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Role of Association of Yanovskii Anionic σ Adducts in Their Oxidation with Quinones

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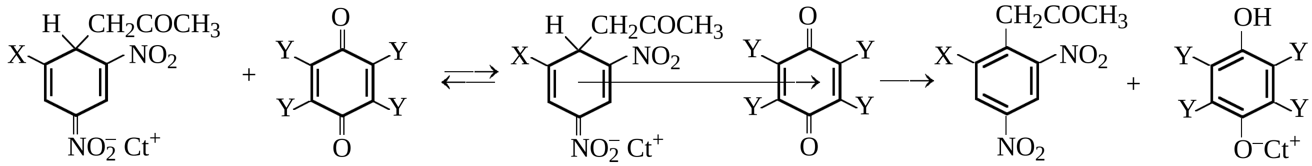
Abstract—In oxidation of 1,3-dinitro- and 1,3,5-trinitrobenzene acetonate σ adducts (Yanovskii complexes) with sodium, potassium, and tetrabutylammonium cations in acetonitrile and tetrahydrofuran (290–313 K), ion pairs are less reactive than free ions, which is explained by charge redistribution in the ring of the σ adducts, decreasing the electron-donor power of the associated anion. Separation of the apparent rate constants into ionic and ion-pair contributions showed that the reactivity of the ion pairs depends on the radius of their cation. The revealed kinetic regularities are interpreted on the basis of AM1 semiempirical quantum-chemical calculations of the ions and ion pairs with lithium cation.

Anionic σ adducts of electron-deficient arenes exist in solutions as solvated ions and ion pairs of different types with different abilities to solvolysis [1] and reactions with electrophiles [2] and oxidants [3]. However, the role of association in oxidation of σ adducts, which is one of efficient ways of introduction of C–C bonds in aromatic systems, have scarcely been studied. Moreover, there has been lack of information in literature about quantitative characteristics of the ions and ion pairs of σ adducts.

In this connection we performed a spectrophotometric study of the kinetics of oxidation of sodium (a), potassium (b), and tetrabutylammonium (c) 1-acetonyl-2,4-dinitro-6-X-cyclohexa-2,5-dienides [X = H (**I**), NO_2 (**II**)] with 1,4-benzoquinone (**III**) and 2,3,5,6-tetrabromo-1,4-benzoquinone (**IV**) in MeCN and THF.

The oxidation reaction has an overall second order and involves formation of a donor–acceptor ion-pair intermediate **V** whose accumulation and consumption can be followed by the absorbance in the region of 12 000 cm^{-1} [4].



Ia–Ic, IIa–IIc **III, IV** **Va–Vc, VIa–VIc** **VII, VIII** **IXa–IXc, Xa–Xc**

X = H (**I, V, VII**), NO_2 (**II, VI, VIII**); Y = H (**III, V, IX**), Br (**IV, VI, X**); $Ct^+ = Na^+$ (a), K^+ (b), $[N(C_4H_9)_4]^+$ (c).

In acetonitrile (ε 36.0), where σ adducts are mostly present as free ions, the rate constant is independent of the concentration of σ adducts [k_2 (**Ib**) $(2.19 \pm 0.06) \times 10^{-1}$ l mol^{-1} s^{-1} (298 K)]. In THF the rate constant decreases with increasing concentration of σ adducts (Table 1), on account of increasing fraction of the tight ion pair.

The reactivity of ions and ion pairs was estimated by the Acree equation [5].

$$k_{app} = k_i\alpha + k_{ip}(1 - \alpha).$$

Here k_{app} is the apparent second-order rate constant, k_i and k_{ip} are the oxidation rate constants of ions and

Table 1. Second-order rate constants for oxidation of σ adducts **Ia**–**Ic** and **IIa**–**IIc** in THF (298 K)

$c_{ad} \times 10^4$, M	**Ia**		**IIa**		**Ib**	
	$k_2 \times 10$, l mol^{-1} s^{-1}	α	$k_2 \times 10^2$, l mol^{-1} s^{-1}	α	$k_2 \times 10$, l mol^{-1} s^{-1}	α
7.14	1.71 ± 0.08	0.275			2.94 ± 0.09	0.179
6.66	1.83 ± 0.04	0.283	1.00 ± 0.02	0.310	3.47 ± 0.13	0.185
5.55	1.91 ± 0.10	0.305	1.03 ± 0.01	0.334	3.63 ± 0.08	0.203
3.33	1.98 ± 0.06	0.374	1.18 ± 0.03	0.407	4.54 ± 0.11	0.263
2.22	2.33 ± 0.11	0.435	1.99 ± 0.01	0.471	5.05 ± 0.09	0.322
1.33			2.52 ± 0.13	0.557	5.23 ± 0.12	0.415
0.67	2.63 ± 0.12	0.637	3.54 ± 0.25	0.674	5.37 ± 0.09	0.588
0.62	2.67 ± 0.14	0.648				
0.50	2.87 ± 0.09	0.685	7.74 ± 0.04	0.728	5.50 ± 0.29	0.678
0.33			11.7 ± 0.40	0.781		

$c_{ad} \times 10^4$, M	**IIa**		**Ic**		**IIc**	
	$k_2 \times 10^2$, l mol^{-1} s^{-1}	α	$k_2 \times 10$, l mol^{-1} s^{-1}	α	$k_2 \times 10^2$, l mol^{-1} s^{-1}	α
7.14	2.44 ± 0.02	0.286	1.78 ± 0.06	0.472	0.398 ± 0.024	0.448
6.66	3.08 ± 0.03	0.294	2.01 ± 0.02	0.483	0.729 ± 0.051	0.459
5.55	3.06 ± 0.01	0.317	2.10 ± 0.05	0.514	0.843 ± 0.032	0.484
3.33	4.53 ± 0.13	0.388	2.13 ± 0.03	0.601	0.991 ± 0.012	0.576
2.22			2.39 ± 0.06	0.669	1.03 ± 0.02	0.644
1.33	9.81 ± 0.15	0.535	2.54 ± 0.13	0.751	1.29 ± 0.05	0.728
0.67	29.2 ± 1.4	0.653	2.58 ± 0.02	0.842	1.57 ± 0.08	0.825
0.62	39.7 ± 1.3	0.694			2.30 ± 0.03	0.833
0.50			2.72 ± 0.08	0.873	2.40 ± 0.14	0.858
0.33	61.8 ± 2.2	0.763	3.21 ± 0.12	0.908	2.98 ± 0.70	0.897

ion pairs, respectively, and α is the dissociation degree of σ adducts, determined by conductometry.

The k_i values for σ adducts **Ia**–**Ic** are higher than k_{ip}, and k_{ip} increase in the order $K^+ > Na^+ > [N(C_4H_9)_4]^+$. This result can be explained in terms of the increasing radius of solvated cation, which enhances steric hindrances to formation of intermediate **V** and thus slows down the reaction. The dependence of $k_{app}/(1 - \alpha)$ on $\alpha/(1 - \alpha)$ for 1,3,5-trinitrobenzene σ adducts is not linear (Fig. 1), and, therefore, the apparent rate constants are impossible separate into ionic and ion-pair contributions by the Akri equation.

The plots of $\ln k_i/k_{ip}$ on $\ln K_d$ (K_d is the dissociation constant) for σ adducts **Ia**–**Ic** (Fig. 2) are straight lines with positive slopes, which, too, suggests that the reactivity of ion pairs increases with increasing degree of binding of the anion with the cation.

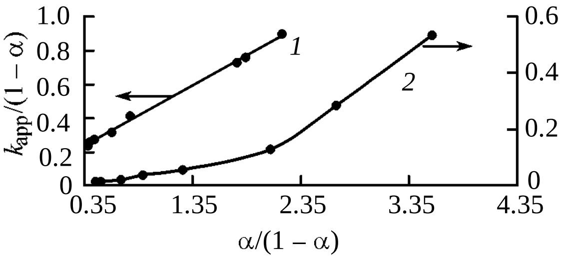


Fig. 1. Plot of $k_{app}/(1 - \alpha)$ vs. $\alpha/(1 - \alpha)$ for σ adducts. (*1*) Compound **Ia** and (*2*) compound **IIa**.

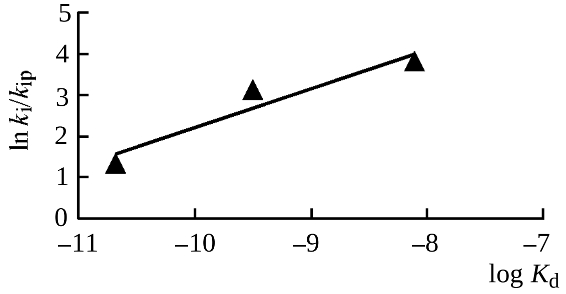


Fig. 2. Plot of $\ln k_i/k_{ip}$ vs. $\ln K_d$ for σ adducts **Ia**–**Ic**.

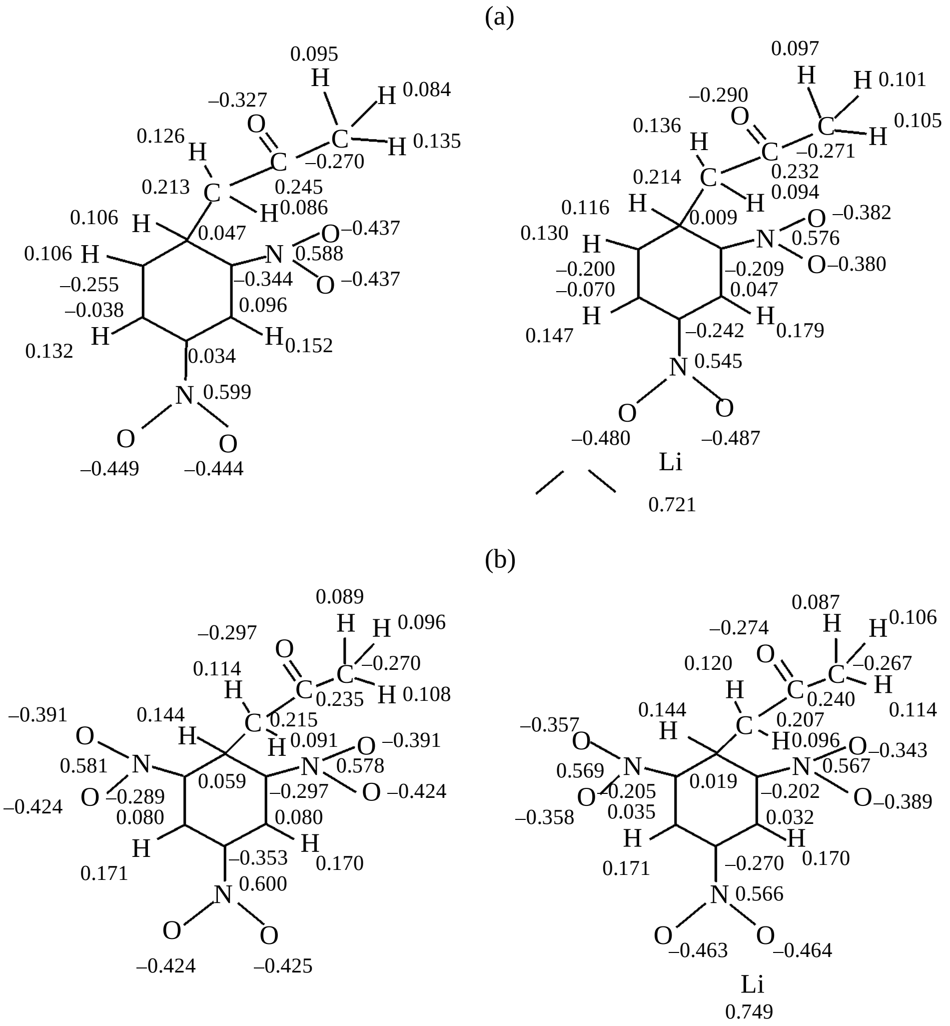


Fig. 3. Atomic charges in the anions and ion pairs of σ adducts, calculated by the AM1 method. (a) Structure **I** and (b) structure **II**.

It should be noted that dissociation stronger affects the rates of oxidation of 1,3,5-trinitrobenzene σ adducts compared with 1,3-dinitrobenzene σ adducts. Thus, as the concentration of σ adducts changes from 7.14×10^{-4} to 3.33×10^{-5} M, the oxidation rate constant of σ adduct **IIc** increases 7.4 times and that of adduct **Ic**, 1.8 times.

One of the reasons for the reduced reactivity of ion pairs compared with an ions may lie in the charge redistribution induced by association of the anion with the cation, which, according to [6], involves oxygen atoms of the 4-NO_2 group. The AM1 semiempirical calculation of the ions and ion pairs of σ aducts **I** and **II** with lithium cation located at a distance of 2.42 Å from oxygen atoms of the 4-NO_2 group placed increased negative charge on the 4-NO_2 group and reduced negative charge on the ring and the 2(6)-NO_2 groups (Figs. 3a and 3b). The energy of the highest occupied molecular orbital (E_{HOMO}) for ion pairs and ions are –8.08 and –4.83 eV, respectively, which suggests a lower electron-donor ability of ion pairs compared with free ions.

It is interesting that on addition of dibenzo-18-crown-6 (**XI**) the oxidation rate decreases, whereas the bathochromic shifts of the absorption maxima of σ adducts points to formation of solvent-separated ion pairs and solvated ions from the tight ion pairs (Table 2). This is apparently explained by formation of so-called crown-separated ion pairs in which the metal cations are located in the crown ether cavity, but the distance between the cation and the anion remains unchanged: $\text{Ct}^+\text{An}^- + \textbf{XI} \rightleftarrows \text{Ct}^+\textbf{XI}\text{An}^-$.

Analysis of the activation parameters of oxidation of σ adducts **Ia**–**Ic**, measured in the range 290–313 K in THF (Table 3), showed that the energy E_a and the

Table 2. Dependence of the oxidation rate of σ adduct **Ib** on the concentration of crown ether (c_{ce}) in THF (298 K)

c_{ad}/c_{ce}	$k_2 \times 10$, l mol^{-1} s^{-1}	λ_{max}, nm
0	5.34 ± 0.12	541.1
1 : 0.2	5.39 ± 0.18	542.3
1 : 1	4.65 ± 0.05	543.4
1 : 5	2.49 ± 0.15	549.9
1 : 10	2.65 ± 0.98	556.2

changes in the activation enthalpy $\Delta H^{\neq}$ and entropy $\Delta S^{\neq}$ decrease with increasing radius R of solvated cation. Thus, as R and, consequently, the dissociation constant of σ adduct increase (Table 4), the entropy difference between the starting and transition state increases, and, since the reaction is entropy-controlled, it is slowed down.

Table 3. Termodynamic parameters of oxidation of σ adducts **Ia**–**Ic** in THF (298 K)

Cation	E_a, kJ/mol	$\Delta H^{\neq}$, kJ/mol	$\Delta S^{\neq}$, kJ mol^{-1} K^{-1}	$\Delta S^{\neq}T$, kJ/mol	$\Delta G^{\neq}$, kJ/mol	α
Na^+	50.8 ± 0.7	48.4 ± 0.2	–97.8 ± 0.7	29.1	77.0 ± 0.4	0.435
K^+	48.1 ± 0.8	45.6 ± 0.5	–101.1 ± 1.2	30.1	75.2 ± 0.7	0.415
$[N(C_4H_9)_4]^+$	29.2 ± 2.6	26.7 ± 2.1	–168.4 ± 2.6	50.2	77.1 ± 1.0	0.472

Table 4. Dissociation constants (K_d), ionic (k_i), and ion-pair (k_{ip}) rate constants of oxidation of σ adducts **Ia**–**Ic** (298 K)

σ Adduct	$K_d \times 10^5$, M	$k_i \times 10$, l mol^{-1} s^{-1}	$k_{ip} \times 10$, l mol^{-1} s^{-1}	r	k_i/k_{ip}
Ia	7.46	3.54 ± 0.18	1.14 ± 0.28	0.997	3.1
Ib	2.60	5.07 ± 0.10	4.56 ± 0.37	0.985	1.3
Ic	30.1	3.32 ± 0.21	0.272 ± 0.093	0.999	12

Thus, we found that ion pairs of σ adducts are less reactive than free ions, which is explained by the fact that association increases the negative charge on the ring and decreases the negative charge on the 4-NO_2 group. The reactivity of ion pairs decreases with increasing ionic radius of their cation.

EXPERIMENTAL

Kinetic and spectral measurements were performed on a Specord M-40 spectrophotometer by the procedure in [7] in temperature-controlled cells 0.1 to 5 cm thick. The rates of oxidation of σ adducts were followed by the decrease of optical density in their absorption maxima. All measurement were performed under pseudo-first-order conditions at 50–100-fold excesses of oxidant.

Conductometric measurements were performed be means of an R-5010 ac bridge and a specially designed cell with parallel-plate platinum electrodes. The concentrations were measured to an accuracy of 0.2% and the electrical conductivities, 0.8–2%, depending on concentration. The λ_0 and K_d (λ_0 is equivalent electrical conductivity) were calculated by the program in [8].

Quantum-chemical calculations were performed by the HyperChem 4.5 program, AM1 semiempirical method, Polak–Ribiere optimization algorithm, gradient 10^{-4}.

The Yanovskii σ adducts and quinones were synthesized by the procedures in [9] and [10], respectively. Their structures were proved by electronic, ^{1}H NMR, and IR spectroscopy. The solvents were purified according to [11], and their purities were controlled by the refractive indices measured on an IRF-22 refractometer.

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