Anion Radical Formation in the Reaction of 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with Tribenzylamine in Acetonitrile

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Kinetics of the reaction of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with tribenzylamine in acetonitrile has been measured spectrophotometrically. The product of this reaction is a stable anion radical of DDQ. The reaction is relatively slow, due to a considerable steric hindrance in both quinone and amine molecule. Activation parameters indicate a charge separation in the transition state. The mechanism of the reaction has been proposed.

Key words: quinone anion radical, kinetics, reaction mechanism, activation parameters

Benzoquinones are commonly known as electron acceptors used in chemical synthesis. Ubiquinones and plastoquinones are involved in processes of energy storage and utilization and therefore play a vital role in biological systems [1]. Some of these reactions are considered as simple models for biochemical processes. In some photosynthetic redox reactions semiquinone radical anions are produced [2]. Moreover, in respiration process the oxidation of ubisemiquinone radical anion is also a key step [3]. A significant number of papers deals with theoretical calculations of the structure and thermochemical data for some quinones used as model compounds of naturally occurring substances [4,5]. There are also some data concerning fluorescence of benzoquinone radical anion [6]. However, there are only a few papers concerning the mechanisms of model reactions, in which anion radicals of quinones are formed. Usually radical anions in chemical systems are generated using electrochemical and photochemical methods. The most common method for chemical generation of anion radicals is the reaction of neutral molecules with alkali metals. An excellent overview of the formation and reactions of transient radical pairs was published by Kochi [7]. The lifetime of such intermediates is usually very short – in the range of picoseconds. Radical anions resulting from electron transfer from nucleophile to quinone molecule form mainly ion pairs – both contact and solvent-separated – depending on the system studied [8].

The spectrochemical data for a radical anion of DDQ has been presented by Foster [9]. Recently, a kinetic study on ion pair formation between chloranil radical anion and alkaline metal cations has been published [10]. In all these reactions anion radicals were generated using γ-irradiation, flash photolysis [11] or pulse electrolysis [10].

Halogenosubstituted quinones reacting with primary and secondary amines usually give rise to substituted quinones and/or charge-transfer complexes [1]. However, in some reaction systems the process is more complex – in the first, rapid step, an anion radical of quinone is formed, then vinylic substitution takes place and substituted aminoquinones are formed. Nevertheless, when a haloquinone reacts with tertiary amine or other π-donor or n-donor, there is no possibility of substitution reaction taking place. In such cases, in which a single electron transfer process (SET) is involved, charge-transfer complexes or ions (anion radicals and cation radicals) are formed. Charge-transfer complexes have been found to be intermediates in many reactions of quinone derivatives with amines. The usual pathway consists of the formation of EDA complex followed by subsequent substitution of quinone by amine molecule:

Quinone + amine $\rightarrow$ EDA complex $\rightarrow$ mono-substituted product $\rightarrow$ disubstituted product

The first step of this reaction is fast and reversible [1,12,13]. DDQ forms a quite stable anion radical that has been identified as an intermediate in vinylic substitution reaction [14].

In purpose to investigate a model reaction, in which a radical anion of quinone is formed, we have chosen DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone) because of its greater electron affinity in comparison to other simple benzoquinone derivatives [15]. Reduction potential of DDQ (*vs* SCE) is 0.51 V, and it is considerably greater when compared with 0.01 V for 2,3,5,6-tetrachlorobenzoquinone (chloranil), therefore, this should facilitate anion radical generation. Acetonitrile has been chosen because its solvating properties should stabilize charged anion radicals of quinone and cation radicals of amine.

EXPERIMENTAL

DDQ (Merck) was recrystallized two times from chloroform (m.p. 213–215°C). Purity of this compound was checked by means of TLC. Tribenzylamine (commercial product – Koch-Light Laboratories Ltd) was used as received (m.p. 91–94°C). Acetonitrile (Romil far UV solvent) was used without any further purification. DDQ anion radical potassium salt was synthesized according to the procedure of Torrey [16]. To the saturated solution of 0.5 g DDQ in cold acetone, 0.5 g of solid KI was added gradually. Green precipitate was formed immediately, which was then filtered off, washed with cold acetone and dried *in vacuo*. UV-VIS spectrum of this compound is identical with the one presented by Grampp [11]. UV-VIS spectra were recorded on Hewlett-Packard diode array spectrophotometer HP 8452A. The kinetic measurements were done on the same apparatus fitted with thermostated cell holder. Fresh solutions of the substrates were made for each set of measurements. All errors are the calculated standard deviations. IR spectra were recorded on BRUKER IFS 113v. NMR spectra were recorded on VARIAN Gemini 300 VT. Mass spectra were recorded on AMD INTECTRA Mass Spectrometric System, AMD 604/402. Melting points were measured on Boetius apparatus.

RESULTS AND DISCUSSION

DDQ reacts with primary and secondary amines forming 2,5-disubstituted products in multistep reaction. In some of these reactions charge-transfer complexes or σ-complexes have been found to be the intermediates. However, when a tertiary

amine reacts with DDQ, there is no possibility of substitution in the quinone ring. Therefore, in such reactions one can expect a formation of either charge-transfer complex or, in the case of a complete electron transfer, a pair of anion radical of the quinone and cation radical of the amine. The reactions of anion radical formation are usually fast.

A mixture of equal volumes of the solution of DDQ [0.001 M] in acetonitrile with a solution of tribenzylamine [0.1 M] in acetonitrile turns slowly red. The UV-vis spectrum of this mixture shows maxima characteristic for DDQ anion radical (λ_{max} = 348 nm, 458 nm, 548 nm, and 588 nm) and their positions and intensities are identical with those obtained by Foster [9] and Grampp [11]. The time resolved spectrum shows 2 isosbestic points (368 nm and 384 nm). The anion radical seems to be very stable, even under aerobic conditions. This can be attributed to conjugative stabilization by two double bonds in quinone molecule. The use of polar aprotic acetonitrile ($\varepsilon = 36$) probably also stabilizes highly polar species formed in this reaction.

However, we were not able to isolate the product of the reaction in solid state, probably due to its decomposition during the normal work-up. This reaction is surprisingly slow, as compared with the reaction of DDQ with imidazole in acetonitrile, where anion radical has been found to be an intermediate [14]. In the latter case an anion radical is formed in a very fast reaction and then the vinylic substitution takes place giving rise to disubstituted benzoquinone. It might be pointed out that low rate values could be caused by a substantial steric hindrance in both tribenzylamine molecule and quinone molecule.

The kinetic measurements were made using 5 tribenzylamine concentrations (0.005–0.025 M) and 6 temperatures (15–50°C). The concentration of tribenzylamine was at least 10 times larger than the concentrations of the quinone (0.0001 M), ensuring pseudo-first-order conditions. Kinetic curves were well exponential. Calculated second-order rate constants are collected in Table 1. The reaction studied was monitored at two wavelengths characteristic for the product – anion radical of DDQ (348 nm and 548 nm). Activation parameters were calculated using the mean value of the second order rate constants.

Table 1. Second rate order rate constants for the reaction of DDQ (0.0001 M) with tribenzylamine in acetonitrile.

Temperature	k_2 [dm^3·mol^{-1} s^{-1}] λ_{max} = 348 nm	k_2 [dm^3·mol^{-1} s^{-1}] λ_{max} = 548 nm	k_2 [dm^3·mol^{-1} s^{-1}] average
15	0.0389	0.0387	0.0388
20	0.0429	0.0408	0.0419
25	0.0441	0.0474	0.0457
30	0.0644	0.0703	0.0674
35	0.0740	0.0781	0.0761
50	0.122	0.130	0.126

The plot of k_{obs} *vs* [TBA] shows no deviation from the straight line. The activation parameters for this reaction has been calculated using Eyring equation. The free enthalpy of activation is 80.4±3.4 kJ/mol, enthalpy of activation 25.1±2.5 kJ/mol, and the entropy of activation – 185±8 JK^{-1} mol^{-1}. Large negative value of the entropy of activation indicates that there exists a considerable charge separation in the transition state. When the reaction is carried out in polar acetonitrile, we can conclude that such a separation causes a better solvation of highly polar transition state as compared with that of the reacting molecules. Negative value of the entropy of activation also indicates a better ordering of the encounter complex as compared with the reactants. Taking into account all the experiments performed, together with the results of kinetic measurements, we would like to propose the following mechanism of the reaction studied.
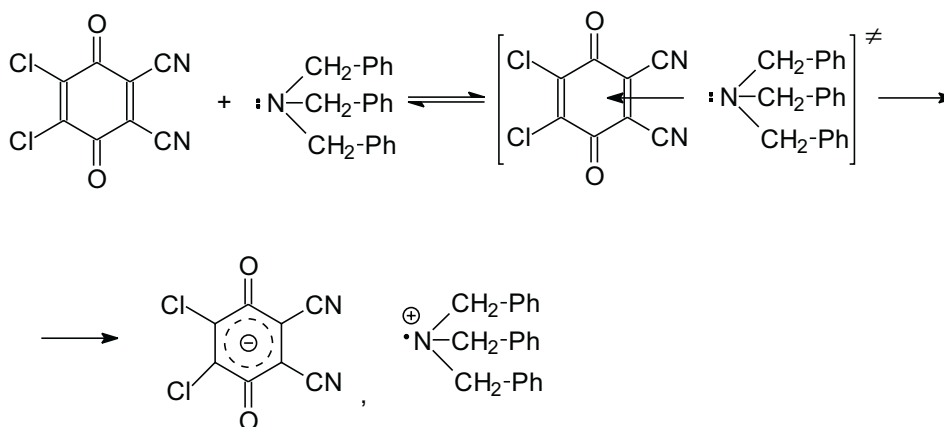
Scheme 1. Mechanism of the reaction of DDQ with tribenzylamine in acetonitrile.

The nucleophilic attack of tribenzylamine molecule takes place perpendicularly to the plane of the quinone molecule. At first, the encounter complex is formed, and its structure probably resembles that of charge-transfer complex. Due to significant electron affinity of the DDQ molecule, lone pair electron of the tribenzylamine molecule is being completely transferred to the quinone molecule, and as a result of this process an ion pair anion radical – cation radical is formed.

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