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Abstract

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KINETICS AND MECHANISM OF THE HOMOGENEOUS CATALYTIC REDUCTION OF QUINONES BY CARBON MONOXIDE IN SOLUTIONS

In works ([1], [2]) it was shown that the rate of reduction of quinones by hydrogen in a neutral medium varies in parallel with the values of their oxidation-reduction potentials (φ_0). The same dependence was found by Noynkhoffer and Pelts in the reduction of a series of quinones by carbon monoxide on palladized carbon in acidic media ([3]). The same authors found the opposite dependence when hydrogen was used for this purpose; moreover, *n*-benzoquinone and toluquinone were not hydrogenated. Rosenblatt carefully checked these experiments and obtained analogous results ([4]). Some authors find a direct relationship between φ_0 and the energy of the molecular orbitals of quinones ([5]), the difference in resonance-energy values ([6]), or the number of possible structures of the oxidized and reduced forms ([7], [8]).

Table 1

Effect of the nature and concentration of acids on the values of oxidation-reduction potentials* (φ_0, mV)
Solvent: water–dioxane (3 : 7)

No.	Oxidant	$HClO_4$, mol/l	$HClO_4$, mol/l	HCl, mol/l	HCl, mol/l
		0.025	0.98	0.068	0.272
1	*n*-Benzoquinone	615	705	645	685
2	Toluquinone	570	650	605	635

No.	Oxidant	$HClO_4$, mol/l	$HClO_4$, mol/l	HCl, mol/l	HCl, mol/l
3	β-Naphthoquinone-4-sulfonic acid	495	615	540	575
4	β-Naphthoquinone	500	580	510	540
5	α-Naphthoquinone	450	500	445	465
6	Phenanthrenequinone	–	–	420	440
7	H_2PdCl_4	670	620	550	505

* The values of φ_0 correspond to equality of the concentrations of the oxidized and reduced forms.

In studying the mechanism of reduction of *n*-benzoquinone by carbon monoxide, we previously showed that the reaction proceeds homogeneously and is activated by complex salts of palladium ([9]). Similar regularities are observed in the oxidation of ethylene in the presence of Pd(II) salts in aqueous solutions ([10–12]).

In the present work, a study was made of the influence of the structure and magnitude of the oxidation–reduction potentials of certain quinones on the kinetics and mechanism of their reduction by carbon monoxide. Solutions of H_2PdCl_4 served as the catalyst; the solvent was aqueous-dioxane mixtures. The quinones were purified by methods described in the literature ([13]) and had tabulated characteristics. The experimental procedure was described by us in ([14]). All experiments were carried out at 20° and a stirring intensity of 600 oscillations/min. The potential values are given relative to the normal hydrogen electrode.

The high catalytic activity of complex compounds of Pd(II) is associated with the ease of their reduction by carbon monoxide in aqueous solutions to elemental Pd and with the possibility of oxidation of the latter by quinones having a sufficiently high oxidation-reduction potential. If $\varphi_{\text{ox quin}} > \varphi_{\text{ox cat}}$, then reduction of the quinone occurs; if $\varphi_{\text{ox quin}} < \varphi_{\text{ox cat}}$, Pd(II) is reduced by carbon monoxide and the process ceases.

Since the potential of the system

$$Pd - 2e + 4Cl^- \rightleftarrows [PdCl_4]^{2-} \tag{1}$$

varies over wide limits depending on the concentration of Cl^- ions in solution, and the pH of the medium strongly affects φ_0 of the quinone–hydroquinone

Fig. 1. Effect of HCl concentration on the rate of reduction of *p*-benzoquinone (1), toluquinone (2), α-naphthoquinone (3), β-naphthoquinone (4). Solvent: water–dioxane (3:7); catalyst H_2PdCl_4: $1.57 \cdot 10^{-4}$ mole/liter (1, 2); $6.28 \cdot 10^{-4}$ mole/liter (3, 4).

Figure 1: Fig. 1. Effect of HCl concentration on the rate of reduction of *p*-benzoquinone (1), toluquinone (2), α-naphthoquinone (3), β-naphthoquinone (4). Solvent: water–dioxane (3:7); catalyst H_2PdCl_4: $1.57 \cdot 10^{-4}$ mole/liter (1, 2); $6.28 \cdot 10^{-4}$ mole/liter (3, 4).

system (Table 1), by varying the concentration of HCl one can find the optimal reduction conditions.

It is seen from Fig. 1 that, as $\varphi_{0\text{quin}}$ decreases, the maxima on the curves of reaction rate versus HCl concentration shift toward higher HCl concentrations. At the same time, the activity of the contact solution on the ascending branch of the curve for α-naphthoquinone, for example, is lower than for *p*-benzoquinone, whereas on the descending branch it is the reverse (Table 2).

Since, in the course of reduction, as the concentration of hydroquinone increases, the potential of the system gradually (and at the end of the experiment rapidly) shifts in the negative direction, during the experiment conditions arise successively that are characteristic for the reduction of quinones with lower values of oxidation–reduction potentials. As noted above, the concentrations of Cl^- ions (and, consequently, the degree of complexation of Pd(II) salts) that ensure maximum reduction rates for the indicated quinones are different. The course of the kinetic curves for reduction of *p*-benzoquinone at HCl concentrations of 0.003, 0.068, and 0.272 mole/liter is therefore not the same (Fig. 2). When the HCl concentration in the solution is low, the catalyst is gradually destroyed (reduced to the metal), and the reaction proceeds with a decreasing rate (Fig. 2, 1). At high concentrations, the decrease in potential creates more favorable conditions (see Table 2), and the reduction rate increases continuously, especially sharply at the end of the experiment (Fig. 2, 3). At intermediate acid concentrations the reaction rate is constant (curve 2).

Fig. 1. Effect of HCl concentration on the rate of reduction of *p*-benzoquinone (1), toluquinone (2), α-naphthoquinone (3), β-naphthoquinone (4). Solvent: water–dioxane ($3:7$); catalyst H_2PdCl_4: $1.57 \cdot 10^{-4}$ mole/liter (1, 2); $6.28 \cdot 10^{-4}$ mole/liter (3, 4).

Table 2

Reduction of quinones by carbon monoxide in a water–dioxane mixture ($3:7$)

No.	Quinone	Standard oxidation-reduction potential, mV	$[H_2PdCl_4]$, mole/liter	[HCl] at maximum point, mole/liter	Reduction rate, ml/min. $[Cl^-]$, mole/liter: 0.027	Reduction rate, ml/min. $[Cl^-]$, mole/liter: 0.40	Reaction order with respect to CO	Literature source (φ_0)
1	*p*-Benzoquinone	703	$1.57 \cdot 10^{-4}$	0.027	19.2	2.4	1.30	(13)
2	Toluquinone	653	$1.57 \cdot 10^{-4}$	0.027	20.0	5.0	1.33	(15)
3	β-Naphthoquinone-4-sulfonic acid	628	$6.28 \cdot 10^{-4}$	0.130	0.5	> 0.5	> 1.00	(16)
4	β-Naphthoquinone	547	$6.28 \cdot 10^{-4}$	0.200	0.8	4.4	0.92	(16)
5	α-Naphthoquinone	494	$6.28 \cdot 10^{-4}$	0.380	0.4	11.0	0.43	(15)
6	Phenanthrenequinone	471	$6.28 \cdot 10^{-4}$	0.380	~ 0.1	~ 0.3	0.65	(15)

Thus, the position of the maximum on the curve of reaction rate versus HCl concentration indicates the optimum composition of the Pd(II) complexes catalytically active for the given oxidizing agent.

In parallel with the decrease in the value of φ_0 of the complex, its stability increases and, consequently, the introduction of CO into the inner coordination sphere is hindered. Chloride complexes of Pd(II) in aqueous solutions are hydrated (and hydrolyzed) to a significant extent (17); therefore the exchange of CO with the inner-

with spherical ligands may in general be represented by the following scheme*:

$$[PdCl_{4-n}(H_2O)_n]^{n-2} + n\,CO \rightarrow [PdCl_{4-n-m_2}(H_2O)_{n-m_1}(CO)_m]^{n-2-m_2} + m_1 H_2O + m_2 Cl^-, \quad (2)$$

(I) (II)

where $m = m_1 + m_2$.

Figure 2

Figure 2: Figure 2

The stage of CO insertion in acidic media for quinones with a high oxidation-reduction potential is limiting. This is indicated by the value of the reaction order with respect to CO (Table 2).

Fig. 2. Reduction of *n*-benzoquinone by carbon monoxide in an acidic aqueous dioxane medium. Dioxane—70 vol.%; H_2PdCl_4—$1.57 \cdot 10^{-4}$ mol/l; HCl: 1—0.003; 2—0.068; 3—0.272 mol/l; 1′, 2′, 3′—potential curves.

For *n*-benzoquinone and toluquinone, the position of the rate maximum (Fig. 1) coincides with the maximum complexation of Pd to $[PdCl_4]^{2-}$ ([18]). The difference in the oxidation-reduction potentials of these quinones ($\Delta\varphi_0$) is 56 mV. In the presence of an oxidizing agent, equilibrium (I) shifts to the right. Therefore, in a solution of *n*-benzoquinone Pd(II) is more strongly complexed than in the presence of toluquinone. This leads to the fact that on the ascending branch of the curve, where the concentration of complex-forming ligands is insufficient, the rate of reduction of toluquinone is lower than that of benzoquinone. On the descending branch, however, the picture is reversed, and the weaker oxidizing agent reacts at a higher rate (Table 3).

Table 3

Activity of the contact solution in the reduction of *n*-benzoquinone and toluquinone
in HCl solutions
Catalyst—$1.57 \cdot 10^{-4}$ mol/l

[HCl], mol/l	Reduction rate (W), ml/min: *n*-benzoquinone	Reduction rate (W), ml/min: toluquinone	W toluquinone / W *n*-benzoquinone	[HCl], mol/l	Reduction rate (W), ml/min: *n*-benzoquinone	Reduction rate (W), ml/min: toluquinone	W toluquinone / W *n*-benzoquinone
0.003	12.5	8.0	0.64	0.068	13.3	16.2	1.22
0.007	15.0	11.6	0.77	0.136	8.5	12.0	1.41
0.013	17.6	17.5	1.00	0.272	3.5	6.8	1.94
0.027	19.2	20.2	1.05	0.544	1.5	3.0	2.00

ClO_4^- anions do not form complexes with Pd(II) ([19]); therefore, in an $HClO_4$ medium a potential is realized that is close to the oxidation-reduction potential of the system $Pd - 2e \rightleftarrows Pd^{2+}$ (Table 1). Quinones with low φ_0 are incapable of being reduced under these conditions, and destruction of complex II occurs with precipitation of elemental Pd:

$$[PdCl_{4-n-m_2}(H_2O)_{n-m_1}(CO)_m]^{n-2-m_2} \rightarrow Pd^0 + m\,CO_2 +$$

$$+ 2m\,H^+ + (n - m_1 - m)\,H_2O + (4 - n - m_2)\,Cl^-, \qquad (3)$$

and the process thereby ceases. It has been observed that the rate of reaction (3) increases sharply in the presence of an oxidizing agent.

Depending on the conditions, Pd either precipitates at once as a black solid or remains for some time in solution as part of a zero-valent complex**, similar to the recently described carbonyl complex of Pd^0 ([20]).

Attempts to reduce quinones with an oxidation–reduction potential $\varphi \leqslant 0.04$ V (n-quinondioxime, tetrahydroxyquinone, anthraquinone and

* Hydrolysis of the aquo complex in acidic media may probably be neglected.
** More detailed results will be published by us later.

a series of its derivatives) were not successful. Evidently, to carry out this process it is necessary to lower the potential of system (I) to a value at least equal to the potential of the quinone–hydroquinone system, which can be achieved only with a considerable excess of Cl^- ions in solution. However, in this case the stability of the Pd(II) chloride complex increases so much that the rate of CO insertion becomes vanishingly small.

Apparently, reduction of the quinone must be preceded by the formation of an intermediate unstable complex with the catalyst; therefore the kinetics of the process is influenced not only by the value of φ_0, but also by the structure of the molecule being reduced. Thus, the rate of reduction of α-naphthoquinone is higher than that of β-naphthoquinone and its sulfonic acid, although the latter are stronger oxidants.

A study of the influence of the composition of the solvent water–dioxane shows that the activity of the contact solution for all quinones increases with an increase in the fraction of the organic component in the mixture. At the same time, there is an inverse relationship between the φ_0 of the quinone and the ratio of the reduction rates in solutions with 30, 50, and 70% dioxane (Table 4).

Table 4

Influence of the composition of the water–dioxane solvent on the rate of reduction of quinones by carbon monoxide*

No.	Quinone	HCl concentration, mol/l	Reaction rate in water–dioxane solvent, ml/min 7 : 3 (1)	Reaction rate in water–dioxane solvent, ml/min 1 : 1 (2)	Reaction rate in water–dioxane solvent, ml/min 3 : 7 (3)	Ratio of rates (1) : (2) : (3)
1	*p*-Benzoquinone	0.068	8.7	8.7	12.6	1 : 1.0 : 1.4
2	Toluquinone	0.068	9.0	11.0	16.2	1 : 1.2 : 1.8
3	α-Naphthoquinone-4-sulfonic acid	0.136	0.9	0.9	1.9	1 : 1.0 : 2.1
4	β-Naphthoquinone	0.272	0.9	3.0	5.8	1 : 3.3 : 6.5
5	β-Naphthoquinone	0.272	0.6	2.5	9.0	1 : 4.2 : 15.0

* The concentrations of H_2PdCl_4 correspond to those indicated in Table 2.

These data make it possible to suppose that dioxane, while not being a participant in the reaction, affects the kinetics of complex formation in solution, since with a change in its concentration both the activity coefficient of HCl and many physical characteristics of the binary solvent change ([21,22]).

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Note: Figure translations are in progress. See original paper for figures.