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REACTIONS OF PHOTOINDUCED 9-ARYLOXY-1,10-ANTHRAQUINONES.

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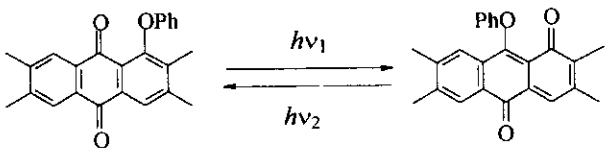
Abstract The reactions of ana-anthraquinones with nucleophiles have been studied in order to find the photochromic compounds with the lowest fatigue. The primary stage of the reaction between 9-aryloxy-1,10-anthraquinones and nucleophiles (water, alcohols, primary amines) is the reaction of nucleophilic 1,4-addition. The electron withdrawing substituents in the anthraquinone increase and the electron donor ones substantially decrease the reaction rate constant favouring the stability of photoinduced 1,10-anthraquinones. All the experimental data on the reactivity of ana-quinones are in a fairly well agreement with the results of AM1 calculations of the electronic properties of ana-quinones.

INTRODUCTION

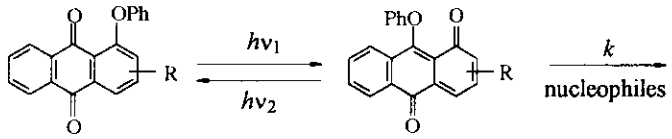
Photochromism of phenoxy derivatives of anthra- and naphthacenequinone is due to the photoinduced isomerization of the yellow para-quinone form to the ana-quinone coloured form.[1,2]



The absence of back thermal reaction is the main advantage of this photochromic process[2]. A very important feature of the photochromic compounds is the absence of side thermal and photochemical reactions of both photochromic forms. It is known that ana-naphthacenequinones are significantly more stable than ana-anthraquinones. The ana-anthraquinones have long been unknown owing to their high reactivity[2]. There are only some reports about successful synthesis of 1,10-anthraquinone derivatives[2-10]. Ana -

anthraquinone can be stabilised by introducing donor [7-10] or bulky substituent in position 9 of anthraquinone[3-6] It was established that position 9 of ana-anthraquinones is the most active in reactions with nucleophiles[2,3,5,8,9,11-13]

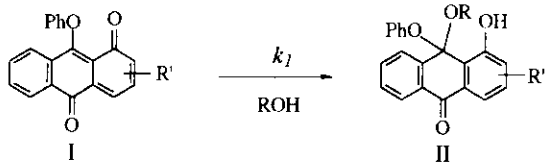
Therefore a high fatigue of the photochromic 1-phenoxyanthraquinones is due mainly to the reaction of ana-anthraquinone form with a traces of water or other nucleophiles.



The reactions of ana-anthraquinones with model nucleophiles (methanol, primary amines) have been studied in order to find the photochromic anthraquinones with the lowest fatigue.

REACTION PRODUCTS

The primary stage of the reaction between 9-phenoxy-1,10-anthraquinones and alcohols is the nucleophilic 1,4-addition[12]



UV spectra of adducts are characterised by intensive long wavelength absorption band with a maxima in the range 350-390 nm. Under the action of UV light adducts II eliminate phenol molecule and convert to the 9-alkoxy-1,10-anthraquinones. These data are in agreement with the results of our AM1 calculations (Figure 1). It is seen from Figure 1, that reaction of 1,4-addition is the exo-ergic process. The reaction of phenol elimination is the ando-ergic one and can be realised only photochemically.

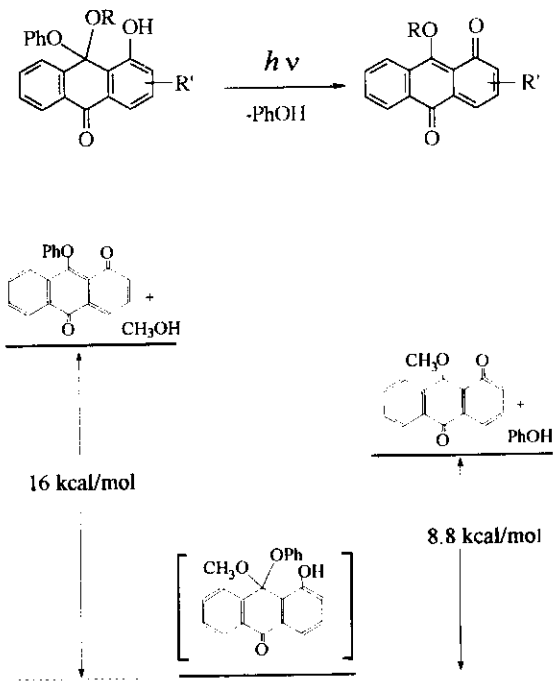
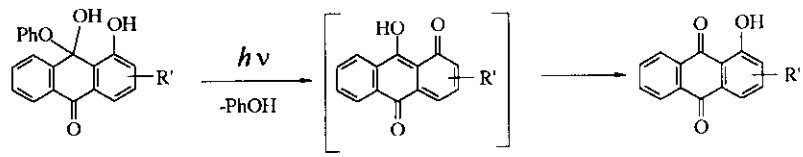


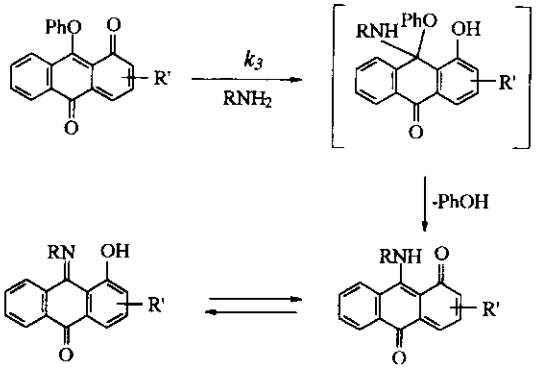
FIGURE 1 Thermodynamics of the reaction of 9-phenoxy-1,10-anthraquinone with methanol. Results of AM1[14] calculations, using MNDO85 program[15]

The similar results were obtain for the reaction of 1,10-antraquinones with water. The adducts are less stable in this case and their formation was detected only spectroscopically. The long wavelength absorption band maxima are in the range of 330-370 nm for the adduct of 1,10-anthraquinones with water. Under the action of UV light adducts convert to the 1-hydroxy-9,10-anthraquinones



The reaction of 9-phenoxy-1,10-anthraquinones with the primary aliphatic and aromatic amines results in the formation of 9-alkyl(aryl)amino-1,10-anthraquinones that are in a tautomeric equilibrium with 1-hydroxy-9,10-anthraquinone-9-alkyl(aryl)imines.[13]

The results of quantum chemical calculations confirm the addition-elimination mechanism of the reaction



Indeed, the reaction of the 1,4-addition of amines is exo-ergic process (Figure 2), and the minimum at the potential energy surface fits the adduct (Figure 3) of 1,10-anthraquinone with amine.

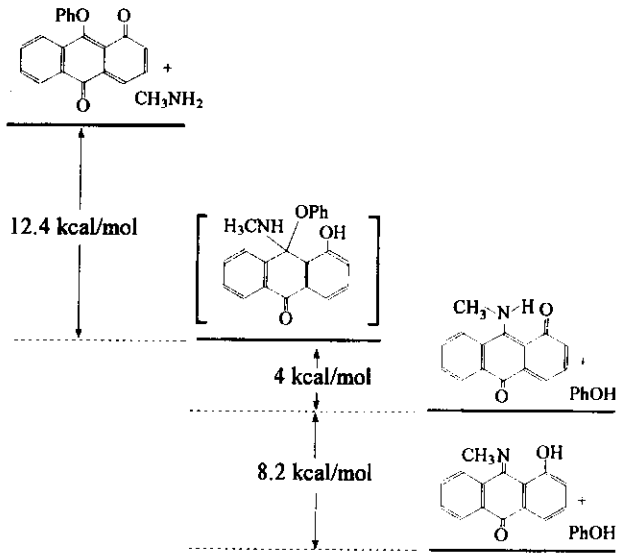


FIGURE 2 Thermodynamics of the reaction of 9-phenoxy-1,10-anthraquinone with methanol. Results of calculations by AM1 method.

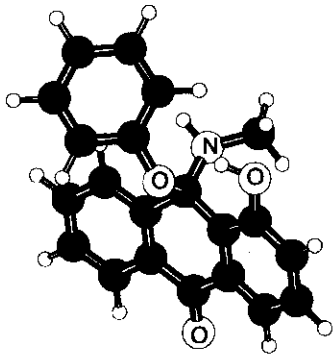


FIGURE 3 A computer generated drawing of the intermediate, 9-phenoxy-9-methylamino-1-hydroxy-10-anthrone.

REACTION KINETICS

Therefore the primary stage of the reaction between 9-phenoxy-1,10-anthraquinones and nucleophiles (water, alcohols, primary amines) is the reaction of nucleophilic 1,4-addition. The nature of nucleophiles effects significantly the rate constant of 1,4-addition. The rate constant is decreased by about four orders of the magnitude upon transition from alkyl amines to alcoholes (Table I).

TABLE I Rate constants of the reactions with methanol (k_1), water (k_2) and iso-propylamine (k_3) in toluene at 298 K and the results of AM1 calculations for 9-phenoxy-1,10-anthraquinone derivatives.

R′	k_1, $M^{-1} s^{-1}$	k_2, $M^{-1} s^{-1}$	k_3, $M^{-1} s^{-1}$	q	ρ_{LUMO}	E_{LUMO}
2-NO_2	4.2	-	$(2.1\pm0.2)\times10^4$	0.19	0.17	-2.63
4-NO_2	-	-	$(5.8\pm0.5)\times10^3$	0.20	0.19	-2.54
H	0.3	0.02	150±10	0.16	0.17	-1.95
2-OCH_3	-	-	21±1	0.15	0.17	-1.85
4-OCH_3	7×10^{-3}	-	5.4±0.5	0.14	0.17	-1.82
2-$NHCH_3$	3×10^{-4}	-	4.0±0.2	0.14	0.18	-1.75
naphthace-nequinone	$\approx10^{-5}$	-	-	0.14	0.15	-1.83

It is seen from Table I, that the substituents in anthraquinone effect the rate constants of the reactions with alcohol and amine similarly. The electron withdrawing substituents in the anthraquinone increase and the electron donor ones substantially decrease the reaction rate constant favoring the stability of photoinduced 1,10-anthraquinones (Table I).

As mentioned above, the ana-naphthacenequinone is significantly less reactive than ana-anthraquinones. Even the most stable 2-aminosubstituted 9-phenoxy-1,10-anthraquinone has about an order of magnitude higher value of the rate constant of the reaction with methanol.

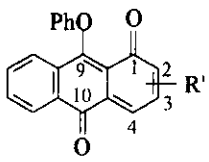
DISCUSSION

According to the perturbation theory and taking into account only boundary MO of reactants[16] one can estimate the interaction between reactants

$$\Delta E = \Delta q_a \Delta q_b \Gamma / \varepsilon + \Delta E_{solv} + \frac{2(c_a^{HOMO})^2 (c_b^{LUMO})^2 \gamma_{ab}^2}{\varepsilon_{HOMO}^a - \varepsilon_{LUMO}^b},$$

where Δq_a and Δq_b are the total charges of atoms a and b; Γ is the term of Coulomb interaction between atoms a and b; ε is a local dielectric constant; ε_{LUMO} and ε_{HOMO} are the energies of the electrophile LUMO and the nucleophile HOMO.

This formula and the "rule of non-intersection"[16] are the basis of a lot of correlations between the values of the rate constant and properties of reactants. Our experimental results correlate fairly well with a data of quantum chemical calculations of charge distribution and other properties of ana-quinones



Positive charges are localized only on the carbon atoms C_1, C_{10} ($q \cong 0.3$) and C_9 ($q = 0,15$) of ana-anthraquinone. Other carbon atoms have the negative charges. It is

one of the reason of the high reactivity of the position 9. From the other hand, the most preferable position for nucleophile attack is the atom with a largest value of the electron density in the lowest unoccupied molecular orbital (LUMO).[16] Indeed, the p_z-AO of C_9 gives the main contribution to the LUMO of 9-phenoxy-1,10-anthraquinone. The boundary electronic densities are equal to 0.17 for C_9, 0.14 for C_4 and 0.06 for C_2.

It is seen from Table I that structure of ana-quinones effects significantly the rate constant of nucleophilic addition. This effect correlate with the charge on reaction center. The value of boundary electronic density (ρ_{LUMO}) practically does not depend on the substituent nature. It was found that the substitution influences mainly the energy of the boundary MO (Table I). Significantly less reactivity of ana-naphthacenequinones is in the agreement with the smaller values of C_9 charge and ρ_{LUMO} (Table I). Figure 4 demonstrates a fairly well correlation of 1,4 addition rate constant with the data for ana-quinone LUMO.

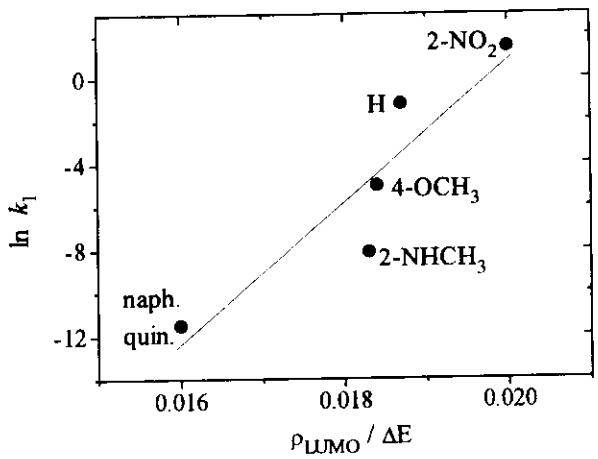


FIGURE 4. Correlation of the rate constant of the ana-quinone reaction with methanol with a data for ana-quinone LUMO.

Therefore the photoinduced form of photochromic phenoxy-quinones can be stabilized significantly by introducing the donor substituents in the quinone rings. All the experimental data on the reactivity of ana-quinones are in a fairly well agreement with

the results of AM1 calculations of the electronic properties of ana-quinones.

ACKNOWLEDGMENTS

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