

Reaction of Pentacyanocobaltate(II) with Derivatives of *p*-Benzoquinone

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Reaction of various substituted 1,4-benzoquinones with $\text{Co}(\text{CN})_5^{3-}$ in aqueous solution has been studied. The reaction has been shown to proceed via redox addition mechanism. Thermodynamic considerations point to the conclusion that the standard redox potential of the benzoquinone is the most important factor governing the variation of the reactivity with the change of substituents.

Introduction

In a previous communication¹ it was shown that $\text{Co}(\text{CN})_5^{3-}$ reacts with *p*-benzoquinone with formation of a bridge species, the original oxidant forming a bridge between two $\text{Co}(\text{CN})_5$ units. This reaction has been classified as proceeding by redox addition mechanism, i.e. by a concerted redox and coordination process.

In processes of this type, the ability of the substrate to be coordinated and its redox strength (given by the value of the standard redox potential of the appropriate process) determine the course of the reaction as well as the nature and stability of the products. To follow these effects the reaction of a series of substituted *p*-benzoquinones with $\text{Co}(\text{CN})_5^{3-}$ was investigated.

Experimental

Materials

Substituted *p*-benzoquinones were purified by sublimation and recrystallized from benzene or ethanol.

2-phenyl-1,4-benzoquinone was prepared according to Kvalnes² and nitranilic acid according to Nef.³

KCN was purified by ethanol precipitation from its aqueous solution.

Polarographic Measurements

These were performed as described previously.¹

Spectra

Infrared spectra were taken in nujol on a Unicam SP200 or Perkin Elmer grating infrared Model 257. A

Unicam Model SP800 spectrophotometer was used for recording the visible and ultraviolet spectra. The method for preparation of the solutions of unstable species was that described previously.¹

Potentiometric titrations

These were performed in inert atmosphere with a bright platinum electrode combined with a saturated calomel electrode using QTK compensator (Metra-Blansko, Czechoslovakia). All titrations were carried out at 0°C to minimize the decomposition of the products.

Kinetic Measurements

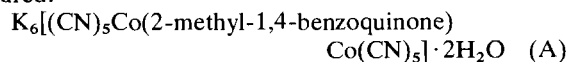
The rate of the decomposition of the substances prepared was followed spectrophotometrically or polarographically using the technique described in the previous papers.¹

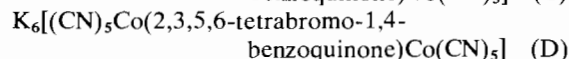
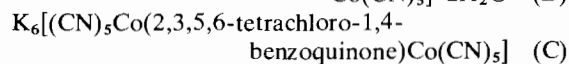
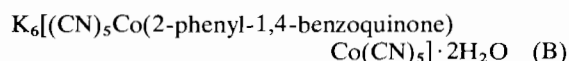
Preparations

All preparations were carried out in the atmosphere of purified argon using the Schlenk-type technique.⁴

3 g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 ml of water, the solution was carefully deaerated and cooled to 0°C. 30 ml of a deaerated solution of 4.1 g KCN was added. The corresponding quinone was then added either in stoichiometric amount (2Co:1 quinone) dissolved in benzene or ethanol (in the case of methyl derivatives) or in ten-fold excess of the solid compound. When the reaction was finished the nonaqueous phase or the surplus of solid was separated. From the resulting deep red solution the product was precipitated by the addition of 100 ml of precooled, deaerated ethanol. The precipitate formed was washed with ethanol and ether, quickly redissolved in a small volume of precooled water and reprecipitated with ethanol. The final product thus obtained was washed with ethanol and ether and dried in vacuum over P_2O_5 .

In this way the following new compounds were prepared:





The compounds were analyzed as in the previous case¹. The results of the analysis are summarized in Table I.

Results

From the series of quinones investigated the following react in the same way as *p*-benzoquinone to give compounds of general formula $[(CN)_5Co \cdot Q \cdot Co(CN)_5]^{6-}$ (I):

2,3,5,6-tetrachloro-1,4-benzoquinone (Cl-Q)

2,3,5,6-tetrabromo-1,4-benzoquinone (Br-Q)

2-methyl-1,4-benzoquinone (CH₃-Q)

2-phenyl-1,4-benzoquinone (φ -Q)

On the other hand no reaction with $Co(CN)_5^{3-}$ was observed for the following compounds:

2,5-dimethyl-1,4-benzoquinone

2,3,5-trimethyl-1,4-benzoquinone

2,3,5,6-tetramethyl-1,4-benzoquinone

nitranilic acid (3,6-dinitro-2,5-dihydroxo-1,4

benzoquinone)

chloranilic acid (2,5-dichloro-3,6-dihydroxo-1,4

benzoquinone)

2,3,5,6-iodo-1,4 benzoquinone reacts in a complicated way, primarily the iodine-carbon bond being attacked

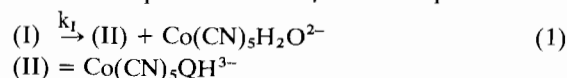
by $Co(CN)_5^{3-}$. As products of this reaction $Co(CN)_5I^{3-}$ (predominant), $Co(CN)_5H_2O^{2-}$ and species of the type (I) with 1,4-benzoquinone as bridging ligand are formed.

Partial reduction was observed for sodium anthraquinone- β -sulphonate (products were not followed in detail). 1,4-naphthoquinone seems to react in a different way, one $Co(CN)_5^{3-}$ unit being consumed per molecule of naphthoquinone.

The same general reaction pattern as observed with 1,4-benzoquinones was found also with 1,4-dinitrobenzene;⁵ the product of this reaction is, however, very unstable. Dinitrobenzene differs also in that its reaction with $Co(CN)_5^{3-}$ proceeds much more slowly than that with benzoquinones.

The properties of the isolated bridge species are summarized in Table II.

All the bridge species (I) isolated show the same pattern of electrochemical and spectrochemical behaviour, the differences observed reflect the changes in the composition of the organic ligand. Analogously to the previously described compound resulting from the reaction with 1,4-benzoquinone, all compounds of the type (I) show a four electron reduction in the potential region typical for Co^{III} pentacyanocomplexes. Similarly, all compounds (I) decompose in the solution in two steps. The first step can be represented as



The kinetic data for this reaction are summarized in Tables IV to VI. The analysis of the data shows that

TABLE I. Elemental analyses of the complexes.

	Co		C		N		H		X	
	calc.	found	calc.	found	calc.	found	calc.	found	calc.	found
(A):	15.31	15.26	26.49	26.1	18.17	18.03	1.31	1.52		
(B):	14.15	14.04	31.74	31.92	16.82	16.71	1.45	1.61		
(C):	13.73	13.86	22.38	22.09	16.31	16.15	–	–	16.52	16.48
(D):	11.37	11.49	18.54	18.83	13.52	13.42	–	–	30.84	30.76

TABLE II. Some properties of the $K_6[(CN)_5Co \cdot Q \cdot Co(CN)_5]$ species.

Q	ν (cm ⁻¹) 0.1M KOH	$E_{1/2}$ (SCE) (mV) 0.1M KOH, 25°	$k_1 \times 10^4$ (s ⁻¹) 0.1M KOH, 25°
unsubstituted ¹	23000	-1591	1.9
CH ₃ -Q	23400	-1583	5.75
φ -Q	23600	-1550	7.9
Cl-Q	23900	-1513	9.8
Br-Q	24000	-1471	25.2

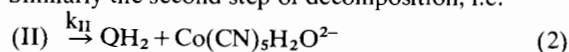
TABLE III. Some properties of the $\text{K}_3[\text{Co}(\text{CN})_5\text{QH}]$ species.

Q	ν^a (cm^{-1})	$E_{1/2}(\text{SCE})^a$ (mV)	$E_{1/2}$ oxid. SCE (mV)		$k_{\text{II}} \times 10^4{}^c$ (s^{-1})
			Pt vibr. ^b	Hg ^c	
unsubstituted ¹	3200	-1531	+1020	+20	5.4
	36100				
$\text{CH}_3\text{-Q}$	32300	-1515	+1000	-74	8
	36000				
Cl-Q	29900	-1520	+1050	-	5
	35700				
Br-Q	29900	-1531	+1030	-	5
	35700				

^a pH 9.5; 0.1M NaCl. ^b pH 9.5; 1M NaCl. ^c pH 9.2; 0.1M NaCl.

the reaction is acid-catalyzed. The $k_{\text{H}_3\text{O}^+}$ values are given in Table X, $k_{\text{H}_3\text{BO}_3} = (1.2 \pm 0.2) \times 10^{-3} \text{ mol}^{-1}\text{s}^{-1}$ and is the same for all substances studied.

Similarly the second step of decomposition, i.e.



is an acid-catalyzed reaction (see Tables VII-IX), $k_{\text{H}_3\text{O}^+}$ values are given in Table X, $k_{\text{H}_3\text{BO}_3} = (1.4 \pm 0.2) \times 10^{-4} \text{ mol}^{-1}\text{s}^{-1}$ and is again independent of the nature of Q.

Unlike the bridge compounds, (II) can be oxidized at the electrode, the potential of this process being dif-

ferent from that of the parent hydroquinone. This implies that the organic ligand is being oxidized while bonded in the complex. Complexes of the type (II), derived from tetrachloro and tetrabromobenzoquinone are oxidized at such positive potentials that the process cannot be seen at dropping mercury electrode. Values for platinum vibrating electrode are given in Table III. The mechanism of the oxidation process is the same as that described for $\text{K}_3[(\text{CN})_5\text{Co}(\text{OC}_6\text{H}_4\text{OH})]$.¹ Most of the species (II) were not isolated in the pure form and their properties were studied in the solution. (See Table III for summary of their properties.)

TABLE IV. Dependence of k_1 upon pH. Buffer acid concentration = 0.05M; ionic strength = 0.1M; 25°C.

Q pH	$k_1 \times 10^4 \text{ s}^{-1}$			
	Cl-Q	Br-Q	$\text{CH}_3\text{-Q}$	$\varphi\text{-Q}$
10.80	-	-	760	-
11.20	661	-	354	515
11.60	240	435	142	192
11.90	105	380	58	87.5
12.20	66.5	175	28.5	44.5
12.40	37.5	79.5	23	32
12.80	17.5	43.5	7.65	12.5
13.0	10.0	25.0	5.8	7.6

TABLE V. Dependence of k_1 upon acid concentration. pH = 11.60; ionic strength = 0.8M; 25°C.

Q [H_3BO_3], M	$k_1 \times 10^4 \text{ s}^{-1}$			
	Cl-Q	Br-Q	$\text{CH}_3\text{-Q}$	$\varphi\text{-Q}$
0.05	23.0	40.5	12.5	17.5
0.10	24.3	41.2	13.2	18.0
0.15	25.0	42.0	13.7	18.7

TABLE VI. Dependence of k_1 upon ionic strength. pH = 11.60; buffer acid concentration = 0.05M; 25°C.

Q (M)	$k_1 \times 10^4 \text{ s}^{-1}$			
	Cl-Q	Br-Q	$\text{CH}_3\text{-Q}$	$\varphi\text{-Q}$
0.1	240	435	142	192
0.3	95.5	158	50	71
0.5	50	89	27.5	36.5
0.8	23	40	12.5	17.5

TABLE VII. Dependence of k_{II} upon pH. Buffer acid concentration $\times 0.05\text{M}$; ionic strength $\times 0.1\text{M}$; 25°C.

Q pH	$k_{\text{II}} = 10^4 \text{ s}^{-1}$			
	Cl-Q	Br-Q	$\text{CH}_3\text{-Q}$	$\varphi\text{-Q}$
8.50	22.7	21.0	37.2	44.7
8.70	15.5	14.5	27.0	31.7
8.90	12.1	11.5	16.0	22.0
9.20	6.3	5.5	8.70	11.0
9.50	2.3	3.2	4.8	6.15
9.60	2.05	2.1	3.9	4.3 ₅

TABLE VIII. Dependence of k_{II} upon acid concentration. pH = 9.50; ionic strength = 0.8M; 25°C

Q [H ₃ BO ₃], M	$k_{II} \times 10^5 \text{ s}^{-1}$			
	Cl-Q	Br-Q	CH ₃ -Q	φ -Q
0.05	3.55	5.40	7.80	10.0
0.10	4.20	6.00	8.50	10.70
0.15	5.00	6.50	9.20	11.50

TABLE IX. Dependence of k_{II} upon ionic strength. pH = 9.50; buffer acid concentration = 0.05M; 25°C.

Q (M)	$k_{II} \times 10^5 \text{ s}^{-1}$			
	Cl-Q	Br-Q	CH ₃ -Q	φ -Q
0.1	23.0	32.0	48.0	61.0
0.3	11.0	16.5	23.5	30.0
0.5	6.5	9.5	13.5	18.0
0.8	3.5	5.5	8.0	10.0

TABLE X. Values of $k_{H_3O^+}$ for reactions (1) and (2). Buffer acid concentration = 0.05M; ionic strength = 0.1M; 25°C.

Q	$k_{H_3O^+} \times 10^9$	$nk_{H_3O^+} \times 10^7$
unsubstituted ¹	1.8 ± 0.3	8.4 ± 0.4
Cl-Q	9.8 ± 0.4	8.4 × 0.4
Br-Q	24.4 ± 0.4	8.4 ± 0.4
CH ₃ -Q	5.2 ± 0.4	13.5 × 1.0
φ -Q	7.6 ± 0.15	18.2 ± 0.8

Discussion

The results obtained show two distinct types of behaviour of substituted benzoquinones: one group reacts very easily and rapidly with $\text{Co}(\text{CN})_5^{3-}$ whereas the second one, mostly poly-methylated species, do not undergo the reduction at all.

In cases where the reaction proceeds, the mechanism is the same as that described for the unsubstituted benzoquinone itself, i.e. redox addition mechanism resulting in the formation of bridge species of the type (I).

This conclusion has been reached on the basis of the nature of the isolated products as well as from the observed electrochemical behaviour of the products. The latter shows unambiguously that a redox process takes place during the formation of (I) and specifies the reaction as a redox addition* in which the redox

* In contrast, a nucleophilic addition would merely shift the parameters of redox reaction and would not change the general pattern of the reduction of reaction products.

process has been completed, i.e. compounds of the type I are to be looked at as Co^{III} complexes with *p*-hydroquinone dianion as a bridge ligand.

In the case of substituted quinones which do not react with $\text{Co}(\text{CN})_5^{3-}$ at all, the failing of the reaction is due to unfavourable thermodynamic situation of the system and not due to the kinetic inertness as even a prolonged reaction time does not result in any detectable decrease of concentration of the reacting species.

The thermodynamic stability of the products of a redox addition with complete electron transfer is given by:



$$\Delta G^\circ = \Delta G^\circ - F(E_R^\circ - E_S^\circ) \quad (4)$$

E_R° and E_S° are the standard redox potentials of the couples $R-R^+$ and $S-S^-$, respectively and ΔG_C° corresponds to the hypothetical coordination process



It is obvious that the ability of the components to coordinate after the electron transfer is a decisive factor for a redox addition process and it might even overbalance the unfavourable value of $(E_R^\circ - E_S^\circ)$, i.e. great ΔG_C° might make such processes possible which according to the values of standard redox processes would not proceed as simple redox reaction.

If the reaction of a series of substrates S with the same reduction agent R is compared, the change of both ΔG_C and E_S° with the change in the nature of S has to be considered. In the present case of substituted quinones, such values E_S° are to be chosen which correspond to a simple electron transfer process $Q \rightarrow Q^-$ which, together with coordination of one $\text{Co}(\text{CN})_5$ unit, represent the first, and decisive, step in the reaction followed. The appropriate E_S° values cannot be obtained in water as complicated protonation and dimerization reactions influence strongly the apparent redox potentials. However, in nonaqueous solvents the reduction potentials of quinones reflect correctly the effect of substitution upon the electron affinity of the compounds.

Values of E° for a series of quinones, measured in acetonitrile, are given in Table XI. In a simplified way we may think of these values as reflecting the electron affinity of the π -system of the quinone, including, of course, the change of delocalization of π electrons when going from the quinone (Q) to the semiquinone anion (Q^-). These values are thus proportional to the $(E_R^\circ - E_S^\circ)$ values of eq. 4, and it is reasonable to assume that their differences can be used as the measure of the change of redox strength of the quinones in the reaction with $\text{Co}(\text{CN})_5^{3-}$.

The coordinating ability of the semiquinone anion towards the $\text{Co}(\text{CN})_5$ unit would, to the greatest part, depend upon the properties of the lone electron pairs on oxygen. However, due to the delocalization of the

TABLE XI. Half-wave potentials of substituted quinones and dissociation constants of corresponding hydroquinones.

Q	$(E_{1/2})_I^a$	$(E_{1/2})_{II}^a$	pK ^b	Reaction with $\text{Co}(\text{CN})_5^{3-}$
2,3,5,6-Br-Q	0.00	-0.72	<4.6 ^e	+
2,3,5,6-Cl-Q	+0.01	-0.71	<5.0 ^e	+
2- <i>p</i> -Q	-0.50	-1.03	9.6 ^e	+
unsubstituted	-0.51	-1.14	9.85 ^c	+
2-CH ₃ -Q	-0.58	-1.10	10.05 ^c	+
2,5-CH ₃ -Q	-0.67	-1.27	10.38 ^d	-
2,3,5,6-methyl-Q	-0.84	-1.45	11.25 ^c	-

^a Values measured in acetonitrile at 25°, satd. calomel electrode (M.E. Peover, *J. Chem. Soc.*, (4540, 1962). $(E_{1/2})_I$ corresponds to the $\text{Q} \rightarrow \text{Q}^-$ reaction. $(E_{1/2})_{II}$ to the $\text{Q}^- \rightarrow \text{Q}^{2-}$ reaction. ^b pK value of the first dissociation step of hydroquinone in aqueous solution at 25° C. ^c J.D. Baxendale and H.R. Hardy, *Trans. Faraday Soc.*, 49, 1140 (1953). ^d C.A. Bishop, and L. K. J. Tong, *J. Am. Chem. Soc.*, 87, 501 (1965). ^e Values estimated on the basis of additivity principle using the values for substituted phenols.

π system in the semiquinone anion the possibility of the π -bond formation between oxygen and cobalt ($\text{Co} \rightarrow \text{O}$) also exists. There is no direct way to determine ΔG_C° values or their general trend. The σ -contribution to ΔG_C° values would be expected to increase in the sequence of substituents halogen-hydrogen-mono-methyl-polymethyl, as can be deduced from the pK values measured for the corresponding hydroquinones (see Table XI). The π -contribution given by the ability of the semiquinone anion to accommodate π -electrons from cobalt, would, however, decrease in the same direction. The general trend of absolute values of $(E_{1/2})_I$ and of $(E_{1/2})_{II}^*$ with the change of the substituent, as well as the calculated values of or-

bital energies,⁶ show a decreasing electron affinity of the π -antibonding system with increasing number of methyl group, making thus the π -contribution to the Co-oxygen bond smaller. The σ and π contributions to the ΔG_C° oppose thus each other and it is reasonable to assume, that the change of ΔG_C° with substitution on the quinone would be rather small and the contribution of ΔG_C° to the overall stability of the products could be expected to be roughly constant within the series.

The most striking fact in the series studied is the abrupt change in reactivity when going from mono-methyl derivative to polymethyl-derivatives. The above discussion leads to the conclusion that this is most probably due to the unfavourable value of E_S° for the dimethyl quinone. The difference in E_S° between the mono- and di-methyl derivatives amounts to ca. 2 kcal what is enough to make the product of the first reaction step unstable to such an extent that the reaction does not proceed to any detectable extent under the experimental conditions used.

This result implies very interesting conclusions about the nature of the first reaction step, which are being now tested experimentally.

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* The $(E_{1/2})_{II}$ values are strongly influenced by the electron pairing energy in the singly occupied π -orbital of semiquinone, generally, however, their absolute values reflect the tendency of the semiquinone to accommodate electrons.