Kinetic Effects of Electrolytes in Oxidation of Sodium, Potassium, and Tetrabutylammonium 1-Acetonyl-2,4-dinitrocyclohexa-2,5-dienides with 1,4-Benzoquinone

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Abstract — The kinetics of oxidation of sodium, potassium, and tetrabutylammonium 1-acetonyl-2,4-dinitrocyclohexa-2,5-dienides with 1,4-benzoquinone in acetonitrile and tetrahydrofuran was studied spectrophotometrically. The reaction is of the first order with respect to the substrate and quinone and of the total second order. In the course of the process, a charge-transfer complex with an absorption maximum at about 716 nm is formed, accelerating the reaction. The rates of its accumulation and consumption increase with increasing concentrations of reactants and decrease on addition of sodium or tetrabutylammonium perchlorate. The factors facilitating association of σ adducts in solution (increase of the concentration in THF, addition of NaClO₄ or [N(C₄H₉)₄]ClO₄), decelerate oxidation owing to decrease of the negative charge in the cyclohexadienide ring of the contact ion pair of the σ adduct as compared to the free ion.

Oxidation of anionic σ adducts of nitroarenes with quinones, on the one hand, is of interest as a route to substituted α -phenyl ketones, because this process occurs under relatively mild conditions and with a fairly high yield [1]. On the ohter hand, quinones and their one-electron reduced species play a key role in studies of electron transfer and conversion of biological energy [2–5]. For example, in photosynthetic processes they act as electron acceptors [6]; also, they are constituents of oxyreductases [7]. Much attention is also given to the mechanism of hydrogen transfer in reactions involving quinones. Various types of hydride transfer are discussed in the literature, and in some cases the intermediate stage is formation of a charge-transfer complex detected by a characteristic absorption band in the electronic spectra [8]. Since σ adducts are organic π -electron donors and quinones are π acceptors, oxidation of σ adducts can be interpreted in terms of donor-acceptor interaction between the reactants.

We have studied previously [9, 10] the kinetic and thermodynamic features of oxidation of σ adducts with quinones and suggested a bimolecular reaction scheme involving formation of a charge-transfer complex, with the ionic mechanism of hydrogen transfer. We have also studied the effect of solvents on the reaction rate [11, 12] and found that the major effect on the oxidation rate constant is exerted by the electrophilicity of the medium.

σ Adducts are ionic compounds occurring in weakly polar media both as free ions and as ion pairs [13, 14]; their reactivity is different. As shown in [14–16], the shift of the ion-pair equilibrium (including that induced by addition of salts) affects both the rate and the regio- and stereoselectivity of the reaction. Therefore, we suggest that addition of electrolytes should also affect the rate of reaction of σ adducts with quinones. Study of the kinetic effects of electrolytes (salt effects) will give a deeper insight into the reaction mechanism and allow the choice of the optimal reaction conditions.

Thus, the goal of this work was to study the kinetics of the reaction of sodium, potassium, and tetrabutylammonium 1-acetonyl-2,4-dinitrocyclohexa-2,5dienides (**Ia–Ic**, respectively) with 1,4-benzoquinone in solvents of different polarity (acetonitrile, THF) in which these compounds are relatively stable and sufficiently soluble and to examine the influence of sodium and tetrabutylammonium perchlorates on the reaction rate.

To gain insight into the reaction mechanism, we performed a systematic kinetic analysis [17]. The semilogarithmic anamorphoses of the kinetic curves

of consumption of σ adduct **Ib** in acetonitrile at various initial concentrations of Ib are parallel straight lines; at the σ adduct concentration varied from 10^{-3} to 10^{-5} M, the rate constant remains practically unchanged [k $(3.13 \pm 0.09) \times 10^{-3} \text{ s}^{-1}$], which suggests the first order of the reaction with respect to the substrate (n 1.02 \pm 0.02). The linear dependence of the rate constant on the quinone concentartion proves the first order of the reaction with respect to the oxidant also ($n 1.02 \pm 0.04$). The kinetic curves of consumption of **Ib** at its different initial concentrations cannot be made coincident by shifting along the x axis, and the plot of the initial reaction rate vs. time of addition of a fresh portion of the σ complex is a convex curve (Fig. 1). Hence, the reaction course is influenced by intermediate III [scheme (1)] [17]. The increase in the rate constant from $(0.96\pm0.02) \times 10^{-3}$ to $(1.25\pm0.06) \times 10^{-3}$ s⁻¹ on adding 2,4-dinitrophenylacetone (IV) confirms participation of this compound in the transition state. Calculations of the rate constants of the first and second stages of the process showed that the limiting stage is formation of the intermediate $(k_1 \ 2.76 \times 10^{-4}, k_2 \ 5.73 \times 10^{-4} \ s^{-1})$, which is practically irreversible $(k_{-1} \ 10^{-17} \ s^{-1})$.

On mixing the reactants, a broad absorption band appeared in the range 714–833 nm, belonging to charge-transfer complex **III** of quinone with the σ adduct. By normalization and differentiation of the spectrum, we determined the position of the band maximum: about 716 nm. Apparently, this complex has a stack structure stabilized by electrostatic interactions similarly to complexes of quinones with other organic π donors [18]. With increasing concentration of the σ adduct the rates of formation and consumption of the intermediate increase (Fig. 2).

The hydride transfer in the course of transformation of the charge-transfer complex into the reaction products can occur either in a one two-electron stage or in steps via formation of radicals and radical anions. However, addition of radical scavengers (hydroquinone, nitrosobenzene) and removal of oxygen from the reaction mixture did not affect significantly the reaction rate $[k (4.98 \pm 0.12) \times 10^{-4} \text{ s}^{-1}$ without argon bubbling and $(4.89 \pm 0.01) \times 10^{-4} \text{ s}^{-1}$ with argon bubbling], which suggests the predominantly ionic character of the process under these conditions.

Thus, the reaction can be described by scheme (1):





Fig. 1. Initial reaction rate vs. time of addition of a fresh portion of σ adduct Ib.

To examine the influence of electrolytes on this process, we have studied the dependence of the spectral characteristics of the reactants and of the reaction rate on the concentration of sodium or tetrabutylammonium perchlorate. In acetonitrile, σ adducts Ia and Ic mostly exist as free ions and solvent-separated ion pairs. In less polar THF, sodium and potassium ions form with the anion contact ion pairs whose visible absorption spectra differ from those of the free ions: λ_{max} 586 nm for free ions, 539 nm for contact ion pairs with the sodium ion, and 551 nm for contact ion pairs with the potassium ion (Table 1). Despite the fact that, according to conductometric data, the σ adduct with tetrabutylammonium ion Ic is an electrolyte of medium strength ($K_{\rm dis}$ 3.01 × 10⁻⁴ in THF), its spectral characteristics in both solvents are similar to those of the solvent-separated ion pairs and free ions. This is due to the fact that the bulky $[N(C_4H_9)_4]^+$ ion (r 3.5 Å) does not affect significantly the electronic state of the anion owing to the large distance between the positively charged nitrogen center and the negatively charged oxygen atoms of the nitro groups. For the same reason, addition of $[N(C_4H_9)_4]$. ClO₄ to solutions of σ adducts **Ib** and **Ic** in acetonitrile and **Ic** in THF does not affect their absorption spectra (Table 1). The absorption maximum in the spectra of σ adducts **Ia** and **Ib** in THF at a large excess of the salt shifts toward longer waves owing to a decrease in the content of contact ion pairs on replacement of Na⁺ and K⁺ in the initial adduct by $[N(C_4H_9)_4]^+$:

$$An^{-}K^{+} + [N(C_{4}H_{9})_{4}]^{+} \rightleftharpoons An^{-}[N(C_{4}H_{9})_{4}]^{+} + K^{+}.$$
 (2)

Addition of sodium perchlorate causes a hypsochromic shift of the absorption maxima of σ adducts **Ia** and **Ic** due to formation of stronger contact ion pairs of the anion with the sodium ion. In THF, the ion-pair equilibrium is shifted at $C_{\text{salt}}/C_{\text{ad}} = 0.5$, and in CH₃CN this ratio is 3. At higher concentrations of sodium perchlorate, higher associates consisting of three, four, etc., ions are formed, as indicated by a small bathochromic shift of the absorption maxima at a 100–200-fold excess of the salt.

Variation of the ratio of the ions and ion pairs in solutions of σ adducts on adding salts should affect the rate of their oxidation by the mechanism of simultaneously acting primary and secondary kinetic electrolyte effects. The increase in the concentration of $[N(C_4H_9)_4]ClO_4$ does not noticeably affect the oxidation rate of Ic in both solvents and of Ia and Ic in CH₃CN, since in these solutions no shift of the ionpair equilibrium was observed. As was expected from the equation $\ln k = \ln k_0 + 2Z_A Z_B A I^{1/2}$ [where k is the rate constant at a given ionic strength I, k_0 is the rate constant at I = 0, Z_A and Z_B are the charges of the reacting species, and A is the constant of the Debye– Hückel theory (for solution in THF, A 17.62)], for the reaction between the σ adduct anion and the quinone molecule the logarithm of the second-order rate constant is practically independent of the square root of the solution ionic strength (Fig. 3).

Addition of sodium perchlorate affects not only the ionic strength of solution but also the degree of association of the σ adduct. As the concentration of the like ion on its addition to a solution of σ adduct **Ia** in THF is increased, the content of the contact ion pairs increases, and the oxidation rate decreases. A similar trend is observed on adding NaClO₄ to solutions of **Ib** in CH₃CN and THF.

In contrast to acetonitrile solutions in which there is no association and the rate constant is independent of the σ adduct concentration, in THF the observed rate constant decreases with increasing degree of association $1/\alpha$ of σ adduct **Ib** (Table 2).

Our experimental data show that the σ adducts in the form of ion pairs are less reactive than the free



Fig. 2. Kinetic curves of accumulation and consumption of the intermediate at various concentrations of σ adduct Ib (C_{ad}) in MeCN. C_{ad} , M: (1) 1×10^{-5} , (2) 1.8×10^{-5} , (3) 1×10^{-4} , (4) 2×10^{-4} , (5) 4×10^{-4} , and (6) 1×10^{-3} .



Fig. 3. Logarithm of the rate constant of reaction of σ adduct **Ic** with benzoquinone as a function of the square root of the ionic strength of the solution (addition of [NBu₄]ClO₄) in CH₃CN.

ions. A PM3 calculation of the energy of the highest occupied molecular orbital in **Ib**, the major contribution to which is made by the ring carbon atoms, gave for the free ion and ion pair the values of -4.83 and -8.56 eV, respectively. Thus, the decrease in the negative charge in the cyclohexadienide ring and its increase on the nitro group under the influence of the cation weaken the reductive activity of the σ adduct. Owing to decrease in the electron-donor power of the ring, the accumulation and consumption of the intermediate decelerate (Fig. 4) with increasing concentration of NaClO₄.

The cation exchange between σ adduct **Ic** and $[N(C_4H_9)_4]ClO_4$ decelerates its oxidation in THF, and the exchange between **Ic** and NaClO₄ accelerates its oxidation in CH₃CN and THF (Table 2). Hence, the solution of **Ic** contains contact ion pairs which are less

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$ \begin{array}{c ccmp, \\ no. \\ no. \\ c_{shl'} C_{ad} \ \lambda_{max1} \ \lambda_{max2} \ k \times 10^1 \ \lambda_{max1} \ \lambda_{max1} \ \lambda_{max2} \ k \times 10^1 \ \lambda_{max1} \ \lambda_{max1} \ \lambda_{max2} \ k \times 10^1 \ \lambda_{max1} \$		Г <u> </u>	r	r	[]			[]		r	 _		F	г
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$ \mathbf{Ic} = \begin{bmatrix} 0.5 & 361 & 580 & 1.99 \pm 0.07 & 361 & 580 & 2.22 \pm 0.05 & 355 & 543 & 2.49 \pm 0.15 & 357 & 562 & 2.47 \pm 0.17 \\ 1 & 361 & 579 & 1.95 \pm 0.03 & 361 & 580 & 2.27 \pm 0.05 & 354 & 535 & 2.18 \pm 0.18 & 359 & 562 & 2.28 \pm 0.03 \\ 3 & 359 & 577 & 1.93 \pm 0.03 & 361 & 580 & 2.39 \pm 0.05 & 354 & 535 & 1.86 \pm 0.12 & 361 & 569 & 1.92 \pm 0.1 \\ 10 & 358 & 574 & 1.92 \pm 0.03 & 361 & 580 & 2.39 \pm 0.05 & 354 & 535 & 1.88 \pm 0.08 & 362 & 574 & 1.94 \pm 0.09 \\ 20 & 358 & 573 & 361 & 580 & 2.36 \pm 0.04 & 354 & 535 & 1.88 \pm 0.08 & 362 & 574 & 1.94 \pm 0.09 \\ 20 & 358 & 573 & 361 & 580 & 2.36 \pm 0.04 & 354 & 535 & 1.88 \pm 0.08 & 362 & 574 & 1.94 \pm 0.09 \\ 20 & 358 & 573 & 361 & 580 & 2.32 \pm 0.01 & 354 & 535 & 1.88 \pm 0.01 & 361 & 577 & 1.71 \pm 0.06 \\ 50 & 357 & 569 & 1.86 \pm 0.07 & 361 & 580 & 2.32 \pm 0.01 & 354 & 535 & 1.80 \pm 0.13 & 361 & 579 & 1.69 \pm 0.09 \\ 100 & 356 & 567 & 361 & 580 & 2.32 \pm 0.01 & 354 & 535 & 1.67 \pm 0.03 & 361 & 579 & 1.69 \pm 0.09 \\ 100 & 356 & 567 & 361 & 580 & 354 & 535 & 1.67 \pm 0.03 & 362 & 580 & 2.54 \pm 0.05 \\ 200 & 360 & 580 & 1.81 \pm 0.05 & 360 & 580 & 1.81 \pm 0.02 & 363 & 580 & 2.54 \pm 0.05 & 362 & 580 & 2.54 \pm 0.05 \\ 0.5 & 360 & 580 & 1.85 \pm 0.13 & 360 & 580 & 1.82 \pm 0.13 & 361 & 569 & 2.59 \pm 0.03 & 362 & 580 & 2.44 \pm 0.09 \\ 1 & 360 & 580 & 1.79 \pm 0.08 & 360 & 580 & 1.76 \pm 0.03 & 357 & 559 & 2.71 \pm 0.05 & 362 & 580 & 2.44 \pm 0.00 \\ 3 & 360 & 580 & 360 & 580 & 1.76 \pm 0.09 & 355 & 527 & 2.73 \pm 0.05 & 362 & 580 & 2.44 \pm 0.00 \\ 3 & 360 & 580 & 2.01 \pm 0.11 & 360 & 580 & 1.91 \pm 0.06 & 354 & 526 & 2.75 \pm 0.06 & 362 & 580 & 2.44 \pm 0.00 \\ 20 & 359 & 577 & 360 & 580 & 1.86 \pm 0.05 & 355 & 535 & 2.83 \pm 0.01 & 362 & 580 & 2.34 \pm 0.00 \\ 20 & 359 & 577 & 360 & 580 & 1.86 \pm 0.05 & 355 & 535 & 2.83 \pm 0.01 & 362 & 580 & 2.34 \pm 0.00 \\ 200 & 356 & 569 & 1.95 \pm 0.11 & 360 & 580 & 1.86 \pm 0.05 & 355 & 536 & 2.81 \pm 0.01 & 362 & 580 & 2.34 \pm 0.00 \\ 200 & 356 & 569 & 1.95 \pm 0.11 & 360 & 580 & 1.84 \pm 0.05 & 355 & 536 & 2.81 \pm 0.01 & 362 & 580 & 2.34 \pm 0.00 \\ 200 & 356 & 569 & 1.95 \pm 0.11 & 360 & 580 & 1.84 \pm 0.05 & 355 & 536 & 2.81 \pm 0.01 & 362$	Ib	0	361	580	2.11 ± 0.09	361	580	2.11 ± 0.09	357	554	3.63 ± 0.09	356	551	3.18 ± 0.09
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		0.5	361	580	1.99 ± 0.07	361	580	2.22 ± 0.05	355	543	2.49 ± 0.15	357	562	2.47 ± 0.12
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$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		3	360	580		360	580		355	536		362	580	2.46 ± 0.02
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		5	360	580	2.01 ± 0.11	360	580	1.76 ± 0.09	355	527	2.73 ± 0.05	362	580	2.44 ± 0.02
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$		10	359	579	1.99 ± 0.02	360	580	1.91 ± 0.06	354	526	2.75 ± 0.06	362	580	2.46 ± 0.06
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200 356 569 360 580 355 536 362 580		100	356	569	1.95 ± 0.11	360	580	1.84 ± 0.05	355	536	2.81 ± 0.01	362	580	2.34 ± 0.06
		200	356	569		360	580		355	536		362	580	

Table 1. Positions of absorption maxima (λ_{max} , nm) and oxidation rate constants (k, dm³ mol⁻¹ s⁻¹) of σ adducts **Ia–Ic** as influenced by the ratio of the salt and adduct concentrations C_{salt}/C_{ad} (298 K)

Table 2. Rate constant of oxidation of σ adduct **Ib** as influenced by its concentration in THF (298 K)

$C_{\rm ad} imes 10^4$, M	$k_{\rm app} \times 10^3, \ {\rm s}^{-1}$	α
1.83	4.89 ± 0.02 4.78 ± 0.04	0.29
9.31	1.34 ± 0.05	0.13
12.61	1.43 ± 0.04	0.11

reactive than those with the sodium and potassium ions, owing to steric hindrance produced by the tetrabutylammonium ion in formation of the charge-transfer complex. For the same reason, σ adduct **Ic** in both solvents is oxidized more slowly than **Ia** and **Ib**. Thus, oxidation of the σ adducts is a bimolecular reaction with intermediate formation of a chargetransfer complex. The primary kinetic electrolyte effect does not noticeably influence the reaction rate, and the secondary effect consists in shifting the ionpair equilibria in solutions of σ adducts in the presence of salts. In the reaction under consideration, the free ions are more reactive than the ion pairs.

EXPERIMENTAL

The Yanovskii σ adducts and 1,4-benzoquinone were prepared by procedures described in [19] and [20], respectively. Their structure was proved by electronic, ¹H NMR, and IR spectroscopy. The solvents were dehydrated according to [21]; their purity was



Fig. 4. Kinetic curves of accumulation and consumption of the intermediate at various $C_{\text{salt}}/C_{\text{ad}}$ ratios in CH₃CN. $C_{\text{salt}}/C_{\text{ad}}$: (1) 0, (2) 10, and (3) 50.

checked refractometrically with an IRF-22 device. Sodium perchlorate was purified and dried according to [22].

Tetrabutylammonium perchlorate. A 2-1 beaker was charged with 500 g of a tetrabutylammonium hydroxide solution (ω 10%), 50 ml of H₂O was added, and HClO₄ was gradually added with stirring to pH 5.5. The resulting precipitate was filtered off on a Büchner funnel and washed by stirring with doubledistilled water for 4 h. The washed product was filtered off and dried at temperature no higher than 60°C. Yield 90%.

The reaction kinetics was monitored spectrophotometrically [23]. The spectra were taken on a Specord M-40 spectrophotometer.

The oxidation rate of σ adducts was monitored by the decrease in the optical density in the absorption maximum of the adduct. The concentration of the charge-transfer complex was monitored by absorption at 833 nm, because its absorption maximum (716 nm) is overlapped by absorption of the σ adduct. The measurements were performed under pseudo-firstorder conditions at a 50–100-fold excess of benzoquinone.

The first- and second-order rate constants were calculated following the recommendations in [24].

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