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Synthesis and Transformations of Liquid Redoxites

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Abstract

Problems of synthesis and transformations of liquid redoxites have been considered in extraction systems and in systems that contain cations of metals of variable valence. A new method has been put forward to reduce (or to oxidize) cations of *d*-elements in water solutions of their salts by a liquid redoxite that is present in an organic phase. The procedure can be employed in extraction and separation processes for cations of metals, in the systems where redox processes occur at the phase boundary, and also for organic syntheses that represent a redox process.

INTRODUCTION

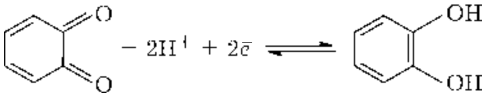
The urgency of studies on redoxites does not weaken in the course of time. However, insights available in the literature apply mostly to investigations of systems of solid redoxites [1–3]. Problems of synthesis and the properties of liquid redoxites are discussed much less often, and they typically relate to studying the properties of oxidation-reduction systems themselves [4]. Our Institute was the first to begin a research into liquid redoxites with reference to extraction systems, where redox processes take place, and this is our priority direction. These liquid redoxites are the systems, where oxidation-reduction processes occur at the interface between aqueous and organic phase; meanwhile, the reducer (or the oxidizer) represents the solution of an organic reversible oxidation-reduction system in the relevant solvent, while the reduced (or the oxidized) cation of metal resides in the aqueous phase.

Our task in view is to create systems of liquid redoxites that are capable, while they reside in the organic phase, to reduce (or to oxidize) cations of *d*-elements in the aqueous phase with no contamination of the aqueous phase by the reducer (or by the oxidizer). The viability of such a reduction procedure is determined by the fact that the reducer and the reduced form, while being in different phases, can be easily separated in space.

The urgency of the problem involves all its components: the development of science, of practice, and scientific novelty. The development of science is determined by the circumstance that the research level that has been achieved in this field to date is controlled by the research of organic oxidation-reduction systems themselves, regardless the fact that they are involved in the interaction with cations of *d*-elements in water solutions. In our opinion, the problem requires a comprehensive approach that is based upon the achievements of organic chemistry (chemistry of oxidation-reduction systems themselves), inorganic chemistry (chemistry of *d*-elements in water solutions), electrochemistry (redox potentials of cations of metals as well as those of oxidation-reduction systems and how these potentials depend on the conditions of the medium), as well as chemistry of metal complexes (in view of the fact that complex formation is possible between organic system and the cation of *d*-element). Studying the interactions with liquid redoxites in extraction systems is the one that represents the development of science in the given field. Development of practice consists in solving the applied problems of inorganic chemistry: reduction (oxidation) of cations of metals in water solutions with no contamination by their reducer (the oxidizer). Practical importance for organic chemistry consists in the opportunity to reduce (or to oxidize) organic compounds by water solutions of salts of metals (*d*-elements) and to synthesise products that cannot be obtained by alternative methods familiar in organic chemistry; to put it another way, the so-called "extraction synthesis" of organic compounds. Scientific novelty lies in the fact that investigation of systems of liquid redoxites with reference to extraction processes and the processes at the interface of water solutions of salts of metals of variable valence in contact with organic oxidation-reduction systems is yet to be performed regularly. The problem like this was not put forward before.

As is implied by the examination of literary data on liquid redoxites, the modern-day level applies to investigate the transformations inside an organic oxidation-reduction system itself. The following questions are of primary importance during this research. The first, the primal problem is to study the redox potentials of organic oxidation-reduction systems [5]. The second problem is to study an effect of electron-donation and electrophilic groups on the redox potential of the redoxite [6, 7]. The third question lies in the variation of the redox potential of a given system as the pH increases from 7 to 11 [8, 9], and at last, the fourth question is an effect of solvent and of many other factors on the redox potential of the redoxite [10].

Although extraction processes that involved the liquid redoxites were not investigated so far, it has been known (to take an illustration, for *ortho*-quinone–pyrocatechol system) that each specific ingredient of an oxidation-reduction system, *i.e.* as an individual material, not a system, is an extractant that forms either derivatives of metals with respect to a hydroxyl group for pyrocatechol, or π-complexes with orthoquinone.



Accordingly, a reduced form, that is pyrocatechol, with C_8–C_{16} alkyl radicals available inside, was applied as extractants for cations of metals with a constant oxidation state [11–13]. The oxidized form, orthoquinone, is capable to form both neutral complexes with iron and platinum metals [14], and paramagnetic complexes of metals [15, 16] in anhydrous and oxygen-free medium of organic solvents. It is obviously possible to combine complexing capacity of this system with its oxidation-reduction properties to extract and separate cations of elements with variable oxidation state and with the associated redox potentials. Meanwhile, allowance should be made for the fact that the conditions of an extraction process often differ from those conditions that the reactions of complex formation were examined.

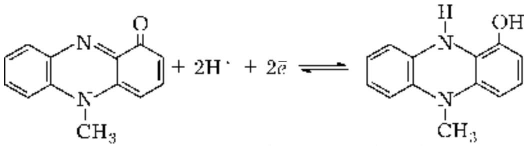
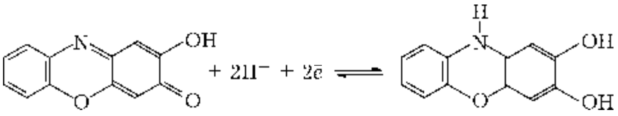
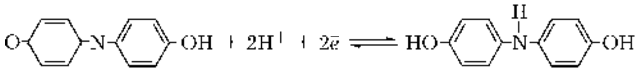
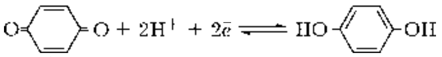
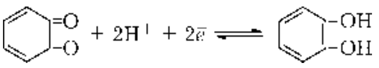
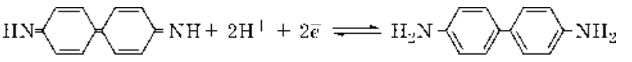
Given the conditions of extraction, at the phase boundary for cations of metals with a variable oxidation state, redox processes that result in a changed oxidation state of metal may take place along with the processes of extraction of metal cation by the system that constitutes a redoxite. In so doing, either ions of metal with a lower oxidation state, or with a higher oxidation state, or both of them together (which depends on the rates of complex formation of the oxidized and reduced forms of the ion of metal and on the stability of complexes) will pass into the organic phase. The extraction does not have to occur for certain cations of *d*-elements, but the redox process will be realized. In so doing, the reduced form of metal ions (if the redox potential of the oxidation-reduction system is below than that of metal cation) will be accumulated in the aqueous phase, while the reducer stays in the organic phase together with the oxidized form. In this case, the reduced form of metal ions remains in the aqueous phase and it can be easily separated from the organic reducer. This is the fundamental difference between these redox processes and the processes that occur in a single phase (in water), when it is necessary to separate the reducer and the reduced form from each other by a certain chemical method.

Liquid redoxites can find application in hydrometallurgy of gold and platinum metals, of uranium, and in alternative systems where a redox process occurs with the involvement of cations of metals with a variable oxidation state and with a fixed redox potential.

Creating systems of liquid redoxites with fixed potentials and properties has its origins in the modification and the improvement (according to the purposes in view) of oxidation-reduction systems that have been known so far and that are represented by different classes of organic compounds. Depending on the magnitude of the redox potential of ions of metals [17, 18] a proper organic oxidation-reduction system can be selected for their reduction (or oxidation). Applied to organic oxidation-reduction systems that are known to date, the redox potentials [5] vary over a wide range: at pH 0, they are mostly in an interval 0−1 V; and they decrease as we go to pH 7. Literary data on the potentials for higher pH values have been received preferentially by extrapolation, although there are sparse experimental data for the range of pH values of 7−11 [8, 9]. Organic reversible oxidation-reduction systems (Table 1) can be used as the actuation medium of re-

TABLE 1

Redox potentials of certain organic oxidation-reduction systems

No.	Semireaction	E^0, V	E^7, V
	Derivatives of phenazine		
1		0.235	−0.034
2	Other N- and C-derivatives	0.05−0.35	−0.034 ... −0.385
	Oxazines		
3	 Phenoxazone	0.35	–
4	Alternative oxazines	0.583−0.380	0.047 ...−0.051
	Indophenols		
5	 Indophenol	0.649	0.228
6	2,6-Dichlorondophenol	0.668	0.217
7	Diphenylamine	0.76	–
8	4-Nitrodiphenylamine	1.03	–
9	4-Sulphodiphenylamine	0.85	–
10	 Parabenzoquinone	0.699	0.285
11	 Orthobenzoquinone	0.79	–
	Benzidines		
12		0.921	–
13	3,3'-Dimethylbenzidine	0.873	–
14	3,3'-Diethoxybenzidine	0.79	–
15	3,3'-Dichlorobenzidine	0.936	–

doxite. The redox potentials that have been received in the work of Clark [5] show the following notation: E^0 is the potential at pH 0, E^7 is that at pH 7.

For the semireactions that are given in Table 1 and that have been written generally as

$$A + 2H^+ + 2\bar{e} \rightleftharpoons AH_2$$

the dependence of the potential of the oxidation-reduction system on the pH takes the following form:

$$E = E_0 + \frac{RT}{nF}\ln\frac{[A][H^+]}{[AH_2]}$$

where E_0 is the standard redox potential; R is the gas constant; T is absolute temperature; F is Faraday constant; n is the number of transferred electrons; [A], $[H^+]$, $[AH_2]$ are the respective concentrations of the oxidized form, of hydrogen ions, and of the reduced form.

Varying the pH, we can reach lower potentials and we can increase the reduction properties of the organic oxidation-reduction system. Meanwhile, it is necessary to make allowance for the circumstance that the redox potential of ions of metals also varies with an increase in the pH [19]. The equation for E makes allowance only for the main ingredients of the reaction. Actually, normal reaction in many organic oxidation-reduction systems is complicated by way of the formation of alternative products, for example, by semiquinones in quinone–hydroquinone systems.

Many organic oxidation-reduction systems that are familiar thus far can also be extractants since they contain several functional groups that are prone to complex formation, and the formed complexes are soluble in organic solvents. Nevertheless, these systems not all are involved either in chemistry of extraction, or in chemistry of redox processes with *d*-elements included. Practice shows more likely abandoning the systems of extractants with the capacity for redox transformations in contact with ions of metals that alter oxidation state. (This is considered a complication, as this leads to a change in the composition of the extractant.) It is our belief that such systems yield additional opportunities for chemistry of extraction processes, since they allow changing the oxidation state of cations of *d*-elements and separating them on this basis. It is clear that these different opportunities should be associated with specific problems. One of them involves the reduction of cations of *d*-elements in water solutions by organic reducers that are in an organic phase.

LIQUID REDOXITES AROUND ALKYLATED DIHYDROXY DERIVATIVES OF BENZENE

From a large number of reversible systems that are not in use so far as liquid redoxites, we chose 1,2-dihydroxybenzene (pyrocatechol) containing hydrophobic substituents in the benzene ring as a reducer for cations of transition elements. We made this choice based on the fact that oxygen atom has not so large number of oxidation states as, for example, sulphur, nitrogen, and phosphorus in the appropriate organic compounds, where oxidation state of an atom of a functional group varies. In addition to oxidation-reduction properties, this system shows the extractant properties owing to the availability of two functional hydroxyl groups that are in *ortho*-position, which makes a chelating ligand of it. This system is reversible, the oxidized and the reduced forms thereof are relatively stable, since it does not include functional groups, which incorporate elements with a set of difficult-to-stabilise oxidation states, or the elements that oxidize with the destruction of the oxidation-reduction system.

The variation of the redox potential of an organic oxidation-reduction system is influenced upon by the groups that are included in it. Table 1 arranges oxidation-reduction systems in the increasing order of their redox potential. It is also possible to track an effect of substituents on the potential in each system. As we take into account the fact that the effect of a substituent in the system on the dissociation constant of the reduced form of the redoxite is variable for different systems, we cannot anticipate any fixed change in the potential that is constant for different systems, although the order of the change is always the known value. We can observe a common order of the changing redox potentials of oxidation-reduction systems upon the introduction of substituents. Electron-donating substituents (those of alkyl, alkoxyl, and hydroxyl nature) that enter the system reduce its redox potential and thus enhance the reduction properties of the system. On the contrary, electrophilic groups (sulpho, nitro, and halogen) raise this potential and enhance the oxidizing properties of the oxidation-reduction system. Sometimes, by way of changing the substituents alone within the same oxidation-reduction system we can reach the variation in the redox potential that is identical to that in going from one oxidation-reduction system to another. So, the incorporation of nitro groups into diphenylamine (E_0 = 0.76) makes its redox potential 270 mV higher. The same change in the potential is evidenced in going from the oxidation-reduction system of indophenol (E_0 = 0.649) to the benzidine system (E_0 = 0.921). To put it otherwise, as we work with an oxidation-reduction system, we can modify its potential by means of the introduced substituents of a different nature.

The various groups that are incorporated in an oxidation-reduction system affect not only the redox potential, but also the solubility of the system in water. It is common knowledge that sulpho and nitro groups enhance the water solubility, while alkyl and alkoxyl groups make it lower.

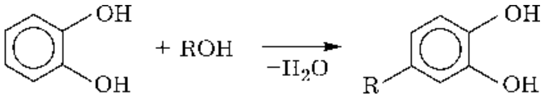
To work with liquid redoxites, we first need to obtain them. We began developing new methods of synthesis of these systems. The point is that the preparation methods that are described in the literature were worked up for water-soluble oxidation-reduction systems. These systems cannot be liquid redoxites. Therefore, as we started the synthesis of initial oxidation-reduction systems around pyrocatechol, we assumed that tertiary alkyl radicals would be introduced into it that show the highest electron-donating effect among alkyl radicals and that lower the redox potential to the greatest degree. These groups impart hydrophoby to the organic system, which allows a more complete separation of the reducer and the reduced form of a metal ion (once it remains in the aqueous phase).

The introduction of tertiary alkyl groups into pyrocatechol occurred through alkylation of pyrocatechol by tertiary alcohols. When alkylating by isostructured primary alcohols under specified conditions, a similar rearrangement occurs to form tertiary alkyl groups during the synthesis. The course of such a rearrangement is described in the literature and it is determined by the circumstance that three alkyl groups more completely extinguish a positive charge on the carbocation during the formation of the carbocation from alcohol in the alkylation reaction. Because of this, it is more stable than carbocations of other structure that are formed in the same reaction. This is responsible for the structure of the compound **1** from 2-methylpropanol and of the compound **4** from 2-ethylhexanol that are given in Table 2. The formation of these cations occurs under the Scheme 1.

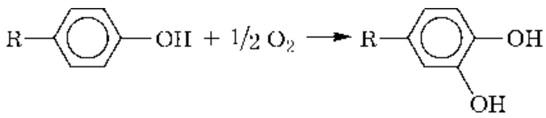
The synthesis processes used for the most part industrially produced alcohols, but we synthesized certain alcohols, namely, 3-methyl-pentanol-3 and 3-methylnonanol-3 (the compounds **3** and **6** respectively, see Table 2), by the procedure of organomagnesium synthesis from 2-butanone and 2-octanone (Schemes 2 and 3, respectively).

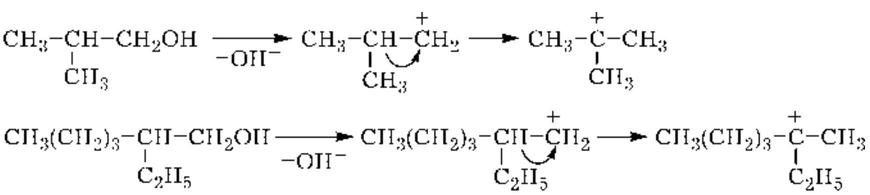
Alkyl pyrocatechols can be prepared both by alkylation of pyrocatechol with alcohol employing an acid catalyst (scheme I), and by oxidation of alkyl phenol (scheme II):

I



II





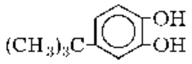
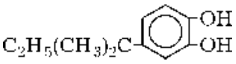
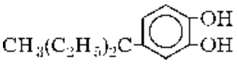
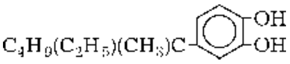
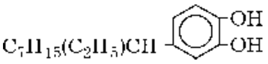
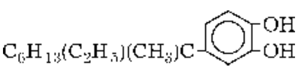
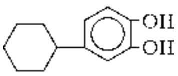
$$CH_3-\underset{CH_3}{CH}-CH_2OH \xrightarrow[-OH^-]{} CH_3-\underset{CH_3}{CH}-\overset{+}{C}H_2 \longrightarrow CH_3-\underset{CH_3}{\overset{+}{C}}-CH_3$$

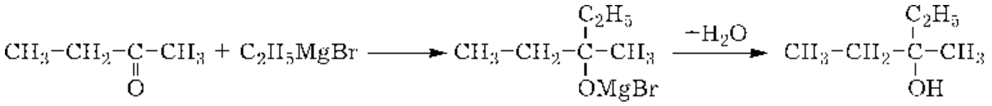
$$CH_3(CH_2)_3-\underset{C_2H_5}{CH}-CH_2OH \xrightarrow[-OH^-]{} CH_3(CH_2)_3-\underset{C_2H_5}{CH}-\overset{+}{C}H_2 \longrightarrow CH_3(CH_2)_3-\underset{C_2H_5}{\overset{+}{C}}-CH_3$$

Scheme 1.

TABLE 2

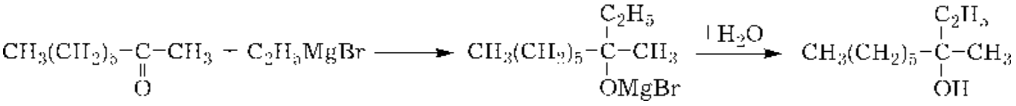
4-Alkylpyrocatechols

Compound	Empirical formula	Source alcohol	Yield, %	T_{boil}, °C/P, mm Hg (T_{melt}, °C)	n_D^{20}
1		2-Methylpropanol	96	137–138/5	1.5330
2		2-Methylbutanol-2	83	153–154/7 (41–42)	1.5323
3		3-Methylpentanol-3	50	154–155/5 (48–49)	
4		2-Ethylhexanol	55	174–175/5	1.5240
5		Decanol-3	60	185–186/6	1.4920
6		3-Methylnonanol-3	43	192–193/4	1.5170
7		Cyclohexanol	65	164–165/5 (85–86)	



$$CH_3{-}CH_2{-}\underset{\underset{O}{\|}}{C}{-}CH_3 + C_2H_5MgBr \longrightarrow CH_3{-}CH_2{-}\overset{\overset{C_2H_5}{|}}{\underset{\underset{OMgBr}{|}}{C}}{-}CH_3 \xrightarrow{-H_2O} CH_3{-}CH_2{-}\overset{\overset{C_2H_5}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH_3$$

Scheme 2.



$$CH_3(CH_2)_5{-}\underset{\underset{O}{\|}}{C}{-}CH_3 - C_2H_5MgBr \longrightarrow CH_3(CH_2)_5{-}\overset{\overset{C_2H_5}{|}}{\underset{\underset{OMgBr}{|}}{C}}{-}CH_3 \xrightarrow{\mathrm{I}\,H_2O} CH_3(CH_2)_5{-}\overset{\overset{C_2H_5}{|}}{\underset{\underset{OH}{|}}{C}}{-}CH_3$$

Scheme 3.

By virtue of the fact that pyrocatechol is alkylated with more difficulties than phenol (especially by higher alcohols), the procedure II is more preferred with the availability of good preparative methods for oxidation of alkyl phenols. However, we failed so far in developing a convenient method for oxidation of alkyl phenols, especially with long alkyl radicals, that may show oxidizing reactions by means of C–C bonds of alkyl radical; therefore, the procedure I was used as the basic one. Synthesis of 4-*tert*-butylpyrocatechol is described in the literature [20]. We have worked out a more advanced way to synthesise 4-alkylpyrocatechols [21], whereby an extensive series of such compounds (see Table 2) has been obtained. The procedure can be realized under commercial conditions, because all mother substances are now produced by the national industry, and the setups and the operations are simple.

We pioneered in testing all the compounds, presented in Table 2, as liquid redoxites [22]. With this end in view, water solutions of salts of *d*-elements, the cations of which show higher redox potentials (E_0 = 0.79), when compared to pyrocatechol system, were mixed with solutions of 4-alkylpyrocatechols in organic solvents (chloroform or diethyl ether).

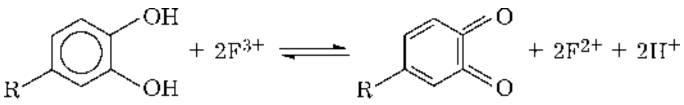
Table 3 illustrates data of elemental analysis for 4-alkylpyrocatechols.

Time for the complete transformation of a metal cation into the reduced form was determined from results of the analysis of the aqueous phase. It was found that this quantitative transformation (with a small excess of redoxite) proceeds with a great velocity. Then it was checked if there are ions of metal in the organic phase. After solvent stripping, the oxidized form of the redoxite, the appropriate alkyl benzoquinone, precipitated from the or-

TABLE 3

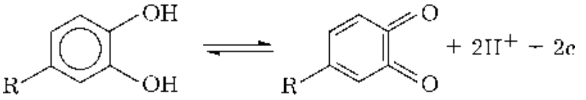
Data of elemental analysis for 4-alkylpyrocatechols

No.	Compound	Empirical formula	C content, mass %		H content, mass %	
			observed	calculated	observed	calculated
1	4-*tert*-Butyl-1,2-dihydroxybenzene	$C_{10}H_{14}O_2$	72.42	72.26	8.38	8.49
2	4-(2-Methylbutyl-2)-1,2-dihydroxybenzene	$C_{11}H_{16}O_2$	73.17	73.30	8.75	8.95
3	4-(3-Methylpentyl-3)-1,2-dihydroxybenzene	$C_{12}H_{18}O_2$	74.35	74.23	9.14	9.34
4	4-(3-Methylheptyl-3)-1,2-dihydroxybenzene	$C_{14}H_{22}O_2$	75.54	75.63	9.82	9.97
5	4-(Decyl-3)-1,2-dihydroxybenzene	$C_{16}H_{26}O_2$	76.63	76.75	10.35	10.46
6	4-(3-Methylnonyl-3)-1,2-dihydroxybenzene	$C_{16}H_{26}O_2$	76.58	76.75	10.30	10.46
7	4-Cyclohexyl-1,2-dihydroxybenzene	$C_{12}H_{16}O_2$	74.82	74.97	8.22	8.38

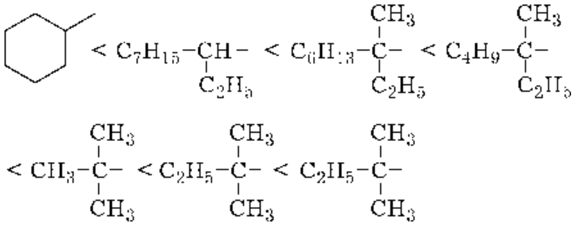


Scheme 4.

ganic phase. It has been found out that redoxites around 4-alkylpyrocatechols show very high reduction activity in relation to a number of cations of *d*-elements. Times for the transformation of cations of metals into the reduced form are extremely small. The effect of liquid redoxite in these systems can be seen as



An influence of alkyl radical R on the properties of a redoxite was examined in a series of 4-alkylpyrocatechols. The nature of alkyl group has its effect not only upon the water solubility of the redoxite, but also upon its reduction activity. We have found that accumulation of alkyl radicals at a carbon atom that is attached to a benzene ring enhances the reduction properties of pyrocatechol system. Depending on the R radical, the pyrocatechols we have studied [22] are arranged within the following succession of the increasing reduction activity:

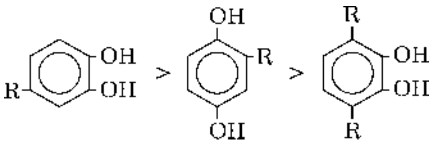


It is evident that the enhancement of the reduction properties is determined by an increase in the electronic density at the carbon atom that is attached to the benzene ring, and this leads to a decrease in E_0 for 4-alkylpyrocatechol. This succession is of practical importance, for there are no experimentally measured values E_0 for these systems.

The interaction of 4-alkyl pyrocatechols with a cation of metal, for example with an ion of iron (III), proceeds according to the Scheme 4.

Change-over to 1,4-dihydroxybenzene (hydroquinone), to a system with a lower redox potential (E_0 = 0.699) relative to pyrocatechol, does not lead as one might expect to the enhancement of the reduction properties in

2-alkyl hydroquinones in comparison to 4-alkylpyrocatechols. The accumulation of electron-donating alkyl radicals in pyrocatechol [23] does not produce either an expected increase in the reduction activity of the system. The activity weakens in the succession of



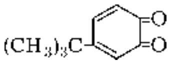
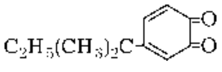
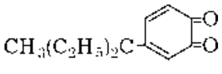
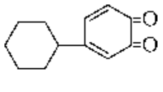
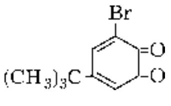
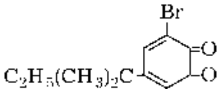
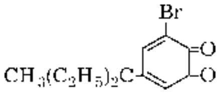
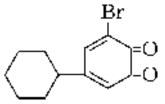
Based on these data, an inference has been made about the steric interference of alkyl radicals that are located at an *ortho*-position to the reaction site that is responsible for the redox process. To put it another way, hydroxyl groups in 2-alkylhydroquinones and 3,6-dialkylpyrocatechols are less accessible and less reactive, than they are in 4-alkylpyrocatechols where the alkyl group is remote from functional hydroxyl groups.

It should be noted that the derivatives of metals with respect to hydroxyl group do not form in all the studied oxidation-reduction systems, because a quinoid structure emerges, which relates, obviously, to a greater exchange rate for electrons than that for ions. These data apply to cations of metals with a higher value of E_0, than it is in the oxidation-reduction systems we have studied.

In our opinion, evidence with respect to steric difficulties in redox processes with the involvement of 3,6-dialkylpyrocatechols can be transferred to cover extraction processes that occur with the involvement of the same systems, but that are not followed by an oxidation-reduction interaction. It is common knowledge that extraction processes with the use of dialkyl pyrocatechols have been widely studying for a long time. Meanwhile, it is diortho-substituted pyrocatechols that are being applied, since only these isomers can be received

TABLE 4

4-Alkyl- and 3-bromo-5-alkyl-1,2-benzoquinones

No.	Compound formula	Yield, %	T_{melt}, °C
1		96	67–68
2		87	51–52
3		91	59–60
4		98	116–117
5		98	117–118
6		85	49–50
7		83	57–58
8		87	79–80

upon the simultaneous introduction of two alkyl groups into pyrocatechol. However, according to our data, it has been just these compounds where hydroxyl groups are less accessible than they are, for example, in 4-alkylpyrocatechols. Therefore, we believe that the application of 4-alkylpyrocatechols in extraction processes holds more promise as compared to 3,6-dialkylpyrocatechols. Extraction without a concurrent redox process can also be observed for elements with a variable oxidation state, but which feature much lower redox potentials, than does the pyrocatechol system and its alkyl derivatives.

OBTAINING 4-ALKYL-*ORTHO*-BENZOQUINONES. EXTRACTION SYNTHESIS WITH THE INVOLVEMENT OF LIQUID REDOXITES

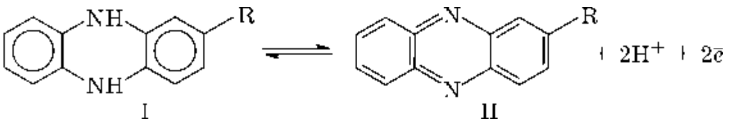
Investigation of the redox processes that involve cations of *d*-elements and organic systems of liquid redoxites has demonstrated that such interactions are applicable not only in inorganic chemistry (to reduce or oxidize cations of metals), but also in organic chemistry. The organic system that is involved in this process yields products of oxidation (reduction) that on frequent occasions are unavailable by alternative methods that are reported in organic chemistry. The analogous redox processes that occur at the phase boundary are spoken of as «extraction synthesis of organic compounds”. They differ from the extraction of organic compounds from an aqueous into organic phase in terms of that the redox processes are followed by not extracting a substance from a certain phase into another one, but by an oxidation-reduction reaction that results in synthesis of a new organic compound. It has been apparent in the above schematic diagram of the reaction between 4-alkylpyrocatechol and cation of iron (III) that the organic phase yields 4-alkyl-*ortho*-benzoquinone. This process underlies a new way we developed to synthesise differently substituted *ortho*-benzoquinones [24].

Procedures to synthesise quinones from various classes of organic compounds have been reported [25]. The best obtaining method of benzoquinone vapour consists in the oxidation of hydroquinone by sodium chlorate [26, 27] and by a mixture of sodium bichromate with sulphuric acid [27, 28]. Alkyl-substituted para-benzoquinones, for example 2-isopropyl-5-methyl-*para*-benzoquinone, can be obtained in a similar way [29]. These methods are too severe for synthesis of alkyl-*ortho*-quinones and they can be accompanied by oxidation of alkyl rad-

TABLE 5

2-Alkyl-5,10-dihydrophenazines and benzo-5,10-dihydrophenazines

No.	Compound formula	Observed, mass %			Empirical formula	Calculated, mass %		
		C	H	Br		C	H	Br
1	4-*tert*-Butyl-1,2-benzoquinone	73.01	7.12		$C_{10}H_{12}O_2$	73.15	7.36	
2	4-*tert*-Amyl-1,2-benzoquinone	74.00	7.79		$C_{11}H_{14}O_2$	74.13	7.92	
3	4-*tert*-Hexyl-1,2-benzoquinone	74.80	8.21		$C_{12}H_{16}O_2$	74.97	8.39	
4	4-Cyclohexyl-1,2-benzoquinone	75.59	7.27		$C_{12}H_{14}O_2$	75.76	7.42	
5	3-Bromo-5-*tert*-butyl-1,2-benzoquinone	49.18	4.32	32.52	$C_{10}H_{11}O_2Br$	49.41	4.56	32.87
6	3-Bromo-5-*tert*-amyl-1,2-benzoquinone	51.12	4.89	29.79	$C_{11}H_{13}O_2Br$	51.38	5.09	31.08
7	3-Bromo-5-*tert*-hexyl-1,2-benzoquinone	53.02	5.47	29.17	$C_{12}H_{15}O_2Br$	53.16	5.58	29.47
8	3-Bromo-5-cyclohexyl-1,2-benzoquinone	53.37	4.63	29.48	$C_{12}H_{13}O_2Br$	53.55	4.87	29.69



Scheme 5.

TABLE 6

2-Alkyl-5,10-dihydrophenazines and benzo-5,10-dihydrophenazines

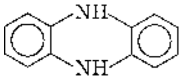
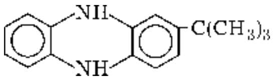
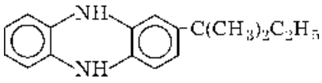
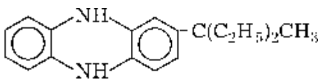
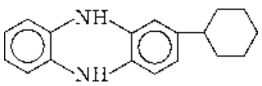
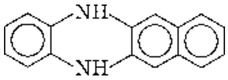
No.	Compound formula	Source dihydroxy compound	Yield, %	T_{melt}, °C	Bishydrochloride T_{melt}, °C
1		Pyrocatechol	98	89–90	211–212
2		4-*tert*-Butyl-pyrocatechol	98	93–94	214–215
3		4-*tert*-Amyl-pyrocatechol	85	96–97	210–211
4		4-*tert*-Hexyl-pyrocatechol	93	98–99	226–227
5		4-Cyclohexyl-pyrocatechol	98	81–82	213–214
6		2,3-Dihydroxy-naphthalene	52	120–121	220–221

TABLE 7

Data of elemental analysis for 2-alkyl-5,10-dihydrophenazines and benzo-5,10-dihydrophenazines

No.	Compound	C content, mass %		Empirical formula	H content, mass %	
		observed	calculated		observed	calculated
1	5,10-Dihydrophenazine	78.89	79.10	$C_{12}H_{10}N_2$	5.31	5.53
2	2-*tert*-Butyl-5,10-dihydrophenazine	80.45	80.63	$C_{16}H_{18}N_2$	7.47	7.61
3	2-*tert*-Amyl-5,10-dihydrophenazine	80.72	80.91	$C_{17}H_{20}N_2$	7.72	7.99
4	2-*tert*-Hexyl-5,10-dihydrophenazine	81.02	81.16	$C_{18}H_{22}N_2$	8.15	8.32
5	2-Cyclohexyl-5,10-dihydrophenazine	81.56	81.78	$C_{18}H_{20}N_2$	7.45	7.63
6	2-Benzo-5,10-dihydrophenazine	82.52	82.73	$C_{16}H_{12}N_2$	5.05	5.21

TABLE 8

Melting points and data of elemental analysis for complexes of 2-alkylphenazines (II) with 2-alkyl-5,10-dihydrophenazines (I)

R	T_{melt}, °C	Observed, mass %		Formula	Calculated, mass %	
		C	H		C	H
H	88.89	79.31	4.80	$C_{24}H_{18}N_4$	79.54	5.01
Br	84–85	55.18	2.78	$C_{24}H_{16}Br_2N_4$	55.41	3.10
$-C(CH_3)_3$	101–102	80.77	6.98	$C_{32}H_{34}N_4$	80.98	7.22
$-C(CH_3)_2C_2H_5$	99–100	81.03	7.39	$C_{34}H_{38}N_4$	81.24	7.62
$-C(C_4H_9)(C_2H_5)CH_3$	103–104	81.61	8.24	$C_{40}H_{50}N_4$	81.87	8.59
cyclo-$C_6H_{11}-$	86–87	81.79	6.95	$C_{36}H_{38}N_4$	82.09	7.27

icals and destruction. Typically, *ortho*-quinones with alkyl substituents are available from alkylpyrocatechols upon their exposure to silver oxide. When alkaline solution of potassium hexacyanoferrate employed as an oxidizer, the yield of a product is low [30], which is caused by the formation of accessory substances, condensation products. Alkyl pyrocatechols show lower redox potentials, than the unsubstituted pyrocatechol, and thus they can be oxidized by weaker oxidizers. This is what forms the basis for the method we suggested [24]. This simple and efficient way has been used to obtain an extensive series of compounds (Table 4) with a good yield and purification degree.

LIQUID REDOXITES AROUND PHENAZINE

The quest to obtain systems of organic redoxites with a very low formal potential E_0 stems from the circumstance that these systems make it possible to reduce a more extensive set of cations of metals. This explains our interest in studying a phenazine system.

Derivatives of phenazine have found wide application as redox indicators. Their formal potentials are typically low and they are in an interval of 0.05–0.30 V [31]. These potentials show negative values in the neutral medium. As we take into consideration the range of application of these compounds, only water-soluble systems that feature hydrophilic substituents in the benzene ring have been studied carefully. We did not describe henazines that include only alkyl substituents within the benzene ring. Electron-donating alkyl radicals result in even stronger lowering the formal potential of the phenazine system and confer hydrophoby on it, which allows the use of this system for processes of oxidation-reduction extraction. We worked up a method of producing 2-alkyl-5,10-dihydrophenazines [32], the oxidation of which may give rise to 2-alkylphenazines. However, the known ways of oxidation led to destruction of the system. Apparently, this is exactly the reason for the fact that synthesis by classical methods of organic synthesis failed for this system and so alkyl phenazines have not been described in the literature. We have found a soft way of oxidation of 2-alkyl-5,10-dihydrophenazines to 2-alkylphenazines [33]. The redox process in the alkyl phenazine system runs according to the Scheme 5.

The resulting 2-alkylphenazines II have been isolated in the form of complexes with initial 2-alkyl-5,10-dihydrophenazines I. The composition of complexes is I : II = 1 : 1, which is similar to the formation of complexes in the quinone – hydroquinone system (1 : 1). We took out a patent for synthesis of 2-alkyl-5,10-dihydrophenazines; the properties of these compounds are given in Tables 6 and 7. The received complexes are characterized in Table 8.

SUMMARY

Investigations that have been made allow one to draw the following basic conclusions.

1. Methods of synthesis of new systems of liquid redoxites have been developed.

2. The possibility has been demonstrated to use these redoxites to reduce certain cations of *d*-elements with higher E_0, than those shown by organic oxidation-reduction systems.

3. A new extraction method for the redox synthesis of organic compounds has been found that employs water solutions of salts of *d*-elements.

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