Kinetic studies on the reaction of 9-aryloxy-1,10-anthraquinones with alkyl and arylamines

Z. V. Leonenko,[a] N. P. Gritsan,[a]* and L. S. Klimenko[b]

[a]Novosibirsk State University, Institute of Chemical Kinetics and Combustion, Siberian Branch
of the Russian Academy of Sciences, 3 ul. Institutskaya, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 352 350
[b]Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences,
9 ul. Akad. Lavrent'eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 354 752

The kinetics of the reactions of 9-aryloxy-1,10-anthraquinone derivatives with aliphatic and aromatic amines was studied. The limiting stage of the reaction is the nucleophilic 1,4-addition. Electron withdrawing substituents in anthraquinone increase and electron donor substituents considerably decrease the rate constant, stabilizing photoinduced 1,10-anthraquinones. The geometric and electronic structures of the amine also affect the rate constant. On going from alkylamines to aniline, the rate constant decreases by more than an order of magnitude. The introduction of electron donor substituents into the aniline molecule leads to an increase in the rate constant, while the introduction of electron withdrawing substituents leads to its decrease. The significant negative activation entropy of the reaction between 1,10-anthraquinone derivatives and *n*-propylamine leads one to the conclusion that the transition state is highly ordered. The reaction occurs easily due to the low activation enthalpy ($\Delta H^{\#}$ = 2÷7 kcal mol^{-1}).

Key words: 9-aryloxy-1,10-anthraquinones, nucleophilic substitution, rate constant, quantum chemical calculations, electron structure.

1,10-Anthraquinone derivatives, owing to their high reactivity, were not known for a long time.[1] There are only a few reports concerning successful synthesis and separation of 1,10-anthraquinone derivatives,[1—9] made possible by screening of position 9 by bulk substituents[2—5] or, in the case of stabilization of 1,10-anthraquinone, by the introduction of electron donor groups into various positions of the molecule including position 9 (Refs. 6—9). In the anthraquinone molecule, position 9 was found to be the most active in reactions with nucleophiles.[1,2,4,7,10—12] Under the action of hydrogen halide, the 1,4-addition of a nucleophile molecule takes place, while the reactions with water, hydrogen sulfide, and the anions of CH-acids resulted in the replacement of the group at position 9.[4,8,10]

Previously we have found[1,11] that the first stage of the reaction between 9-aryloxy-1,10-anthraquinone and alkohols is nucleophilic 1,4-addition to give the corresponding 1-hydroxy-9-alkoxy-10-anthrone. In the reaction of 9-aryloxy-1,10-anthraquinones with primary aliphatic and aromatic amines, an equilibrium mixture of 1,10-anthraquinon-9-amine and 1-hydroxy-9,10-anthraquinon-9-imine is formed. These compounds are formally products of the replacement of the aryloxy group at the position 9 with an amino group.[12,13]

The sole kinetic investigation of the reactivity of 1,10-anthraquinones was carried out for the nucleophilic addition of alcohols to 9-aryloxy-1,10-anthraquinone derivatives.[11] The aim of this study is the kinetic investigation of the reaction of 9-aryloxy-1,10-anthraquinone derivatives with aliphatic and aromatic amines and the elucidation of the relationship between the rate constants and the chemical structures of the reagents.

Experimental

The reaction of 9-aryloxy-1,10-anthraquinones with amines was followed by the variation in time of the long-wave adsorption of 1,10-anthraquinones. 9-Aryloxy-2-methylamino-1,10-anthraquinone was synthesized and isolated using the procedure described earlier.[9,12] Less stable 9-aryloxy-1,10-anthraquinone derivatives were obtained by the irradiation of the corresponding 1-aryloxy-9,10-anthraquinones in the presence of amines. The irradiation of the solutions was carried out with the light of a DRSh-500 high-pressure mercury lamp. The required spectral regions were selected using glass light filters. Electron adsorption spectra were recorded on a Specord UV VIS instrument. Measurements of the rate constants were carried out with a significant excess of amine, hence the kinetic curves were described by the equations of a pseudo-unimolecular reaction. The effective rate constant depends linearly on the amine concentration. In all cases the rate constants of the second-order reaction were determined with an accuracy not less than ±10 %.

When the reactions were fast, *i.e.*, when the half-life of 9-aryloxy-1,10-anthraquinones in the presence of amines was

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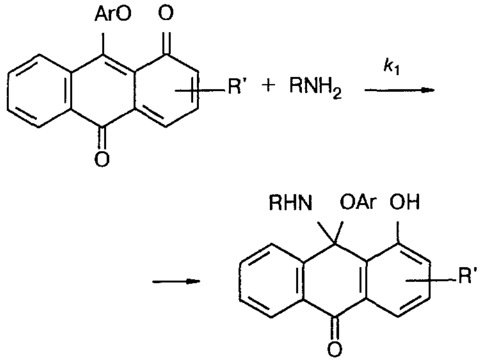
in the range from several milliseconds to seconds, an automatic setup for lamp pulse photolysis[14] was used in the kinetic experiments. The 9-aryloxy-1,10-anthraquinone derivatives were obtained by pulse excitation of the corresponding 1-aryloxy-9,10-anthraquinone.

The temperature of the samples was maintained and varied between 15 and 60 °C with an accuracy of 0.5 °C with a U-8 thermostat. Toluene (reagent grade) was distilled, and hexane was dried over Na and distilled. Acetonitrile was boiled over P_2O_5 for 1 h and distilled.

Quantum chemical calculations of the geometry, distribution of the electron density, and the enthalpy of formation of the examined compounds and assumed intermediates were performed by the AM1 method[15] using a modified MNDO-85 program.[16] For optimization of geometry, the standard procedure[17] was used. The distribution of the electron density was also calculated by MNDO[18] and PM3[19] methods using the program from Ref. 16 and by INDO[20] method using the program from Ref. 21.

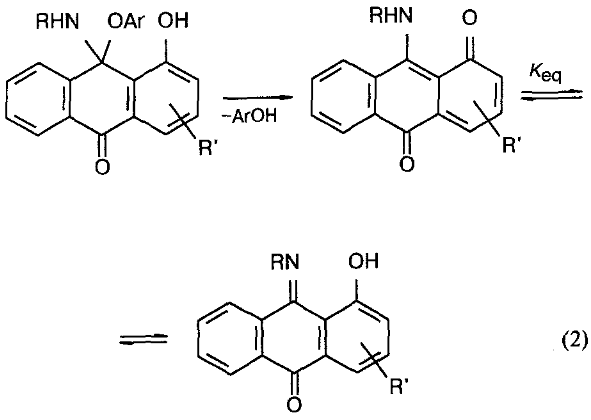
Results and Discussion

The first step of the investigated reaction between 1,10-anthraquinone and amines is a nucleophilic 1,4-addition to form an adduct (tetrahedral intermediate).[12]



(1)

However, in this case the adduct is unstable and rapidly elliminates a phenol molecule to form a substitution product.

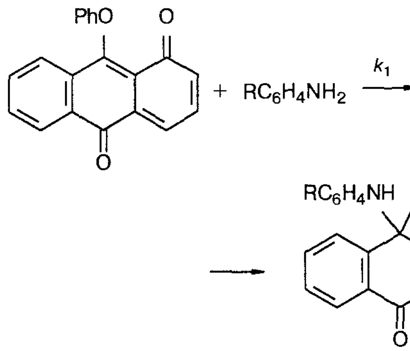


(2)

The formation of the adduct was not followed under stationary conditions at a low temperature (−100 °C) or in the pulse experiments at room temperature. This is because reaction (1) is the limiting stage. Therefore, as in the case of the reaction with alcohols,[11] in this study the rate constant of nucleophilic 1,4-addition was measured.

The nature of the amine has a considerable effect on the rate constant of nucleophilic addition. The rate constants k_1 (L (mol s)$^{-1}$) of the reactions between 2-methylamino-9-(*n-tert*-butylphenoxy)-1,10-anthraquinone and primary amines (RNH_2) in toluene at 305 K for propyl are equal to 24.0±0.2, butyl — 19.0±1.0, isopropyl — 4.0±0.2, benzyl — 21.7±0.1, phenyl — 0.56±0.05. The difference in the rate constants is mainly related to their spatial structure. The rate constants are close for the *n*-alkyl substituents and decrease substantially for the branched isopropyl substituent. The rate constant drops considerably on going from alkylamines to aniline due to the electron effect of the substituent and delocalozation of the unshared electron pair of the nitrogen atom in the aniline molecule.

The electron effect of the substituent on the rate constant of the 1,4-addition reaction was found to be the most pronounced in the series of substituted anilines.



(3)

The introduction of electron donor substituents considerably increases the rate constant of 1,4-addition (Table 1), as it should be for nucleophiles.

The rate constant depends considerably also on the substituents in the anthraquinone ring. The influence of electron donor and acceptor substituents at positions 2 and 4 in the anthraquinone molecule was studied (Table 2). The previously published data[11] on the reaction between substituted 1,10-anthraquinones and methanol are shown for comparison in Table 2. As can be seen, the influence of the nature of the substituents on the rate of both reactions coincides qualitatively. Electron acceptor substituents increase the rate constant, while electron donor substituents decrease it. However, the extent of the influence is less in the case of more reactive amines (Table 2). Moreover, the introduction of substituents at position 4 has a greater effect than that at position 2.

Table 1. Dependence of the rate constant (k_1) and the heat of reaction (ΔH_1) for 1,4-nucleophilic addition of substituted anilines to 9-phenoxy-1,10-anthraquinone on the donor substituents

R	k_1[a] /L (mol s)$^{-1}$	ΔH_1[b] /kcal mol^{-1}	q	ρ_π	ρ_{HOMO}	E_{HOMO} /eV	μ_{theor} /D	μ_{exp} /D
p-OH	$5.9 \cdot 10^3$	−10.1	−0.32	1.66	0.21	−8.28	2.17	—
			0.22[c]	1.71[c]	0.25[c]	−9.85[c]		
p-OCH$_3$	$1.5 \cdot 10^3$	−10.2	−0.32	1.66	0.21	−8.22	2.13	1.87
p-CH$_3$	$3.3 \cdot 10^2$	−10.3	−0.33	1.67	0.23	−8.36	1.42	1.36
H	$1.2 \cdot 10^2$	−10.2	−0.33	1.68	0.27	−8.52	1.54	1.48
			−0.22[c]	1.73[c]	0.36[c]	−10.60[c]		
m-CF$_3$	$1.3 \cdot 10^1$	−10.1	−0.32	1.68	0.29	−9.04	4.05	—
p-COCH$_3$	4.4	−9.7	−0.34	1.71	0.26	−8.78	4.35	4.38
p-NO$_2$	0.4	−9.6	−0.38	1.80	0.29	−9.17	7.60	5.6
			−0.22[c]	1.85[c]	0.36[c]	−11.07[c]		

Note. q — charge value, ρ_π — π-electron density, ρ_{HOMO} — boundary electron density at the nitrogen atom, E_{HOMO} — energy of the highest occupied MO of substituted anilines, μ — dipole moment.

[a] Experimental data. [b] Calculated by AM1 method. [c] Calculated by AM1 and INDO methods.

Table 2. Dependence of the rate constants of the reaction between 9-(n-*tert*-butylphenoxy)-1,10-anthraquinone derivatives and isopropylamine (k_1) and methanol (k_2) in toluene at 298 K on the nature of the substituent in the anthraquinone ring (R')

R'	k_1 /L (mol s)$^{-1}$	k_2 /L (mol s)$^{-1}$	q_C	ρ_{LUMO}	E_{LUMO} /eV
2-NO$_2$	$(2.1\pm0.2) \cdot 10^4$	4.2	0.19	0.17	−2.63
4-NO$_2$	$(5.8\pm0.5) \cdot 10^3$	—	0.20	0.19	−2.54
H	150±10	0.3	0.16	0.17	−1.95
2-OCH$_3$	21±1	—	0.15	0.17	−1.85
4-OCH$_3$	5.4±0.5	$7 \cdot 10^{-3}$	0.14	0.17	−1.82
2-NHCH$_3$	4.0±0.2	$3 \cdot 10^{-4}$	0.14	0.18	−1.75

Note. q_C — charge values calculated by AM1 method; ρ_{LUMO} — boundary electron density at the carbon atom of the reaction centre; E_{LUMO} — energy of the lowest unoccupied molecular orbital of substituted 9-phenoxy-1,10-anthraquinone. E_{HOMO} p-$C_3H_7NH_2$ = −9.8 eV; E_{HOMO} CH_3OH = −11.04 eV.

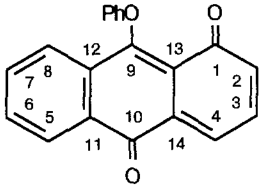
Inert aprotic solvents, such as hexane, toluene, and acetonitrile, thoroughly dehydrated to exclude the reaction of 1,10-anthraquinones with water, were used as the solvents. The increase in solvent polarity in this series leads to an increase in the rate constant, which indicates the better solvation of the transition state and, consequently, its greater polarity in comparison with the initial reagents (however the extent of the effect is small). We obtained the following values of k_1 (L (mol s)$^{-1}$) for the reaction between 2-methyl amino-9-phenoxy-1,10-anthraquinone and isopropylamine: hexane — 3.4±0.1, toluene — 4.0±0.2, acetonitrile — 6.9±0.4.

The temperature dependence of the rate constant of nucleophilic addition was studied for the reaction of the 9-phenoxy-1,10-anthraquinone derivatives with methanol and propylamine. The experimental temperature dependences of the rate constants are well described by Arrenius' law. The experimental values of the pre-exponential factor (A) and the activation energies (E_a), as well as those of the activation entropy ($\Delta S^{\#}$) and enthalpy ($\Delta H^{\#}$) calculated on the basis of these data, are presented in Table 3.

The reaction of nucleophilic addition at the carbonyl group (1,2-addition) is the most typical for carbonyl compounds, including those that are unsaturated.[23,24] In our case, position 9 in ana-anthraquinones is the most active towards nucleophilic agents.[1,2,4,5,7,8,10–12] When it is schielded by a bulk substituent, attack at position 4 becomes possible. Then, in the case of a significant excess of the reagent, position 2 can also be attacked by strong nucleophiles.[4,5] These data correlate well with the results of quantum chemical calculations of the charge distribution in the initial 1,10-anthraquinone.

Table 3. Activation parameters of the rate constants of the reaction of 9-(*n*-*tert*-butylphenoxy)-1,10-anthraquinone with methanol and *n*-propylamine in toluene

Substituent in quinone	Nucleophile	k_{298} /L (mol s)$^{-1}$	logA	E_a /kcal mol^{-1}	$\Delta S^{\#}$ /cal (mol deg)$^{-1}$	$\Delta H^{\#}$ /kcal mol^{-1}
2-$NHCH_3$	CH_3OH	0.0003	9.1±0.6	17.1±0.9	−18.8±1.4	16.5±0.9
2-$NHCH_3$	*n*-$C_3H_7NH_2$	16.2	7.0±0.1	7.9±0.1	−28.4±0.3	7.3±0.2
H	*n*-$C_3H_7NH_2$	510	5.7±0.1	4.1±0.2	−34.4±0.4	3.5±0.2
2-NO_2	*n*-$C_3H_7NH_2$	910	6.8±0.1	2.5±0.1	−29.3±0.3	1.9±0.1



The positive charge is localized at the C(1), C(10) (q = 0.3) and C(9) (q = 0.15) carbon atoms of ana-anthraquinone. The rest of the carbon atoms are negatively charged, and C(4) (q = −0.05) is the least negatively charged.

The position with the highest partial electron density at the lowest unoccupied molecular orbital (LUMO) is known, as a rule, to be the most vulnerable to attack by nucleophilic reagents.[25] In the case of 9-phenoxy-1,10-anthraquinone, the *p*-AO of carbon atom C(9) actually makes the greatest contribution to the LUMO (π-type orbital). The boundary electron density at C(9) is equal to 0.19, while that at C(4) is somewhat lower (0.14), C(2) is still less (0.06) and that at the other carbon atoms is negligibly small (0.002—0.04).

Moreover, the calculations of the heats of 1.2- and 1,4-addition with methanol and methylamine also give evidence for the significant thermodynamic advantage of the 1,4-addition reaction: $\Delta H = -16$ and -3 kcal mol^{-1}, respectively, for 1,4- and 1,2-addition of a methanol molecule and −13 and 0.2 kcal mol^{-1} for the addition of a methylamine molecule. Therefore, the calculated data are in agreement with the fact that for 1,10-anthraquinone derivatives position 9 is the object of the nucleophilic attack.

It is seen from Table 2 that the substituents in the anthraquinone ring have a considerable effect on the value of the rate constant: electron donor substituents reduce it more than an order of magnitude, whereas electron acceptor substituents increase it by over two orders of magnitude. As the rate constant changes, the value of the positive charge at the atom C(9) also changes somewhat. The value of the boundary electron density at C(9) virtually does not depend on the introduction of substituents. However, in this case the energy of the boundary LUMO changes significantly. Upon the introduction of acceptor substituents, its energy decreases and the energy difference between the LUMO of the quinone molecule and the highest occupied MO (HOMO) of a nucleophile (amine or alcohol) molecule is correspondingly decreased. In the case of donor substituents, the LUMO energy of anthraquinone molecules increases, and the energy difference between the LUMO and HOMO of the nucleophile molecule increases.

Substituents in the nucleophilic reagent, *viz.* substituted aniline, also have a significant effect on the rate constant: electron donor substituents increase the rate constant by more than one order of magnitude, while acceptor substituents reduce it by over two orders of magnitude. As this takes place, a satisfactory correlation between the logarithm of the rate constant and the σ-constant of the substituent is observed, with the slope $\rho = -1.78 \pm 0.08$ (the correlation coefficient is equal to 0.995). For electron donor substituents, σ^+ constants are used, while for electron acceptor substituents at the *para*-position the constant is σ^-.

According to a common view, the introduction of substituents leads to a change in the charge at the reaction center. A correlation of the rate constants with the σ^+ constants for electron donor substituents and with σ^- for electron acceptor substituents is believed to indicate the predominant influence of π-electron density on the reaction rate.[24] However, according to the data of quantum chemical calculations (see Table 2), in the case under consideration the introduction of substituents does not lead at all to a significant the change in charge at the reaction center (nitrogen atom). Upon the introduction of substituents at the *meta*- and *para*-positions, neither the π-electron density nor the total charge are really changed. Similar results were obtained using the semiempirical AM1,[15] MNDO,[18] PM3,[19] and INDO[20] methods. All of the considered methods are parameterized in the way that best reproduces the heats of formation of the compounds. Therefore, the charge distribution cannot be reproduced well. However, numerous calculations of the dipole moment of the molecules (an experimental characteristic related to the electron density distribution) are in good agreement of calculated and measured values.[19] For substituted anilines the agreement between the calculated and experimental values of the dipole moments is also satisfactory (see Table 2). A simplified interpretation of the Hammett correlations, which reflect the effect of changes in the charge at the reaction centers on the reaction rates, seems to be inadequate.

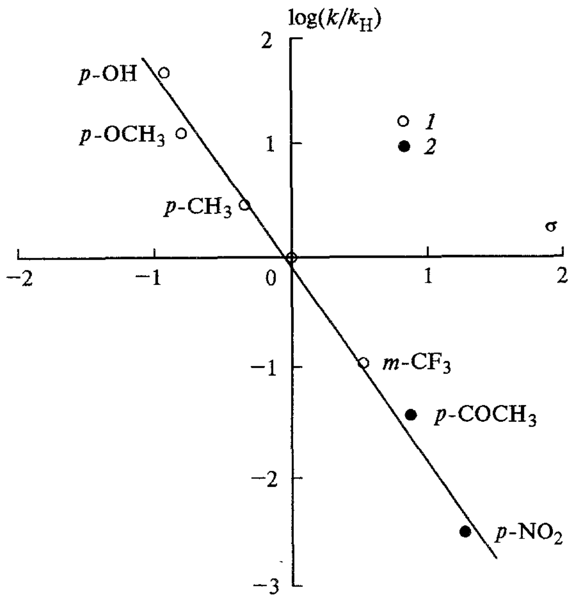


Fig. 1. Dependence of the rate constant of the reaction between substituted anilines and 9-(*n-tert*-butylphenoxy)-1,10-anthraquinone in acetonitrile on the nature of the substituent (*1* — on σ^+, *2* — on σ^-).

All correlations of the rate constants with different reactivity indices (such as charge, boundary electron density) are based on the "rule of non-intersection".[26] This suggests that for similar compounds the ratio of the energies at arbitrary points along the reaction coordinate (including the initial stage of the reaction, when the perturbation theory is valid) is proportional to the ratio of the activation energies. In the framework of the perturbation theory, the interaction energy can be presented as the sum of several components.[25]

$$\Delta E = \Delta q_a \Delta q_b \Gamma / \varepsilon + \Delta E_p + \sum_i^{\text{oc.}} \sum_j^{\text{unoc.}} \frac{2(c_a^i)^2 (c_b^j)^2 \gamma_{ab}^2}{\varepsilon_i - \varepsilon_j}$$

where Δq_a is the total initial charge of atom a; Γ is the term of Coulomb interaction between atoms a and b; ε is a local dielectric constant; ε_i is the energy of the i-th occupied (oc.) MO of the nucleophile; ε_j is the energy of the j-th unoccupied (unoc.) MO of the electrophile. In the simplest case only one term of the sum is taken into account: i — HOMO of the nucleophile, j — LUMO of electrophile. It can be seen that the third term should increase in absolute magnitude both as the boundary electron density increases and as the energy difference decreases.

According to the data of Table 1 there is a correlation between the rate constants and the values of boundary electron density in the substituted anilines. However, as in the case of the introduction of substituents in ana-anthraquinone, the substitution in aniline changes the energy difference between the LUMO of quinone and the HOMO of the aniline molecule considerably. Acceptor substituents decrease the energy difference, while donor substituents increase it. This is bound to lead to an increase in the rate constants when donor substituents are introduced and their decrease when acceptor substituents are introduced, which is indeed observed experimentally.

From the data of Table 3 it follows that the influence of substituents in the anthraquinone ring is due primarily to changes in the activation energy of the reaction. The change in the pre-exponential factor upon the introduction of substituents does not correlate with the change in the rate constant. The very low values of the pre-exponential factors (10^6—10^7 M^{-1} s^{-1}) and the corresponding high negative value of the activation entropy (on the order of 30 entropy units) are noteworthy. Such low $\Delta S^{\#}$ values indicate that the transition state is rigid and highly ordered. It should be mentioned that in the case of the 1,4-nucleophilic addition of methanol, which has a similar mechanism, the absolute value of $\Delta S^{\#}$ is noticeably lower (−19 entr.un.), which appears to be due to the lower rigidity of the transition state in this case.

Therefore, all of the obtained experimental results concerning the influence of the rate constant of the reaction of alkyl- and arylamines with 1,10-anthraquinone derivatives fall into the framework of the viewpoint that the limiting stage of the process is the 1,4-nucleophilic addition of an amine molecule.

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