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Reaction of Semiquinones with Chloroaromatic Compounds

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Abstract—Semiquinones were generated by γ-irradiation of the quinone-containing water–ethanol solutions. The possibility of the reaction of semiquinones with sodium 2,4-dichlorophenoxyacetate and pentachlorophenol was studied. It was found that semiquinones reacted with chloroaromatic compounds to form chloride ions and phenyl radicals active in the abstraction reaction. By means of mathematic modeling the rate constant of the reaction of trimethylbenzosemiquinone with 2,4-dichlorophenoxyacetate was calculated.

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Semiqionones ($Q^{\cdot-}$) are formed during the one-electron reduction of quinones (Q) or oxidation of hydroquinones (QH_2).

$$Q \underset{-e^-}{\overset{e^-}{\rightleftharpoons}} Q^{\bullet-} \underset{-H^+}{\overset{H^+}{\rightleftharpoons}} QH^{\bullet} \underset{-H}{\overset{H}{\rightleftharpoons}} QH_2.$$

Quinones are active participants of the most important biochemical redox processes. Just this process of reversible reduction is the base of biological use of quinones. In the course of electron transport along the respiratory chain in the presence of reducing agents such as pyridinenucleotides ubiquinones transform from the quinone form to hydroquinone and vice versa through the formation of semiquinones. Plastoquinones are exposed to analogous transformations during the electron transport in the processes of photosynthesis [1–3]. Natural and synthetic antioxidants on the basis of biphenols in the course of inhibiting the peroxide oxidation of lipids are transformed to semiquinones. Many quinones are used as medicines for the therapy of cancer and some other diseases [4–6]. The biosystems contain the enzymatic and nonenzymatic pathways of reduction of quinones, vitamins K. Their reduction proceeds through the formation of semiquinones.

Organochlorine compounds are the widespread ecotoxicants. They cause in plant and animal organisms various pathologic distortions whose mechanism in the majority of cases is unknown. Common chemical property of all the organochlorine compounds is their capability of accepting electrons. In the work presented the possibility of the reaction of chloroaromatic compounds with semiquinones including the transfer of electron from semiquinone to the molecule of organochlorine compound is considered.

Semiquinones were generated by means of γ-irradiation of 2 M solutions of 2-propanol containing quinones. Under the action of radiation the active products of water radiolysis such as $OH^{\cdot}$, e_{aq}, H, and H_2O_2 with the radiation-chemical yields 2.7, 2.7, 0.55, and 0.7 molecules/100 eV respectively are formed [7, 8].

Formation of semiquinones in the systems under study proceeds directly by means of the fast reaction (1), and also by oxidation of hydroxyisopropyl radicals with quinone [reaction (4)] the reactions (5) and (15) presented in Table 1. The main contribution (97%) to the generation of semiquinones is provided by the reactions (1) and (4).

The possibility of the reaction of trimethyl-1,4-benzoquinone and 1,4-benzoquinone semiquinones with 2,4-dichlorophenoxyacetate and pentachlorophenol was studied. These processes [reaction (23)] were traced by the formation of Cl^- at low concentrations of 2,4-dichlorophenoxyacetate and pentachlorophenol. Concentration of these substances in solution was 0.001 M, and the concentration of quinones was ten times higher, 0.01 M. Quinones are very effective acceptors of hydrated electrons. Rate constant of the reaction of e_{aq} with 2,5-dimethyl-1,4-benzoquinone k_1 is 3.1×10^{10} l mol^{-1} s^{-1}, ~8.4 times larger than the rate constant of the reaction of e_{aq} with 2,4-dichlorophenoxyacetate [k_{22} 3.7×109 l mol^{-1} s^{-1}].

Table 1. Reactions and their rate constants (k) used in mathematic modeling of the processes of radiolysis of water-2-propanol solution containing trimethyl-1,4-benzoquinone (Q) and 2,4-dichlorophenoxyacetate ($ArCl_2$)

Reaction no.	Reaction	k, l mol^{-1} s^{-1}	References
1	$e_{aq} + Q \rightarrow Q^{-\cdot}$	3.1×10^{10}	[9, 10][a]
2	$H + (Me)_2CHOH \rightarrow (Me)_2\dot{C}OH + H_2$	8.2×10^{7}	[8]
3	$OH + (Me)_2CHOH \rightarrow (Me)_2\dot{C}OH + H_2O$	2.1×10^{9}	[8]
4	$(Me)_2\dot{C}OH + Q \rightarrow (Me)_2CO + Q^{-\cdot} + H^+$	3.6×10^{9}	[10, 11]
5	$H + Q \rightarrow QH^{\cdot}$	6.7×10^{9}	[10][b]
6	$H_2O_2 + (Me)_2\dot{C}OH \rightarrow (Me)_2CO + \dot{O}H + HO^-$	5.0×10^{5}	[8]
7	$e_{aq} + H_2O_2 \rightarrow HO^- + \dot{O}H$	1.2×10^{10}	[12, 13]
8	$QH^{\cdot} + QH^{\cdot} \rightarrow Q + QH_2$	1.4×10^{8}	[14][c]
9	$Q^{-\cdot} + QH^{\cdot} + H_2O \rightarrow Q + QH_2 + HO^-$	1.4×10^{8}	[14][d]
10	$Q^{-\cdot} + Q^{-\cdot} + 2H_2O \rightarrow Q + QH_2 + HO^- + HO^-$	1.6×10^{7}	[14][e]
11	$\dot{O}H + Q \rightarrow HOQ^{\cdot}$	1.0×10^{9}	[15][f]
12	$Q^{-\cdot} + H_2O_2 \rightarrow Q + \dot{O}H + HO^-$	5.0×10^{5}	[8][g]
13	$QH^{\cdot} + H_2O_2 \rightarrow Q + \dot{O}H + H_2O$	5.0×10^{5}	[8][g]
14	$Q^{-\cdot} + H^+ \rightarrow QH^{\cdot}$	2.0×10^{10}	[16][h]
15	$QH^{\cdot} \rightarrow Q^{-\cdot} + H^+$	2.0×10^{5}	[11][i]
16	$(Me)_2CO + e_{aq} \rightarrow (Me)_2\dot{C}OH + HO^-$	6.6×10^{9}	[8]
17	$HO^- + H^+ \rightarrow H_2O$	1.4×10^{11}	[8, 12]
18	$H_2O \rightarrow H^+ + HO^-$	2.52×10^{-5}	[12]
19	$H_2O_2 \rightarrow \dot{O}H + \dot{O}H$	1.33×10^{-7}	[12]
20	$e_{aq} + H^+ \rightarrow H$	2.3×10^{10}	[17, 12]
21	$HOQ^{\cdot} + Q^{-\cdot} + H_2O \rightarrow Q + HOQH_2 + HO^-$	1.4×10^{8}	[14][j]
22	$ArCl_2 + e_{aq} \rightarrow Cl^- + \dot{A}rCl$	3.7×10^{9}	[18]
23	$Q^{-\cdot} + ArCl_2 \rightarrow Cl^- + Q + \dot{A}rCl$	1.13×10^{3}	
24	$\dot{A}rCl + (Me)_2CHOH \rightarrow HArCl + (Me)_2\dot{C}OH$	2.0×10^{7}	[10][k]
25	$\dot{A}rCl + Q \rightarrow ArClQ^{\cdot}$	1.0×10^{9}	[19][l]

[a] Rate constant of the reaction of e_{aq} with 2,5-dimethyl-1,4-benzoquinone. [b] Rate constant for the reaction of H with 1-methylnaphthoquinone. [c] Rate constant for the reaction with Q = tetramethyl-1,4-benzoquinone. [d] Analogously to the reaction no. 8. [e] For semiquinones from tetramethyl-1,4-benzoquinone. [f] For Q=1,4-benzoquinone k_{11} 1.2×10^{9} l mol^{-1} s^{-1}. [g] Analogously to the reaction no. 6. [h] For the reaction of H^+ with acetophenone radical ions. [i] Calculated from pK 4.95 and k_{14}. [j] Analogously to the reaction no. 9. [k] Average value for the reaction of $C_6H_5^{\cdot}$ ($k = 1.2\times10^{7}$ l mol^{-1} s^{-1}) and 4-HO-$C_6H_4^{\cdot}$ ($k = 3\times10^{7}$ l mol^{-1} s^{-1}) radicals with 2-propanol. [l] $C_6H_5^{\cdot}$ radical adds to 1,4-benzoquinone with $k = 1.2\times10^{9}$ l mol^{-1} s^{-1}.

Considering the ratio of concentrations of quinone and 2,4-dichlorophenoxyacetate, and also the rate constants of their reactions with hydrated electrons shows that the rate of reaction (22) is ~84 times lower than the rate of the reaction (1) of e_{aq} with quinone. Hence, the radiation-chemical yield of chloride ions formed by the reaction (22) must be 2.7/84 ≈ 0.03 molecule/100 eV. Yield of chloride ions observed in the experiments (Table 2) is G(Cl^-) 0.41±0.02 molecule/100 eV (pH 6.7) indicating the proceeding of reaction (23). $ArCl^{\cdot}$ radical formed in reaction (23) reacts mainly with the molecule of 2-propanol [reaction (24)] to give $(Me)_2C^{\cdot}OH$ radical which is oxidized with quinone to acetone. It explains the small, but systematical increase in the yield of acetone in 2,4-dichlorophenoxyacetate solutions (Table 2).

While irradiation of 2 M 2-propanol solution containing 0.05 M of 2,4-dichlorophenoxyacetate and 0.001 M of trimethylbenzoquinone the radiation-chemical yield of acetone calculated from the dose dependence (2) presented in Fig. 1 occurred to be significantly higher, 8.86±0.17 molecule/100eV. This value exceeds the summary yield (6.65 molecule/100 eV) of active particles in the course of water radiolysis which initiate the formation of $(Me)_2C^{\cdot}OH$ radicals and further of acetone. In the absence of reaction (23) the yield of acetone must not exceed the

Table 2. Radiation-chemical yields (G) of the products of radiolysis of aqueous 2-propanol solution with the additives of trimethylbenzoquinone and 2,4-dichlorophenoxyacetate at different pH

Product	pH			
	2.4	5.5	6.7	8
	G, molecule/100 eV			
Cl^-	0.17±0.02	0.40±0.03	0.41±0.02	0.23±0.02
$(CH_3)_2CO$	4.76±0.18	4.51±0.19	4.44±0.15	3.48±0.12
$(CH_3)_2CO$[a]	4.54±0.16	4.39±0.16	4.23±0.17	3.22±0.18
Hydroquinone			3.41±0.34	
Hydroquinone[a]			3.52±0.33	
Quinone			–3.51±0.26	
Quinone[a]			–3.34±0.31	

[a] Yields of the products obtained in the absence of 2,4-dichlorophenoxyacetate.

value of 6.65 molecule/100 eV. Hence, under the above-described conditions acetone is formed in the yield 2.21 molecule/100 eV due to the short-chain process including the reactions (23), (24), and (4).

Effect of pH of the solution on the yield of Cl^- ions also confirms the possibility of reaction (23). Hence, in the acid medium the semiquinone undergoes protonation [reaction (26)], and the rate of reaction (23) decreases. Yield of the chloride ions reduces to 0.17±0.03 molecul/100eV at pH 2.4. At such concentrations of H^+ ions the formation of chloride ions is practically completely excluded due to the fast reactions (1) and (20). The formation of chloride ions in the acid medium is possible via reaction (27) though it is less effective.

$$Q^{-\cdot} + H^+ \leftrightarrow QH^{\cdot}\ pK\ 4.95\ [11], \quad (26)$$

$$QH^{\cdot} + ArCl_2 \rightarrow Q + Cl^- + H^+ + {}^{\cdot}ArCl. \quad (27)$$

Reaction (27) is similar to reaction (26) which proceeds due to the electron transfer [20] and has the rate constant $k_{28} \sim 10^6$ l mol^{-1} s^{-1} [21].

$$(CH_3)_2{}^{\cdot}COH + CH_2Cl_2 \rightarrow {}^{\cdot}CH_2Cl + (CH_3)_2CO + H^+ + Cl^-. \quad (28)$$

For the calculation of rate constant for reaction (23) a mathematical modeling of radiolysis was carried out. The modeling was carried out in 2 steps. In the first step the mathematical model of radiolysis of 2 M solution of 2-propanol [reactions (1)–(12)] at pH 6.7 containing trimethylbenzoquinone was designed. This model gave the description of the process consistent with the experimental data. While performing calculations the reported experimental rate constants of radical reactions proceeding in the course of radiolysis of aqueous 2-propanol solution in the presence of quinone were used. In Table 1 the reactions and the values of their rate constants used in the calculations are listed. Figure 2 presents the calculated and experimental dose dependences of accumulation of the main products of radiolysis of aqueous 2-propanol solution with the additive of quinone such as acetone and hydroquinone, and of decomposition of quinone.

In the second stage the model of radiolysis of 2 M aqueous 2-propanol solution containing 0.01 M of quinone was modified considerating the additive of

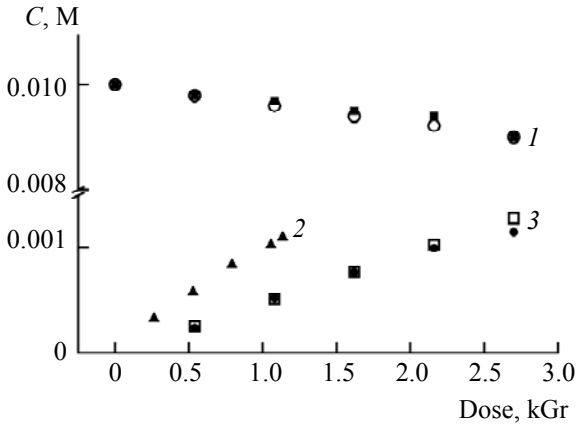

Fig. 1. Dependences of concentrations (*1*) of quinone and (*2, 3*) acetone on the irradiation dose of 2 M 2-propanol solution containing trimethylbenzoquinone and 2,4-dichlorophenoxyacetate (pH 6.7). (■,▲,●) Experimental data, (○, □) calculated data, (*2*) dependence is obtained at the 0.05 M concentration of 2,4-dichlorophenoxy-acetate and 0.001 M of quinone.

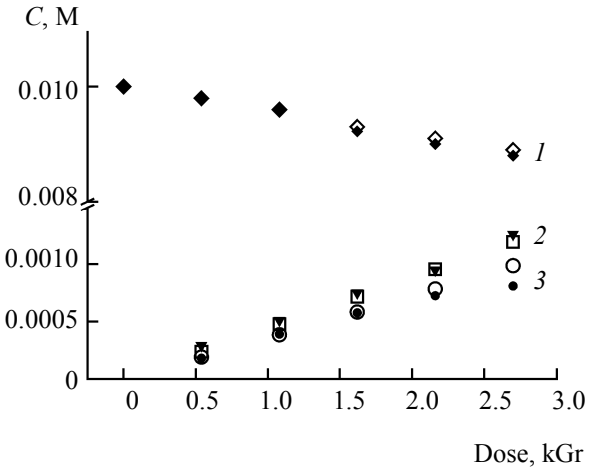

Fig. 2. (♦, ▼, ●) Experimental and (◊, □, ○) calculated values of concentration of (*1*) quinone, (*2*) acetone, and (*3*) hydroquinone depending on the dose of radiation of the 2 M aqueous 2-propanol solution containing trimethylbenzoquinone (pH 6.7).

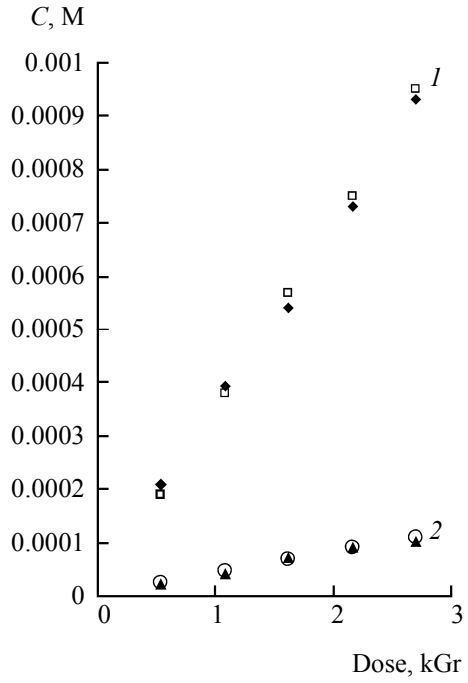

Fig. 3. (♦, ▲) Experimental and (□, ○) calculated values of concentrations of (*1*) hydroquinone and (*2*) chloride ions depending on the radiation dose of 2 M aqueous 2-propanol solution containing trimethylbenzoquinone and 2,4-dichlorophenoxyacetate (pH 6.7).

2,4-dichlorophenoxyacetate (0.001 M), that is of the reactions with participation of this substance and their rate constants. While developing the mathematical model of radiolysis of water–2-propanol solution containing quinone and 2,4-dichlorophenoxyacetate reactions (1)–(25) were used. In the course of calculations the rate constant of reaction (23) was varied. Best agreement of the calculated and experimental dependences of concentrations of the chloride ions, of hydroquinone, of acetone, and of quinone on the radiation dose was achieved at k_{23} 1.13×10^3 l mol^{-1} s^{-1} (Fig. 1, 3). (Such reaction of electron transfer from semiquinone of tetramethyl-1,4-benzoquinone to the O_2 molecule has the rate constant 2×10^8 l mol^{-1} s^{-1} [11]). In reaction (23) the oxidation of semiquinone by means of electron transfer to the 2,4-dichlorophenoxyacetate molecule takes place. It leads to formation of the phenyl σ-radical which is capable of abstracting the hydrogen atom from organic compounds with the high rate constant (about 10^7).

While radiolysis of the quinone-containing 2 M aqueous solution of 2-propanol with the addition of pentachlorophenol (0.001 M) the formation of chloride ions was also observed (Table 3).

At so low concentration of pentachlorophenol practically all hydrated electrons react with quinone. The formation of chloride ions is connected probably with reactions (29), (30).

$$Q^{-\cdot} + C_6Cl_5OH \rightarrow Q + Cl^- + {}^{\cdot}C_6Cl_4OH, \quad (29)$$

$$Q^{-\cdot} + C_6Cl_5O^- \rightarrow Q + Cl^- + {}^{\cdot}C_6Cl_4O^-. \quad (30)$$

Yield of chloride ions in pentachlorophenol-containing solutions also depends on pH value. The highest yield was observed in neutral medium and reached 0.32±0.03 molecule/100 eV. At pH 5 G_{Cl} is 0.19±0.05 molecule/100 eV. Decrease in the yield of chloride ions in the acid medium (pH 5) is connected with the protonation of pentachlorophenol anions (pK 4.7 [22]) and $Q^{-\cdot}$ and the decrease in the rates of the reactions (29,30). Formation of chloride ions is also possible by reaction (31).

$$QH^{\cdot} + C_6Cl_5OH \rightarrow Q + Cl^- + H^+ + {}^{\cdot}C_6Cl_4OH. \quad (31)$$

In the experiments with pentachlorophenol and benzoquinone yield of the chloride ions was ~2 times lower than in the case of trimethylbenzoquinone (Table 3). It shows that semiquinone of trimethylbenzoquinone more eagerly enters in the reaction of electron transfer to pentachlorophenol than semiquinone of benzoquinone what agrees with their redox potentials TMBQ/TMBQ$^{-\cdot}$ = –165 mV, BQ/BQ$^{-\cdot}$ = 99 mV [23].

Table 3. Radiation chemical yields (G) of the products of radiolysis of aqueous 2-propanol solution in the presence of trimethylbenzoquinone, benzoquinone, and pentachlorophenol, pH 7

Product	Trimethylbenzoquinone	Benzoquinone
	G, molecule/100 eV	
Cl^-	0.32±0.03	0.17±0.04
Cl^- [a]	0.19±0.05	
$(CH_3)_2CO$	4.41±0.16	4.56±0.21
$(CH_3)_2CO$ [b]	4.23±0.14	4.33±0.13

[a] Value of the yield at pH 5. [b] Yields of acetone in the absence of pentachlorophenol.

Hence, semiquinones can react with chloroaromatic compounds by electron transfer to the molecule of halogen-containing compound. Such process leads to elimination of chloride ions and formation of phenyl radicals active in the reactions of abstraction of hydrogen atoms. It may be expected that the presence of chloroaromatic contaminants in living systems will favor the development of the free radical processes injuring the biomolecules also due to the interaction of haloaromatic compounds with semiquinones.

EXPERIMENTAL

Bidistilled water and 2-propanol of the "chemically pure" grade were used for preparing the solutions. Sodium 2,4-dichlorophenoxyacetate (pure grade) and 1,4-benzoquinone (pure grade) were recrystallized before use. Trimethyl-1,4-benzoquinone was prepared by oxidation of the corresponding hydroquinone and purified according to the procedure [24]. Before irradiation the solutions were repeatedly saturated with argon in a syringe, and thus air in the solutions was replaced by argon. Irradiation was carried out in sealed glass ampules.

The absorbed dose power according to ferro-sulfate dosimeter was 0.3 Gr s^{-1}. Analysis of the chloride ions was carried out by potentiometric titration with silver nitrate. Before titration the solutions were acidified with nitric acid to pH 3–4. Acetone was analyzed by GLC with flame-ionization detector, carrier gas hydrogen. Concentration of hydroquinone and quinone after irradiation was evaluated spectrophotometrically against the non-irradiated samples. Extinction coefficients were 20033±305 l mol^{-1} cm^{-1} (260 nm) for quinone and 2273±81 l mol^{-1} cm^{-1} (275 nm) for hydroquinone. Radiation chemical yields of the products of radiolysis were calculated from the dependences of their concentrations on the absorbed dose. Computer modeling of radiolysis was carried out by the POMSR packet of specialized programs [25, 26] in which the model of radiolysis is approximated by a system of differential equations. Digital integration of differential equations was carried out by the 4th order Runge–Kutt method.

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