards nucleophilic agents. The kinetic studies have shown substituents in the anthraquinone ring to have a substantial effect on the stubility of ana-quinone. Electron-donor substituents (amino- and methoxy-groups) decrease rate constant of the reaction with nucleophils and, hence, enhance the stability of the photoinduced form[6].

REFERENCES

1 E. Rommel, J. Wirz, Helv.Chim.Acta, 60, 38 (1977).
2. N. P. Gritsan, V. A. Rogov, N. M. Bazhin, V. V. Russkikh and E. P. Fokin, Teor.Eksp.Khim., 15, 290 (1979).
3. N. P. Gritsan, S. A. Russkikh, L. S. Klimenko and V. F. Plyusnin, Teor.Exper.Khim., 19, 455 (1983).
4. Yu. E. Gerasimenko, N. T. Poteleschenko, Zh.Org.Chem., 7, 2413 (1971).
5. N. P. Gritsan, I. V. Khmelinski and O. M. Usov, J.Amer.Chem.Soc. 113, 9615 (1991).
6. N. P. Gritsan, L. S. Klimenko, J.Photochem.Photobiol. A: Chem., 70, 103 (1993).