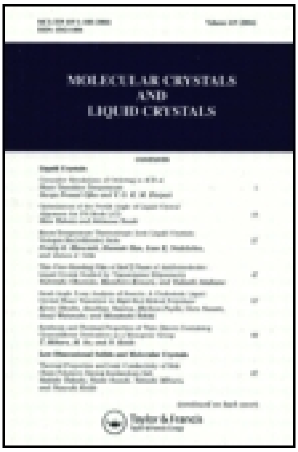


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Photochromic Reactions of 1-Alkylanthraquinones

Zoya Leonenko [a], Lubov Klimenko [a] & Nina Gritsan [a]
[a] Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

Version of record first published: 24 Sep 2006

To cite this article: Zoya Leonenko, Lubov Klimenko & Nina Gritsan (1997): Photochromic Reactions of 1-Alkylanthraquinones, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 297:1, 175-180

To link to this article: http://dx.doi.org/10.1080/10587259708036119

Mol. Cryst. Liq. Cryst., 1997, Vol. 297, pp. 175–180
Reprints available directly from the publisher
Photocopying permitted by license only

PHOTOCHROMIC REACTIONS OF 1-ALKYLANTHRAQUINONES.

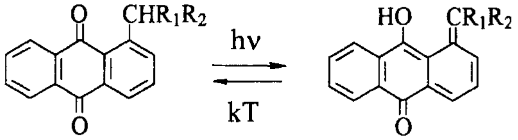
ZOYA LEONENKO, LUBOV KLIMENKO, NINA GRITSAN

Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia

Abstract Under irradiation of 1-alkylanthraquinones, the hydrogen atom of substituted methyl group is transferred to a peri-quinoid oxygen to form the corresponding 9-hydroxy-1,10-anthraquinone-1-methides. It was shown that photochemical reaction occurs through the triplet σπ-biradical. The thermal decay of photoinduced quinone-methides results from three competing parallel processes: intramolecular hydrogen transfer (a thermal back reaction), reaction with a solvent (alcohol), and oxidation by dissolved oxygen. The structure of the transient state and the activation enthalpy for the thermal reaction of hydrogen transfer have been determined quantum chemically.

INTRODUCTION

It is known that 1-methyl-9,10-anthraquinones and some of their derivetives undergo photoenolization to form the deeply coloured 9-hydroxy-1,10-anthraquinone-1-methides.[1-3] These compounds are unstable at room temperature and restore their original structure by a thermal back reaction.



The lifetime of photoproducts depends on the nature of substituents in anthraquinone nuclear and methide group.[1,3] To increase the lifetime of photoproduct, the 1-methylcyano derivatibes of 9,10-anthraquinones (**4**,**5**) were synthesized and their chemical properties were studied.

To understand the influence of chemical structure on the kinetics, the AM1[4] calculations were made, using modified MNDO85 program[5]. The RHF calculations in half electron approximation[6] were performed for the triplet state intermediates.

PHOTOCHEMICAL HYDROGEN TRANSFER

The spectrum of a short-lived intermediate (Figure 1, spectrum 1) has been detected after the nanosecond laser excitation of 1-methylanthraquinone. It was assigned to the triplet σ,π-biradical.[2]

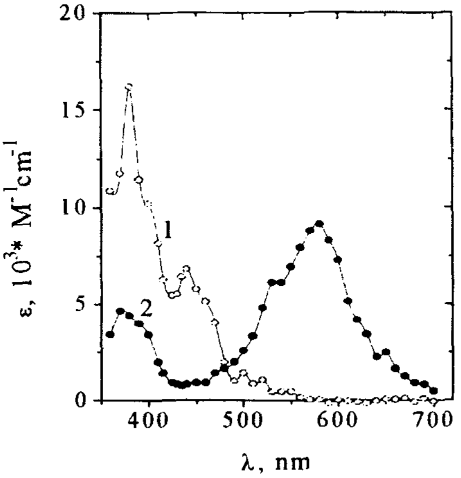


FIGURE 1 Electronic absorption spectra of triplet σπ-biradical (1) and 9-hydroxy-1,10-anthraquinone-1-methide (2) in toluene.

Indeed, there are two minima on the triplet potential energy surface of anthraquinone-methide (Figure 2). One of them corresponds to the $^3\pi\pi^*$ excited state with a plane geometry (Figure 3a). The deepest minimum fits the structure represented in Figure 3b. The plane of methide group is nearly perpendicular to that of anthraquinone nuclear. Two single occupied MO orbitals in this case have the energies -5.04 and -4.68 e.v. The electron of the first σ MO is localized at the carbon atom of

5a at room temperature is described by the first-order equation. In the lamp flash photolysis experiment we have also detected a short-lived intermediate (Table I) with a similar spectrum. Absorbtion recorded under stationary conditions belongs to one isomer, most likely, to the A type.

TABLE I The lifetimes of substituted 9-hydroxy-1,10-anthraquinone-1-methides in ethanol at 290 K (accuracy ±10%).

Comp.	**1**	**2**	**3**	**4**	**5**
τ_A	150 μs	290 μs	2.8 ms	10 s	480 s
τ_B	-	2.5 ms	-	1 ms	5 ms

The rate of thermal decay of **5a** depends on the alcohol nature. When passing from methanol to ethanol, the rate constant (Table II) decreases by a factor of 3, and when passing from ordinary to branched alcohols, this constant decreases by more than an order of magnitude. Photochemical transformations in isopropanol and tert-butanol are reversible. They are irreversible in methanol and ethanol (Figure 5).

TABLE II. Dependence of the rate constant of photoproducts decay (k, s^{-1}) on the nature of alcohol. Accuracy ±10%.

Alcohol	MeOH	EtOH	i-PrOH	t-BuOH
4a	0.75	0.10	0.03	0.05
5a	6.2×10^{-2}	2.1×10^{-3}	3.0×10^{-4}	1.2×10^{-3}

A similar effect of the alcohol nature was observed for the reaction of nucleophilic 1,4-addition of an alcohol molecule to ana-quinones.[7] We specially checked whether the nature of alcohols used influences the rate constant of thermal hydrogen migration in 9-hydroxy-1,10-anthraquinone-1-methide. The rate constants of thermal hydrogen transfer were equal in all alcohols used (methanol, ethanol, 2-propanol, and *tert*-butanol). Therefore, the decay of **4a**, **5a** depends on the nature of alcohols and the photochemical reactions are irreversible in methanol and ethanol. It should be assumed that photoinduced quinone-methides **4a**, **5a** can react with alcohols. The reaction with 2-propanol and *tert*-butanol does not compete with the thermal back transfer of hydrogen. In the case of methanol and ethanol the main contribution to the measered rate constant comes from the reaction with alcohols.

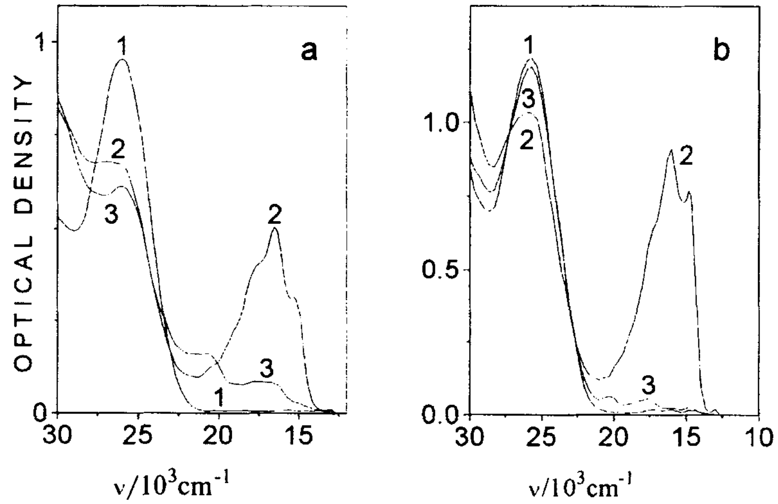
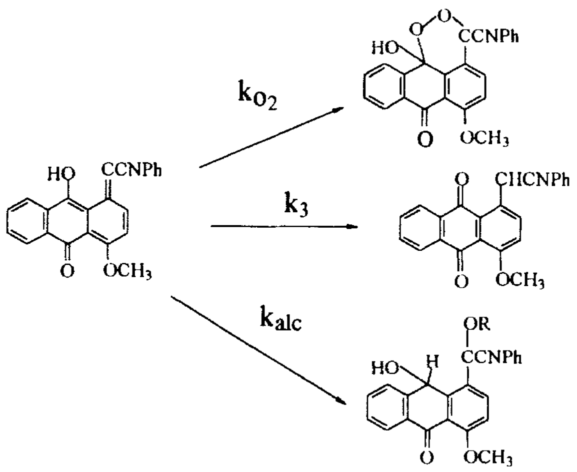


FIGURE 5 Absorption spectrum of quinone **5** (1) and its changes after irradiation for 3s (2) and after thermal decay for 1 h (3) in ethanol (a) and *tert*-butanol (b) in the absence of oxygen.

The lifetime of **5a** depends also on the content of dissolved oxygen (Figure 6). The second order rate constant for the reaction of **5a** with oxygen is 0.42 ± 0.02 l/(mol s). The whole process of 5a decay can be discribed by the following scheme



The rate constants of the three competing processes are presented in Table III.

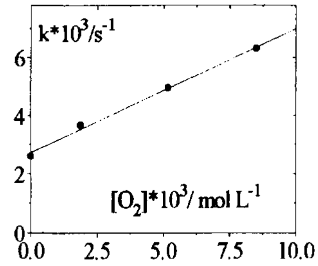


FIGURE 6 Dependence of the rate constant of 9-hydroxy-4-metoxy-1,10-anthraquinone-1-phenylcianomethide decay in ethanol on the concentration of dissolved oxygen at 298 K.

TABLE III The rate constants of the reactions of 9-hydroxy-1,10-anthraquinone-1-(phenylcyano)methide.

k_3, s^{-1}	k_{O2}, l/(mol•s)	k_{MeOH}, l/(mol•s)	k_{EtOH}, l/(mol•s)
$\sim 3\times10^{-4}$	0.42 ± 0.02	6×10^{-2}	2×10^{-3}

Therefore, introdusing strong electron withdrowing substituent to methyl group, we can increase the lifetime of photoinduced form up to 7 orders of magnitude. However, the role of the side reactions becomes importent in this case.

ACKNOWLEDGEMENTS

This work was supported by the Foundation for Fundamental Study of Russia (grant 95-03-08920) and by the Committee of High Education of Russia (program "Chemistry, section "Photochemistry").

REFERENCES

1. N.P. Gritsan, L.S. Klimenko, J. Photochem. Photobiol., A: Chem., 70, 103 (1993).

2. N.P. Gritsan, I.V. Khmelinski, O.M. Usov, J. Amer. Chem. Soc., 113, 9615 (1991).
3. N.P. Gritsan, E.M. Shvartsberg, V.V. Russkikh, I.V. Khmelinski, Zh. Fiz. Khim., 64, 3081 (1990).
4. M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Amer. Chem. Soc. 107, 3902 (1985).
5. A.A. Bliznyuk, A.A. Voityuk, Zh. Struc. Khim., 27, N4, 190 (1986).
6. A.A. Voityuk, Zh. Struct. Khim., 24, N3, 18 (1983).
7. N.P. Gritsan, L.S. Klimenko, Z.V. Leonenko, I.Ya. Managashev, V.I. Mamatyuk, V.P. Vetchinov, Tetrahedron, 51, 3061 (1995).