Coordination Chemistry Reviews, 63 (1985) 241–269
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

TRANSITION METAL COORDINATION COMPOUNDS IN OSCILLATING CHEMICAL REACTIONS

K.B. YATSIMIRSKII and L.P. TIKHONOVA

The L.V. Pisarzhevsky Institute of Physical Chemistry of the Ukrainian SSR Academy of Sciences, Kiev (U.S.S.R.)

(Received 18 May 1984)

CONTENTS

A. INTRODUCTION

Oscillating chemical reactions exhibiting periodic changes in the concentration of components are of interest because of their unusual kinetic behaviour and the possibility of their use as chemical models for oscillating biosystems. Those involving transition metal aquo-ions or coordination compounds as catalysts prove to be systems with reproducible oscillations in the concentrations of several substances.

An oscillating reaction involving the participation of a transition metal compound was first discovered by Belousov [1]. This was an oxidation of citric acid with bromate ion catalyzed by cerium(III) sulfate, in which the ratio of the concentrations of cerium(IV) and (III) varies periodically. Reactions of this type have been further investigated by Zhabotinskii [2,3] who demonstrated a variety of analogous reactions and established the

0010-8545/85/$10.15

requirements which they must satisfy. A detailed study on a cerium(III) sulfate-catalyzed oxidation of malonic (or bromolonic) acid with bromate enabled him to postulate the mechanism for these reactions. Oscillating chemical reactions between organic substrates and bromate ion catalyzed by transition metal aquo-ions or coordination compound redox couples have been designated *Belousov–Zhabotinskii type oscillating reactions*. Zhabotinskii proposed, in addition to the Ce^{4+}/Ce^{3+} couple, the Mn^{3+}/Mn^{2+} couple, 1,10 phenanthroline and 2,2′bipyridyl complexes of iron(II) as catalysts for this type of oscillating reaction *. The papers by Belousov [1] and Zhabotinskii [2] were a great stimulus to extensive studies in this field. At present there are many publications dealing with different oscillating reactions. Some of them are attempts to elucidate and identify more clearly the oscillatory mechanism, and to establish both general regularities and specific features.

Apart from the Belousov–Zhabotinskii type reactions, there are some other oscillating chemical reactions involving transition metal compounds. The main types are:

The Briggs–Rauscher type oscillating reaction is an interaction between iodate, hydrogen peroxide, manganese(II) and malonic acid in an acid medium accompanied by periodic changes in the concentrations of several substances, including the ratio of the concentrations of manganese(III) and manganese(II) [4–6]. This system is regarded to be a combination of the components of the Belousov–Zhabotinskii and Bray–Liebhafsky oscillating reactions [5,6]. Various modifications have been reported [7].

Oscillating redox reactions of inorganic substances and chlorite-ion, in several cases, involve MnO_4^-, $Cr_2O_7^{2-}$, $Fe(CN)_6^{4-}$ [8]. A characteristic feature of such reactions is that the oscillations occur only under flow conditions.

Oscillating redox reactions of transition metal complexes and bromate ions in the absence of an additional reductant (an uncatalyzed reaction).

In these systems a (1,10-phenanthroline)iron(II) complex [9] or a tetraazamacrocyclic copper(II) and nickel(II) complex [10] interact with bromate ion in acid solution and the ratio of the concentrations of components whose metal central ions have different oxidation states changes periodically. Reactions of this type appear to resemble those involving only one reduction–oxidation cycle [11–13]

$$Me^{n+} \rightarrow Me^{(n+1)^+} \rightarrow Me^{n+}$$

The present review primarily covers oscillating chemical reactions between various substrates and bromate ion occurring in the presence of the transi-

---

* For convenience, the metal ions (catalysts) are given in the lowest oxidation state although they undergo alternate reduction–oxidation.

tion metal coordination compounds with chelate or macrocyclic ligands. We attempted to consider some peculiarities in the behaviour of the oscillating reactions which may be of interest from the coordination chemistry viewpoint and, in particular, the participation of metal-ligand complexes containing nitrogen donor atoms. The intermediate metal-chelate complexes, e.g., manganese(III) malonate or acetylacetonate complexes [14,15] are not considered. Some recent research suggests that the role played by coordination compounds in oscillating processes is of interest not only in determining more precisely the kinetics and mechanisms of these reactions but also in revealing new oscillating systems. The incorporation of a coordination compound into an oscillating system may lead to unexpected after-effects, e.g. secondary catalysis (i.e., catalytic step catalysis) [20] or new types of reactions [10].

B. THE BASIC MECHANISM FOR THE BELOUSOV–ZHABOTINSKII REACTION

The Belousov–Zhabotinskii oscillating reactions involve a cerium(II) catalyzed oxidation of malonic acid (or its bromoderivative) by bromate ion. The reaction is the most convenient in elucidating the general regularities of oscillating systems. Qualitative and, to a certain extent, quantitative evaluations of periodic changes are based on the kinetic and thermodynamic data obtained for the individual steps involved.

The oscillating behaviour and the mechanism have primarily been interpreted by Zhabotinskii [3]. Other scientists [15–20] have studied the mechanism and provided additional information on the intricate kinetics involved. The presence of feedback is typical of each controlled bioprocess and, especially, oscillating reactions. An autocatalytic oxidation of the reduced form of a catalyst with bromate ion occurs simultaneously with the accumulation of bromide ions (an inhibitor) followed by reduction of the oxidized form of a catalyst by an organic substrate, and consumption of an inhibitor.

For our discussion we have used the scheme proposed by Field et al. [16], subdividing it, for convenience, into cycles of the oxidation of the reduced form of the catalyst and the reduction of its oxidized form. It is given for a bromate–malonic acid–cerium(III)–sulfuric acid system. The periodic changes in the concentration of cerium(IV) are shown in Fig. 1. The main steps of this reaction are described by eqns. (1)–(10).

(a) The reduction of cerium(IV) involves:

$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HBrO \qquad (1)$$

$$HBrO + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (2)$$

$$HBrO_2 + Br^- + H^+ \rightarrow 2HBrO \qquad (3)$$

$$2\mathrm{HBrO_2} \rightarrow \mathrm{BrO_3^-} + \mathrm{HBrO} + \mathrm{H^+} \tag{4}$$

$$\mathrm{CH_2(COOH)_2} + \mathrm{Br_2} \rightarrow \mathrm{CHBr(COOH)_2} + \mathrm{Br^-} + \mathrm{H^+} \tag{5}$$

$$6\mathrm{Ce(IV)} + \mathrm{CH_2(COOH)_2} + 2\mathrm{H_2O} \rightarrow 6\mathrm{Ce(III)} + \mathrm{HCOOH} + 2\mathrm{CO_2} + 5\mathrm{H^+} \tag{6}$$

$$4\mathrm{Ce(IV)} + \mathrm{CHBr(COOH)_2} + 2\mathrm{H_2O} \rightarrow 4\mathrm{Ce(III)} + \mathrm{HCOOH} + 2\mathrm{CO_2} + 5\mathrm{H^+} + \mathrm{Br^-} \tag{7}$$

(b) The oxidation of cerium(III) proceeds via:

$$\mathrm{H^+} + \mathrm{BrO_3^-} + \mathrm{HBrO_2} \rightarrow 2\,{}^{\bullet}\mathrm{BrO_2} + \mathrm{H_2O} \tag{8}$$

$$\mathrm{H^+} + \mathrm{Ce(III)} + {}^{\bullet}\mathrm{BrO_2} \rightarrow \mathrm{Ce(IV)} + \mathrm{HBrO_2} \tag{9}$$

Reactions (1)–(3) yield free bromine which is necessary to brominate malonic acid via eqn. (5). Bromomalonic acid fairly easily reduces cerium(IV), as shown by eqn. (7). Bromide ions accumulate according to eqns. (5) and (7).

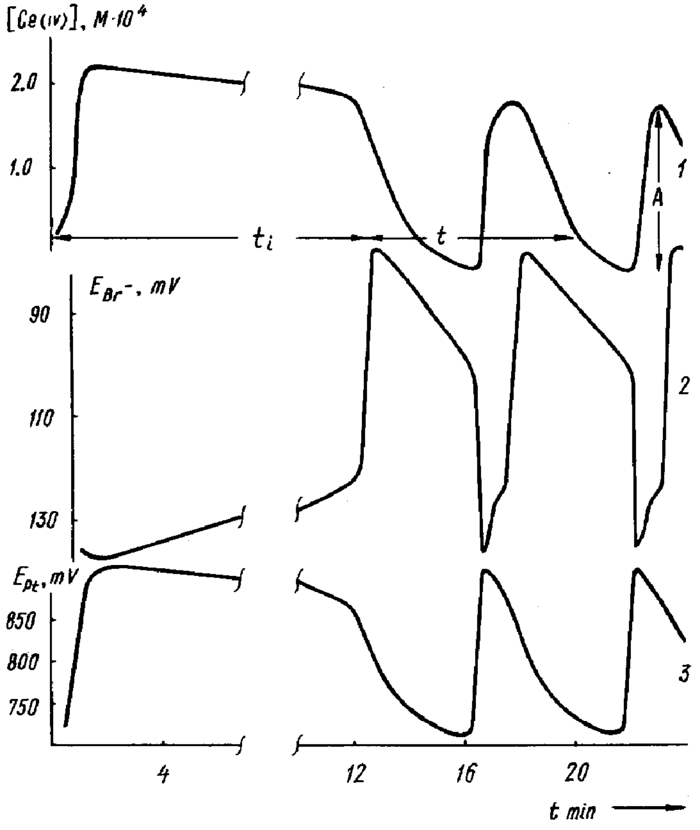


Fig. 1. Plots of cerium(IV) concentration (1), $\mathrm{Br^-}$-selective electrode potential (2) and Pt-electrode potential (3) vs. time. Concentrations: 0.001 mol $\mathrm{l^{-1}}$ $\mathrm{Ce_2(SO_4)_3}$; 0.035 mol $\mathrm{l^{-1}}$ $\mathrm{KBrO_3}$; 0.043 mol $\mathrm{l^{-1}}$ $\mathrm{CH_2(COOH)_2}$; 1,5 mol $\mathrm{l^{-1}}$ $\mathrm{H_2SO_4}$. t_i, induction period; t, oscillation period; A, amplitude of Ce(IV) oscillations.

The presence of Br^- is required to reduce $HBrO_3$, $HBrO_2$ and HBrO by eqns. (1)–(3).

Bromyl radicals ($^{\cdot}BrO_2$) responsible for the oxidation of cerium(III) can only appear at very low concentrations of bromide ions which inhibit reaction (8) consuming $HBrO_2$ by eqn. (3). The accumulation of bromide ions by reaction (7) occurs simultaneously with the formation of cerium(IV) by reactions (8) and (9). When the concentration of bromide ions present in the system reaches a certain critical value, reaction (8) is "switched off" by the competitive reaction (3). Thus, bromide ions switch on and off (i.e, act as a "relay") the oxidation of the reduced form of the catalyst and the reduction of its oxidized form.

At extremely low concentration of bromide ion, cerium(III) is oxidized in cycle (b) and with an increase in its concentration cerium(IV) is reduced in cycle (a). Moreover, a key role for free bromine has been suggested [22]. The induction period * observed in the majority of the Belousov–Zhabotinskii systems is associated with the accumulation of the bromide ion, Br^-, to a critical concentration of bromomalonic acid, largely at the expense of a multistep oxidation [18]. The formation of bromide ions [17,23] occurs via reaction (10), which is a step involved in the overall process (7):

$$BrCH(COOH)_2 + {}^{\cdot}CH(COOH)_2 + H_2O \rightarrow CH_2(COOH)_2 + HO\dot{C}(COOH)_2 + H^+ + Br^- \qquad (10)$$

It follows that the basic steps involving transition metal ions or coordination compounds are oxidation–reduction reactions (9), (6) and (7). Thus, the main requirements that a catalyst must satisfy to be suited for the Belousov–Zhabotinskii reactions are: it must be a one-electron redox couple of a transition metal aquo-ion or coordination compound with a standard oxidation potential ranging from 0.9 to 1.6 V. The reduced form of the catalyst can be oxidized by reaction (9) ($E^0_{^{\cdot}BrO_2/HBrO_2} > 1.33$ V [16]) and its oxidized form is reduced by the organic substrate, reactions (6) and (7). The latter, like reaction (9), occurs largely via the one-electron mechanism.

Apart from the above "thermodynamic" and "stoichiometric" requirements, the catalyst must meet a "kinetic" requirement, i.e., it must have a definite ratio of redox reaction rates.

Besides reactions (1)–(10), some individual steps may involve other conversions of transition metal coordination compounds which are less important for the occurrence of oscillations but which can affect their shape and parameters. These can be exemplified by the reduction of the oxidized

---

* The induction period implies the time required for the onset of oscillations.

catalyst with bromide [24], participation of the catalyst in the bromination of an organic substrate [23], etc.

The main parameters for oscillating reactions, given in Fig. 1, can be formulated as follows:
(a) the induction period is the time elapsed between mixing of all the components of the reaction and the onset of an oscillating state;
(b) the period of oscillations is the time between two minima or two maxima in the plot of a measured characteristic (optical density, platinum electrode potential, etc) versus time;
(c) the amplitude of oscillations is the time interval between maxima and minima of the measured characteristic;
(d) the region of existence of oscillations implies the ranges of concentrations for the main components, in a given oscillating reaction, within which a periodic operation is realized.

C. THE GENERAL CHARACTERISTICS OF TRANSITION METAL COORDINATION COMPOUNDS IN OSCILLATING CHEMICAL REACTIONS.

The choice of new catalysts for oscillating reactions is governed by the basic requirements formulated as follows. Such catalysts must have specific redox potentials dependent on their coordination spheres. The latter determine not only their thermodynamic but also kinetic behaviour. For instance, redox reactions involving some transition metal complexes with nitrogen-containing chelate ligands (namely, 1,10-phenanthroline or 2,2′-bipyridyl) proceed at high rates via an outer sphere electron transfer mechanism, owing to the π-conjugated structure of their coordination sphere [25]. As a result, the rates of individual steps increase and, therefore, the oscillation parameters in these reactions will differ from those of the reactions catalyzed by metal aquo-ions. Complexation of metal ions with chelates, especially, with macrocyclic ligands may also stabilize unusual oxidation states of metal ions (e.g., nickel(III) and copper(III)) which provides unexpected new catalyst redox couples. The contribution of the complexed and dissociated ligand products may bring about new types of oscillating reactions. Various equilibrium forms of metal–chelate or macrocyclic complexes may be present in solutions [26,37]. Shifts in the equilibria affect oscillations. For example, under otherwise equal conditions, a marked change in oscillation parameters was shown [27] even in passing from aquo-manganese(III) to its hydroxo-ion.

At present, 1,10-phenanthroline and 2,2′-bipyridyl iron(II) and ruthenium(II) complexes are used as catalysts in the Belousov–Zhabotinskii oscillation reactions. Reactions catalyzed by 2,2′-bipyridyl Os(II),Cr(II) and Ag(II) complexes [28,29] and 1,10-phenanthroline and 2,2′-bipyridyl Co(II)

TABLE 1

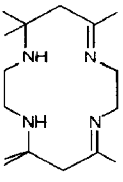
Standard redox potentials (vs. NHE) for 1,10-phenanthroline or 2,2-bipyridyl complexes [28,29,32–35]

Reaction	$E^\ominus$ (V)
$\mathrm{Fe(phen)_3^{3+} + e^- \rightarrow Fe(phen)_3^{2+}}$	1.06
$\mathrm{Fe(bipy)_3^{3+} + e^- \rightarrow Fe(bipy)_3^{2+}}$	0.97
$\mathrm{Ru(phen)_3^{3+} + e^- \rightarrow Ru(phen)_3^{2+}}$	1.29
$\mathrm{Ru(bipy)_3^{3+} + e^- \rightarrow Ru(bipy)_3^{2+}}$	1.25
$\mathrm{Os(bipy)_3^{3+} + e^- \rightarrow Os(bipy)_3^{2+}}$	0.88
$\mathrm{Ag(bipy)_2^{2+} + e^- \rightarrow Ag(bipy)_2^{+}}$	1.45
$\mathrm{Co(phen)_3^{3+} + e^- \rightarrow Co(phen)_3^{2+}}$	0.42

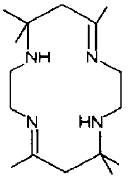
complexes [30] are described. An oscillating reaction between malonic acid and bromate ion takes place in the presence of Cu(II), Co(II) and Ni(II) complexes with aniline as catalyst [30]. However, the changes in the light absorption of solutions were identical within the same spectral region in all cases. In our opinion, the oscillations observed can be attributed to the bromate–aniline system [31] rather than the bromate–malonic acid–metal complex system.

Table 1 lists the standard redox potentials for 1,10-phenanthroline or 2,2′-bipyridyl complexes of transition metals [28,29,32–35]. All redox potentials, except the $\mathrm{Co(phen)_3^{3+}/Co(phen)_3^{2+}}$ couple, meet the requirements established for the catalysts used in the Belousov–Zhabotinskii reactions. With Co(II)-1,10-phenanthroline complexes, the active form of the catalyst in solution differs, from that of the tris-complexes. These complexes were obtained by addition of Co(II) sulfate to the ligand in excess in H_2SO_4 solutions. The nature of the catalytically active Cr(III)–2,2′-bipyridyl complex demands further investigation [29]. To judge from the halfwave reversible polarographic potential for the reaction $\mathrm{Cr(bipy)_3^{3+} \rightleftarrows Cr(bipy)_3^{2+}}$ ($E_{1/2}$ = 0.49 V) [36], the $\mathrm{Cr(bipy)_3^{3}/Cr(bipy)_3^{2+}}$ couple can hardly act as a catalyst.

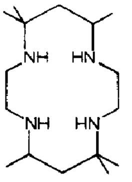
Complexation of transition metal ions with macrocyclic ligands stabilizes the metal oxidation states [37], which must be taken into account in searching for new catalysts for oscillating reactions. We have demonstrated an oscillating chemical reaction between malonic acid and bromate ion in the presence of Cu(II) and Ni(II) complexes with tetraazamacrocyclic ligands of the type



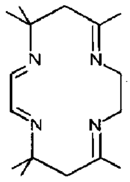
L1



L2



L3



L4

TABLE 2

Halfwave reversible potentials (vs. SCE) for polarographic oxidation–reduction of copper and nickel complexes in acetonitrile solution [38–43]

Ligand/ Redox couple	CuL^{2+}/ CuL^{3+}	CuL^{+}/ CuL^{2+}	NiL^{2+}/ NiL^{3+}	NiL^{+}/ NiL^{2+}
L_1	–	–	0.85	−1.58
L_2	1.18	−1.0	0.98	−1.57
L_3	1.22	−1.0	0.87	−1.57
L_4	–	–	1.05	−0.76

as catalysts. In accordance with the nomenclature cited in [37]: L_1 is Me_6[14]-4,14 diene N_4; L_2 is Me_6[14]-4,11-diene N_4; L_3 is Me_6[14]ane N_4 and L_4 is Me_6[14]-1,3,7-tetraene N_4. The standard redox potential values for the $MeL^{n+}/MeL^{(n+1)}$ couples are not known. Some information on the redox properties of these ions can be obtained from the reversible potentials of polarographic redox waves of the corresponding couples. Apparently, the electron transfer in these complexes involves the central metal ion rather than the ligand [43]. We assume the data obtained in acetonitrile may be used for aqueous solutions. Moreover, the halfwave potential for polarographic reduction of $CuL^{3+} \rightarrow CuL^{2+}$ in acetonitrile and in aqueous solutions were similar [39]. Table 2 lists the halfwave reversible potentials for polarographic oxidation-reduction of nickel(II) and copper(II) complexes in acetonitrile. The CuL^{3+}/CuL^{2+} and NiL^{3+}/NiL^{2+} couples are capable of catalyzing the Belousov–Zhabotinskii reactions on the basis of their halfwave reversible potentials.

The potentials for the MeL^{3+}/MeL^{2+} couples depend [37,40,43] on the nature of the macrocyclic ligand involved (especially on the degree of its unsaturation). Therefore, the conditions for the oscillating reaction can be changed by varying the ligand. It is evident that only a specific set of macrocyclic ligands for a given metal favours the oscillating reaction.

D. OSCILLATING CHEMICAL REACTIONS CATALYZED BY TRANSITION METAL–1,10-PHENANTHROLINE OR 2,2′-BIPYRIDYL COMPLEXES

The catalytic properties of transition metal coordination compounds with 1,10-phenanthroline and 2,2′-bipyridyl have been described only for the reaction between bromate ion and malonic acid. The concentrations of the main components within which oscillations are observed are summarized in Table 3. The regions of existence of concentration oscillations, shown in Figs. 2–5, are more conveniently considered in the coordinates of the oxidant and reductant concentrations. With 1,10-phenanthroline and 2,2′-bi-

TABLE 3

Reactant concentrations within which oscillations are observed in the malonic acid oxidation with bromate ion catalyzed by various catalysts [a]

Catalyst	Metal complex	Concentration (mol l^{-1})			
		H_4SO_4	$KBrO_3$	$CH_2(COOH)_2$	Ref.
$Fe(phen)_3^{2+}$	5.4×10^{-4}	0.4–1.0	0.02–0.25	0.1–2.0	[46,47]
$Fe(phen)_3^{2+}$	4.5×10^{-4}–4.5×10^{-3}	0.283–1.416	0.056–0.341	0.013–0.350	[48]
$Fe(bipy)_3^{2+}$	10^{-4}–10^{-3}	0.45–0.60	0.06–0.15	0.7–3.7	[47]
$Ru(bipy)_3^{2+}$	2×10^{-5}	0.4–2.0	0.045–0.09	0.1–0.4	[44]
$Ru(bipy)_3^{2+}$	2.6×10^{-4}	1.0	0.06–1.10	1.31–0.001	[45]
$Os(bipy)_3^{2+}$ [b]	1.9211×10^{-3}	0.7815	0.0367	0.1104	[28]
$Ag(bipy)_2^{+}$ [c]	2×10^{-6}–4.8×10^{-4}	0.016–0.032	0.0015–0.00225	0.15	[29]
$Co(phen)_3^{2+}$	3.85×10^{-3}–7.15×10^{-2}				[30]
$Co(bipy)_3^{2+}$	2.6×10^{-3}–8.14×10^{-3}				[30]

[a] The limiting concentrations are given for the conditions under which the concentrations of components except those that vary are constant and optimal.

[b] Beside $Os(bipy)_3SO_4$, 0.0195 M 2,2′-bipyridine was added to the solution.

[c] $AgNO_3$ and 0.25 M 2,2′-bipyridine are added to the solution.

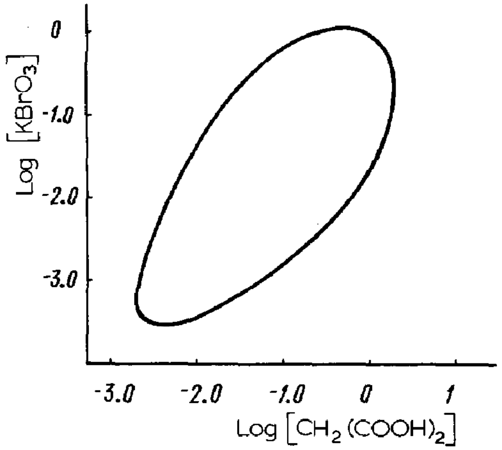


Fig. 2. The domain of existence of oscillations for the $KBrO_3$–$Ce_2(SO_4)_3$–$CH_2(COOH)_2$ system in the coordinates of $KBrO_3$ and $CH_2(COOH)_2$ concentrations [2].

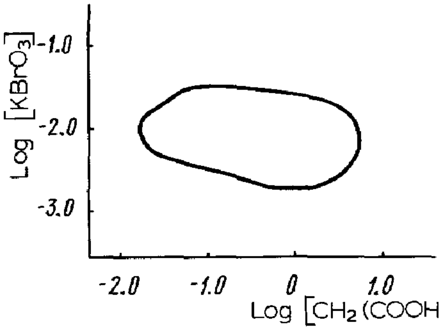


Fig. 3. The domain of existence of oscillations for the $KBrO_3$–$Fe(phen)_3^{2+}$–$CH_2(COOH)_2$ system in the coordinates of $KBrO_3$ and $CH_2(COOH)_2$ concentrations [46].

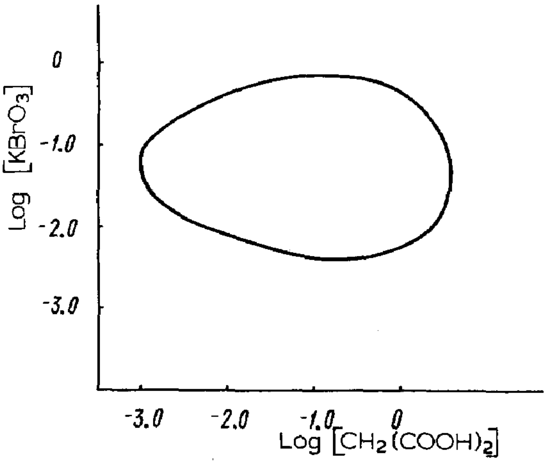


Fig. 4. The domain of existence of oscillations for the $KBrO_3$–$Ru(bipy)_3^{2+}$–$CH_2(COOH)_2$ system in the coordinates of $KBrO_3$ and $CH_2(COOH)_2$ concentrations [45].

pyridyl complexes of iron(II), oscillating chemical reactions occur in rather a narrow range of concentration of bromate ion and malonic acid. The region of existence of oscillations for the systems catalyzed by $Ru(bipy)_3^{2+}$ is similar (in position and size) to those of the systems catalyzed by manganese(II) aqueo-ions [46] or sulfate complexes of Ce(III) [3]. The standard redox potentials for the $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ and $Fe(bipy)_3^{3+}/Fe(bipy)_3^{2+}$ couples are small and nearly the same (see Table 1) while for the $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+}$ couple the standard redox potential resembles those for the Mn(III)/Mn(II) and Ce(IV)/Ce(III) couples, 1.55 and 1.44 V, respectively. It is evident that the concentration limits of components over which the oscillations exist are determined, above all, by the redox potentials of the catalyst couples. Changes in the oscillation parameters varying the concentrations of the main components depend also on the nature of the metal ion and its coordination environment. A marked change in the amplitude of oscillations with time is common for oscillating reactions involving metal complexes, shown in Table 3, and, for the most concentrated conditions studied, there is no induction period. The period and amplitude of oscillation with increasing catalyst concentration were found to be weakly reproducible in these reactions.

Temporal concentration oscillations in a $Fe(phen)_3^{2+}$-bromate–malonic acid have been the most investigated [3,46–49,50]. The sequence of steps (1)–(9) for this reaction is believed to be analogous to that of the reaction catalyzed by Ce(III). The ferroin-catalyzed oscillating system has a narrower concentration limit for bromate ion than has the cerium(III) catalyzed system, and has a different dependence of amplitude of oscillation on K_{ox}/K_{red} with the bromate ion concentration. This is associated with differences in the mechanism of the oxidation of ferroin by bromate ion [49] for example the different effect of radical scavengers: with ferroin, the

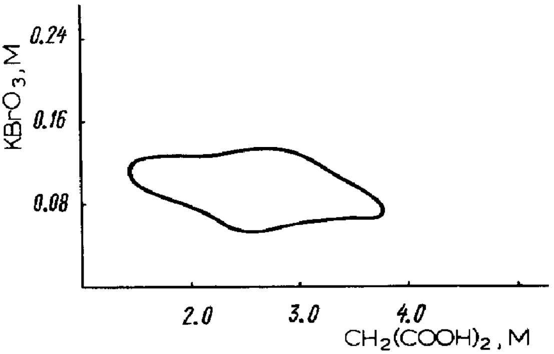


Fig. 5. The domain of existence of oscillations for the $KBrO_3$–$Fe(bipy)_3^{2+}$–$CH_2(COOH)_2$ system in the coordinates of $KBrO_3$ and $CH_2(COOH)_2$ concentrations. Concentrations: 6.7×10^{-4} mol l^{-1} $Fe(bipy)_3^{2+}$; 0.48 mol l^{-1} H_2SO_4.

oscillations are damped by 1% of oxygen in nitrogen, with cerium(III), by pure oxygen [90]. The kinetics of the oxidation of ferroin by bromate ion are complicated and the available experimental results are unambiguous. The reaction stoichiometry and the products obtained by various investigators differ from each other and with those for the oxidation of cerium(III) with bromate ion. For instance, this reaction proceeds via a six-electron oxidation to yield bromide ions [51]:

$$BrO_3^- + 6Fe(phen)_3^{2+} + 6H^+ \rightarrow 6Fe(phen)_3^{3+} + Br^- + 3H_2O \tag{11}$$

A stoichiometry corresponding to a four-electron oxidation

$$BrO_3^- + 4Fe(phen)_3^{2+} + 5H^+ \rightarrow 4Fe(phen)_3^{3+} + HBrO + 2H_2O \tag{12}$$

is possible with a large excess of the oxidant $[BrO_3] > [Fe(phen)_3^{2+}]$, according to ref. 52. At lower concentrations of bromate ion deviations from the above stoichiometry are due to the fact that the oxidation of ferroin occurs simultaneously with its protolytic dissociation. On the other hand, the variations in the kinetic parameters which depend on $[BrO_3^-]/[Fe(phen)_3^{2+}]$ may be associated not only with the possibility of formation of iron(III) tris-phenanthroline and the oxidation of ferroin by $^{\cdot}BrO_2$ similar to reaction (9), but ferroin also may be oxidized with bromate ion via a one-electron mechanism to form $^{\cdot}BrO_2$ [53]:

$$BrO_3^- + Fe(phen)_3^{2+} + 2H^+ \rightarrow {}^{\cdot}BrO_2 + Fe(phen)_3^{3+} + H_2O \tag{13}$$

Recently, in order to interpret differences in the behaviour of oscillating oxidation reactions of malonic acid with bromate ion catalyzed by ferriin–ferroin or ceric–cerous redox couples, a phenanthroline iron(IV) complex was proposed to occur [54]. This suggestion is justified in our opinion, as it accounts for some peculiar features of the corresponding reactions. For instance, the oxidation of malonic acid may proceed via a two-electron mechanism:

$$Fe(IV)L_3 + CH_2(COOH)_2 + H_2O \rightarrow Fe(II)L_3 + CHOH(COOH)_2 + 2H^+ \tag{14}$$

Manganese(IV) may partake in the oxidation of malonic acid with manganese(III) in the same way. The two-electron oxidation of malonic acid with manganese(IV) by a non-radical mechanism generates a higher rate compared to a cerium(IV) catalyzed oxidation of malonic acid which excludes a two-electron path [55]. The formation of an iron(IV) complex may take place via disproportionation:

$$2Fe(III)L_3 \rightleftarrows Fe(II)L_3 + Fe(IV)L_3 \tag{15}$$

and the oxidation of iron(II) with HBrO

$$Fe(II)L_3 + HBrO + H^+ \rightarrow Fe(IV)L_3 + Br^- + H_2O \qquad (16)$$

Considering the dissociation of tris-1,10-phenanthroline iron(II), the oxidation of this complex with $HBrO_2$ may occur via the mechanism proposed [56] for its oxidation with $HClO_2$:

$$Fe(phen)_3^{2+} \rightarrow Fe(phen)_2^{2+} + phen \qquad (17)$$

$$Fe(phen)_2^{2+} + HBrO_2 + 2H^+ \rightarrow Fe(phen)_2^{4+} + HBrO + H_2O \qquad (18)$$

$$Fe(phen)_2^{4+} + Fe(phen)_2^{2+} + 2H_2O \rightarrow [Fe(OH)(phen)_2]_2^{4+} + 2H^+ \qquad (19)$$

This mechanism yielding, eventually, the dimeric species of the complex occurs [56] at a low concentration of the acid and at nearly the same concentrations of the oxidant and ferroin. As in the oscillating systems the concentration of the bromous acid does not exceed that of the catalyst [15] and a ferroin-catalyzed reaction proceeds at lower concentrations of H_2SO_4 than the corresponding reactions catalyzed by cerium(III) or manganese(III) ions. The occurrence of the individual steps (17) and (18) is quite possible. Reaction (19) is not likely to proceed under the conditions of an oscillating process because of the large excess of malonic acid and its rapid reduction via reaction (13). It should be noted that such participation of iron(IV) complexes with 1,10-phenanthroline and 2,2′-bipyridyl is also expected in other reduction reactions of halogenates, e.g., in the reduction of periodate ions catalyzed by the Fe^{3+}/Fe^{2+} couple [57,58].

The occurrence of reactions (17) and (18) simultaneously with an autocatalytic reaction such as (8) or (9) can also be associated with the interruptions of oscillations at low concentrations of bromate and malonic acid [46]. Moreover, the inconstancy of period and amplitude of the oscillations may be due to the existence of individual steps, independent of the concentrations of the key reactants, i.e., bromide ions.

The absence of the induction period in the bromate–malonic acid–ferroin system is associated with reaction 16. The induction period increases with decreasing bromate concentration [46] * leading to a drop in the rate of reaction (1). The induction period increases with a rise in the concentration of malonic acid which may be due to the consumption of hypobromous acid by reactions 20–22:

$$HOBr + Br^- + H^+ \rightarrow Br_2 + H_2O \qquad (20)$$

---

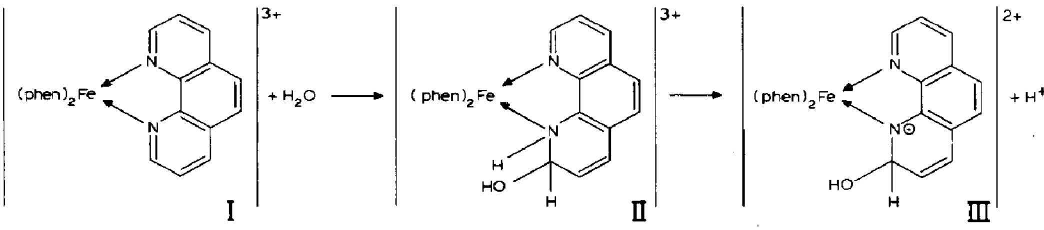
* No induction period has been observed in this reaction by Smoes [48] and Körös et al. [50]. This may, in our opinion, be due to the optimal concentration conditions, i.e. the centre of the region of occurrence of oscillations. It is not quite clear what Körös et al. define as an "introductory" period.

$$Br_2 + CH(COOH)_2 \rightarrow CHBr(COOH)_2 + H^+ + Br \tag{21}$$

$$HOBr + CH_2(COOH)_2 \rightarrow CHBr(COOH)_2 + H_2O \tag{22}$$

The existence and duration of the induction period is believed to be determined by the possibility of formation of an intermediate complex compound between the catalyst and the reactants since the participation of manganese(III) in the form of a malonate complex completely excludes the induction period. The absence of the latter is also characteristic of a bromate–manganese(II)–acetylacetone system catalyzed by a substrate–manganese complex [60]. Assuming partial dissociation of tris-phenanthrolinate iron(II) in reaction (17) forming an iron(II)–monodentate ligand complex [25], one cannot completely exclude participation of a catalyst–substrate intermediate, though it is not probable.

Variations in the coordination environment of the catalyst (e.g., aquation of one or more ligands) may affect one of its oxidation states which may then inhibit the reproducibility of the oscillation parameters. For instance, an increase in the acid concentration in solution destabilizes a non-aquated form of tris-1,10-phenanthroline-iron(III), (I) and leads to an intracomplex reduction involving a "covalent" hydrate, (II) [26]:



(23)

The occurrence of reduction 23 * alongside the oscillating reaction may be one of the reasons for the variation of the oscillation parameters with time.

It follows that the experimental data are not sufficient to interpret the peculiar behaviour of the oscillating system even in the reaction most studied. However, an interpretation based on allowance for variations in the state and structure of the coordination sphere of the catalyst is justified.

The region in which the oscillations occur are described in the coordinates of bromate and malonic acid concentrations for the bromate-malonic acid-tris(2,2′-bipyridyl)ruthenium(II) system (Fig. 4). This resembles systems involving cerium(III) or manganese(III). However, the changes in the basic

---

* We assume that reactions 23 and 25 are possible ways of such catalyst reduction, independent of oscillating reaction components, and they cannot be regarded as an argument pro or contra "covalent hydrate" formation [26,62(a)]. We do not have a direct proof of "covalent hydrate" formation.

oscillation parameters which depend on the concentrations of components are analogous to the relationships characteristic of the ferroin-catalyzed systems. The amplitude and period of oscillations are not constant with time. For instance, within the whole region of existence of the oscillations, the amplitude for $[\mathrm{Ru(bipy)}_3^{3+}]/[\mathrm{Ru(bipy)}_3^{2+}]$ decreases from one oscillation to the next.

The amplitude value, described as the average obtained from 10 oscillations, tends to decrease with increase of concentration of bromate ion. The induction period is observed only at the boundary of the region in which the oscillations exist and is absent at optimal component concentrations. These facts indicate a certain analogy in the mechanisms of the oscillating reactions catalyzed by 2,2′-bipyridyl ruthenium(II) and by 1,10-phenanthroline iron(II).

The stoichiometry of the oxidation of ferroin and tris (2,2′-bipyridyl)ruthenium(II) is the same [51]. We have no information on the mechanism of these reactions. One can, however, expect a resemblance to the mechanism of oxidation of ferroin and tris-(2,2′-bipyridyl) iron(II) with bromate. The latter is visualized as a direct one—electron oxidation of a metal complex with bromate [61]. The oxidation of $\mathrm{Ru(bipy)}_3^{2+}$ with hypobromous acid is likely to proceed by a two-electron mechanism, as does reaction (17), on the basis of the diverse oxidation states of ruthenium [62]. For example bis(2,2′-bipyridyl)ruthenium(IV) is formed in the oxidation of the corresponding ruthenium(III) complex. The reaction, proceeding in the same way as reaction (17), can account for the absence of the induction period under optimal concentration conditions. At low concentrations of bromate ions, this reaction hardly occurs and the induction period is observed. The appearance of the latter at low concentrations of malonic acid cannot only be due to the occurrence of the oxidation of ruthenium(II) with hypobromite ion.

The oxidation of malonic and bromomalonic acids in the course of the oscillating reaction catalyzed by the 2,2′-bipyridyl ruthenium(II) complex may take place both by two-electron and one-electron mechanisms. The latter involves malonic acid radicals. A high rate observed in the oxidation of malonic acid with tris-(2,2′-bipyridyl)ruthenium(III) is evidence in favour of the two-electron mechanism. On the other hand, a rather high standard redox potential for the $\mathrm{Ru(bipy)}_3^{3+}/\mathrm{Ru(bipy)}_3^{2+}$ couple (Table 1) enables the occurrence of reaction (24) [54]:

$$\mathrm{Ru(bipy)}_3^{3+} + \mathrm{CH_2(COOH)_2} \rightarrow \mathrm{Ru(bipy)}_3^{2+} + \dot{\mathrm{C}}\mathrm{H(COOH)_2} + \mathrm{H^+} \qquad (24)$$

The resultant malonic acid radicals seem to induce and quench periodic changes in chemiluminescence during the oscillating chemical reaction catalyzed by tris-(2,2′-bipyridyl)ruthenium(II) [64]. The periodic photoluminescence observed in this reaction may be associated with a change in the state of the ligands in ruthenium(II) and ruthenium(III) complexes.

In aqueous solutions, equilibria of the type of reaction 23 are characteristic of iron and ruthenium complexes with 2,2′-bipyridyl and 1,10-phenanthroline [26]. The ratio of the concentrations of covalent hydrate(II) and unaquated complex (I) is determined by the acid concentration. The photoluminescence of free 2,2′-bipyridyl was found to be related only to covalent hydrate [65]. The periodic changes in $[Ru(bipy)_3^{3+}]/[Ru(bipy)_3^{2+})$ during the oscillating reaction are accompanied by periodic photoluminescence characteristic of the $Ru(bipy)_3^{2+}$ complex at 610 nm [64]. The photoluminescence of Ru $(bipy)_3^{2+}$ in H_2SO_4 solutions diminishes with increase in the acid concentration, (Fig. 6) which may be due to a shift in the equilibrium to the left and a decrease in the concentration of covalent hydrate in solution. On the other hand, the same decrease in the acid concentration decreases the amplitude of the oscillations of $[Ru(bipy)_3^{3+}]/[Ru(bipy)_3^{2+}]$ (Fig. 6) which may also be associated with a drop in the concentration of the aquated catalyst.

The role of aquation of the ligand in determining a reaction mechanism is illustrated by oxidation of 2,2′-bipyridyl iron(II) with bromate [61]. However, the autocatalytic route required for an oscillating process was shown to take place under conditions when the rate of aquation is negligibly small. The oscillating reaction in the bromate–malonic acid-tris(2,2′-

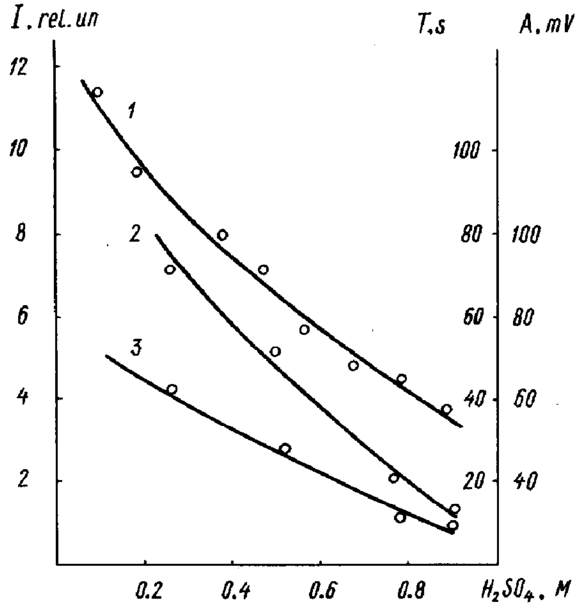
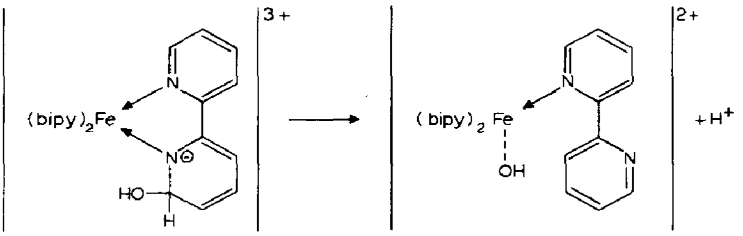


Fig. 6. Plots of photoluminescence intensity of 2,2′-bipyridyl ruthenium(II) aqueous solutions (1), amplitude (2) and period (3) of oscillations in a $KBrO_3$–$Ru(bipy)_3^{2+}$–$CH_2(COOH)_2$ system vs. H_2SO_4 concentration. Concentrations: (1) 10^{-5} mol l^{-1} $Ru(bipy)_3^{2+}$; (2) 0.07 mol l^{-1} $KBrO_3$; 2.6×10^{-5} mol l^{-1} $Ru(bipy)_3^{2+}$; 0.27 mol l^{-1} $CH_2(COOH)_2$.

bipyridyl)iron(II) system proceeds over a narrow range of bromate and malonic acid concentrations (Fig. 5) and low concentrations of H_2SO_4; when the latter is higher than 0.6 mol l^{-1} the oscillations stop, when it is less than 0.05 mol l^{-1}, the amplitude is not detectable. In this case the oscillations occur at the same concentrations of H_2SO_4 and bromate characteristic of a "mixed" mechanism for the oxidation of tris-(2,2′-bipyridyl)iron(II) with bromate ion [61] involving an autocatalytic oxidation of tris-(bipyridyl)iron(II) and non-autocatalytic oxidation of its aquated form. Assuming the participation of an iron(IV) complex in the redox reaction [56,66] the oxidation of the aquated form of the complex can be visualized as follows. The formation of a tris-(2,2′-bipyridyl)iron(II) pseudobase may be followed by a rupture of one of the bonds in the complex to yield a monodentate ligand $Fe(bipy)_2(bipy)^{3+}$



(25)

The monodentate ligand is released:

$$Fe(bipy)_2(bipy)^{2+} + H^+ \rightarrow Fe(bipy)_2^{2+} + Hbipy^+ \qquad (26)$$

which may lead either to a rapid decomposition of $Fe(bipy)_2^{2+}$ or its oxidation similar to that of reaction 18:

$$Fe(bipy)_2^{2+} + HBrO_2 + 2H^+ \rightarrow Fe(bipy)_2^{4+} + HBrO + H_2O \qquad (27)$$

The oxidation of malonic and bromomalonic acids in the course of an oscillating process is likely to proceed only via a two-electron mechanism involving iron(IV) complexes as indicated from the low redox potential for the $Fe(bipy)_3^{+3}/Fe(bipy)_3^{2+}$ couple. Hence, reaction (27) producing an iron (IV) complex must take place together with an autocatalytic reduction of bromate ion. It follows, as the acid concentration rises, the concentration of the pseudobase $Fe(bipy)_2$ (bipy) $*^{3+}$ drops and reaction (27) is barely possible. In this case the oscillations stop because the substrate is not oxidized. On the other hand, a decrease in the acid concentration lowers the concentration of the unaquated complex and, hence, decreases the contribution from the autocatalytic reduction of bromate. It should lessen the amplitude and period of oscillations, which prediction was confirmed experimentally.

An appreciable change in the ratio $Fe(bipy)_3^{3+}//Fe(bipy)_3^{2+}$ is observed, respecially, with increasing catalyst concentration. This fact may be accounted for both by the instability of the tris-(2,2′-bipyridyl) complexes of iron(II) and iron(III) with time and the complicated character of the oxidation of the catalyst.

The participation of *osmium, chromium, silver and cobalt coordination compounds* has been described incompletely Recently, the 1,10-phenanthroline and 2,2′-bipyridyl cobalt(II) complexes were found to act as catalysts in the oscillating reaction between malonic acid and bromate [30]. Unfortunately, this laconic information lacked illustration and is the only report available today.

The oscillating chemical reactions catalyzed by 2,2′-bipyridyl osmium(II) [28] are characterized by a long induction period and a small contribution of the catalyst involved relative to its total concentration (up to 2%). A low standard redox potential for the $Os(bipy)_3^{3+}/Os(bipy)_3^{2+}$ couple (Table 1), and the diverse oxidation states of osmium in complex compounds [62] suggest reaction (28):

$$HOBr + Os(bipy)_3^{2+} + H^+ \rightarrow Os(bipy)_3^{4+} + Br^- + H_2O \qquad (28)$$

This case, however, excludes the induction period which contradicts the experimental data [28]. Reaction 28 can take place only via contribution from a specific form of the catalyst, e.g., $Os(bipy)_2^{2+}$ (cf. iron(II) complexes). If the dissociation

$$Os(bipy)_3^{2+} + H^+ \rightarrow Os(bipy)_2^{2+} + bipyH^+ \qquad (29)$$

proceeds slowly, the induction period may be associated with accumulation of an active form of the $Os(bipy)_2^{2+}$ complex which is further involved in the reduction of malonic acid. A small amount of the osmium complex resulting from the dissociation (29) can partly account for a small contribution of the catalyst involved in the oscillating process.

The shape of the oscillations observed for the BrO_3^-–$CH_2(COOH)_2$–$Cr(bipy)_3^{2+}$ system [28] resembles that of the BrO_3^-–$CH_2(COOH)_2$–$Fe(bipy)_3^{2+}$ system. There is no induction period in the reaction involving chromium(II) complexes, and though the oscillations are observed for a long time, their amplitude diminishes from one oscillation to the next. Unfortunately the available data are not sufficient to determine the composition and form of the catalytically active Cr(III) complex. However, its tris-complex is barely active because of a low standard redox potential for the $Cr(bipy)_3^{3+}/Cr(bipy)_3^{2+}$ couple (see Table 1).

The oscillating chemical reaction between bromate and malonic acid catalyzed by bis(2,2′-bipyridyl)silver(I) [29] is of special interest as it periodically forms a precipitate, $Ag(bipy)_2NO_3$. The latter dissociates to liberate free Ag^+ which removes bromide ions. This process decreases the time of consumption of bromide ions to a critical value and reduces the period of oscillations and the duration of the overall oscillating system.

E. COORDINATION COMPOUNDS OF TRANSITION METALS AS ADDITIONAL CATALYSTS FOR OSCILLATING REACTIONS

The introduction of additional transition metal compounds in the operating oscillatory system allows one to gain some more information on the regularities and the mechanism of the initial oscillating reaction. For instance, addition of microamounts of ruthenium(III) sulfate complexes to a malonic acid–bromate–cerium(III) sulfate system appreciably shortens the period of oscillations and lengthens the induction period (Fig. 7) [20]. Ruthenium(III) complexes, though not contributing to the oscillating process, catalyze the oxidation of malonic and bromomalonic acids and bromide ions with cerium(IV) [69,70] bringing about changes in the oscillation parameters. Alterations in the period of oscillation caused by ruthenium compounds were used in determining microamounts of the latter [71].

Addition of ferroin to a bromate–cerium(III)–malonic acid system (at [Ce(III)]/[Fe(phen)$_3^{2+}$] ranging from 0.09 to 0.14 mol l^{-1}) leads to complete damping of the oscillations [67], attributed to competitive reductions of cerium(IV) with ferroin and the organic substrate. The ferroin ions at a very low concentration (5×10^{-6} mol l^{-1}) act as a redox indicator in the reactions catalyzed by the Ce(III)–Ce(IV) couple. With the initial [Ce(III)]/[Fe(phen)$_3^{2+}$] ratio higher than 0.14, the oscillations of [Ce(IV)]/[Ce(III)] are damped completely.

Ferroin differently affects the "uncatalyzed" oscillating reactions between

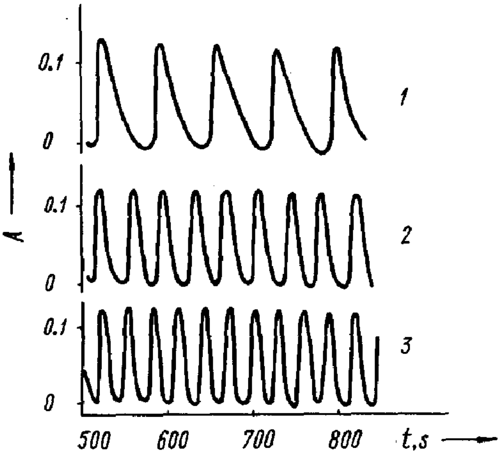


Fig. 7. Effect of sulfate ruthenium(III) compounds on the oscillation period for $KBrO_3$–$Ce_2(SO_4)_3$–$CH_2(COOH)_2$ system [71]. 1, without Ru(III) complexes; 2, 10^{-6} mol l^{-1} Ru(III) complexes; 3, 10^{-5} mol l^{-1} Ru(III) complexes.

aromatic substances and bromate ion [68,72–78]. Tris-(1,10-phenanthroline)iron(II) like tris-(2,2′-bipyridyl)ruthenium(II) completely inhibits the concentration oscillations in the oxidation of trihydroxybenzene, 3-aminophenol, 2,4-diaminodiphenylamine, phenol and aniline [68] with bromate ion. This is in contrast to the action of cerium(III) and manganese(II). The inhibiting action of ferroin and tris-(2,2′-bipyridyl) ruthenium(II) is associated with the low redox potentials of the $Fe(phen)_3^{3+}/Fe(phen)_3^{2+}$ and $Ru(bipy)_3^{3+}/Ru(bipy)_3^{2+}$ couples. This interpretation is consistent with the assumption of the predominant non-radical two-electron oxidation of intermediate organic substrates with iron(IV) and ruthenium(IV) compounds. The absence of organic radicals responsible for oscillations excludes the occurrence of the latter in an uncatalyzed oxidation with bromate ions.

In several papers [73–75], the addition of ferroin is shown to activate the oscillating chemical reactions between aromatic compounds and bromate ion: the number of oscillations and their amplitude are increased and the induction period and the period of oscillations are decreased. The only exception is the oxidation of salicylic and sulfosalicylic acids with bromate ion: the presence of ferroin lengthens the induction period [76]. Moreover, the oscillations are renewed in an uncatalyzed oscillating chemical system after their complete damping upon addition of ferroin. Analogous behaviour with cerium(III) and manganese(II) ions is observed in systems exhibiting an inhibiting effect by ferroin [68].

It follows from the above that ferroin can either inhibit or activate uncatalyzed oscillating reactions depending upon its interaction with an organic substrate (or its conversion products). A rapid interaction of ferroin with polyphenol radicals in the course of the oscillating reaction accounts for a lower sensitivity to stirring, i.e., the action of oxygen as a scavenger [73]:

$$Fe(phen)_3^{3+} + HAr(OH)O^{\cdot} \rightarrow HArO_2 + Fe(phen)_3^{2+} + H^+ \qquad (30)$$

F. OSCILLATING CHEMICAL REACTIONS CATALYZED BY MACROCYCLIC COMPLEXES OF COPPER(II) AND NICKEL(II)

The oxidation of malonic acid with bromate ion proved to be a convenient system in choosing the conditions for oscillating reactions in the presence of transition metal complexes of macrocyclic ligands. Tetraazamacrocycles have been chosen as ligands not only because of their suitable metal redox potentials (see Table 2) but also because of the stability of these compounds in aqueous solutions. The same considerations were taken into account in choosing the metals. For instance, complex compounds of iron(II)–(III) with some tetraazamacrocyclic ligands (i.e., Me[14]ane N_4 and others,) [43] in acetonitrile solutions are characterized by redox potential values ranging from 0.8 to 1.5 V, though they are very unstable in aqueous solutions [77]. Periodic changes in the potential of the platinum and of the bromide-selective electrodes were observed for BrO_3^-–$CH_2(COOH)_2$–CuL^{2+} and BrO_3^-–$CH_2(COOH)_2$–NiL^{2+} systems, in which L is a tetraazamacrocyclic ligand. Copper complexes with the 14-member macrocyclic ligands, Me_6[14]4,14-diene N_4, Me_6[14]ane N_4 and Me_6[14]4,11 diene N_4 and nickel complexes with the same ligands (except Me_6[14]ane N_4) and Me_6[14]1,3,7,11-tetraene N_4 have also been used. Oscillating reactions involving these complexes have some unusual features which distinguish them from other Belousov–Zhabotinskii reactions. Reactions involving macrocyclic complexes are characterized by the total absence of an induction period, the diversity of oscillation forms and a wide range of fluctuations in the amplitude and period of oscillations [10,78–80].

The concentration oscillations observed in the oxidation of malonic acid with bromate ion in the presence of tetraazamacrocyclic copper(II) complexes are damped in character. Periodic changes in the ratio of the concentrations of the oxidized and reduced forms of the catalyst, $[CuL^{3+}]/[CuL^{2+}]$, are confirmed by oscillations in the optical density of solutions at wavelengths of 357 and 500 nm corresponding to $Cu(Me_6[14]4,14\ diene\ N_4)^{3+}$ and $Cu(Me_6[14]4,14\ diene\ N_4)^{2+}$, respectively. Oscillations of $[CuL^{3+}]/[CuL^{2+}]$ are also indicated from periodic changes in the intensity of an ESR signal characteristic of a CuL^{2+} complex. With tetraazamacrocyclic nickel(II) complexes, the oscillations last not less than 1.5–2 hours. The concentration conditions under which oscillations occur in the oxidation of malonic acid with bromate ion, catalyzed by nickel complexes vary with the compounds investigated. For instance, in the system involving $Ni(Me_6[14]\text{–}4,11\ diene\ N_4)^{2+}$ the oscillations were detected only in mixed aqueous–acetonitrile solutions. Such variations were not observed in the series of copper macrocyclic derivatives studied. Changes in the potentials of platinum and bromide-selective electrodes are accompanied by oscillations in the optical density of the solutions at wavelengths of 438 and 590 nm corresponding to transitions of nickel(II) and nickel(III) in macrocyclic complexes of this type [39,81].

In the Belousov–Zhabotinskii oscillating reactions catalyzed by manganese(II) aquo-ions and cerium(III)–sulfate complexes, variations in the initial concentrations of reaction components maredly affect the oscillation parameters and change slightly the shape of the oscillations. The latter is sharply changed with alterations in the initial concentrations of components in the reactions catalyzed by nickel–macrocyclic ligand complexes. In this case the shape, period and amplitude of oscillations are not constant in time; see Fig. 8.

Oscillating reactions involving metal–macrocyclic complexes have not been investigated sufficiently to draw conclusions about their mechanism. As in other Belousov–Zhabotinskii reactions, bromide ions at a concentration of 10^{-5} M switch the oscillations on and off and at high concentrations the oscillations are stopped. Therefore, bromide ion is considered to be the key substance responsible for switching on and off the oxidation of the catalyst and the reduction of its oxidized form.

The role of malonic acid is ambiguous in these reactions: it acts not only as a reductant, but its bromination is responsible for removal of free bromine. When malonic acid is replaced by bromomalonic acid the oscillations are absent and free bromine accumulates in the reaction mixture. In the Belousov–Zhabotinskii reactions the oxidation of bromomalonic acid is regarded as the main source of bromide ions. In the systems considered here, the bromide ions must be formed by some other process. The two-electron reduction of hypobromous acid cannot be completely excluded, similar to reaction (16), if a nickel(I) or copper(I) complex is formed as an intermediate.

$$MeL^+ + HBrO + H^+ \rightarrow MeL^{3+} + Br^- + H^+ \qquad (31)$$

However, the formation of MeL^+ complexes is doubtful because of the

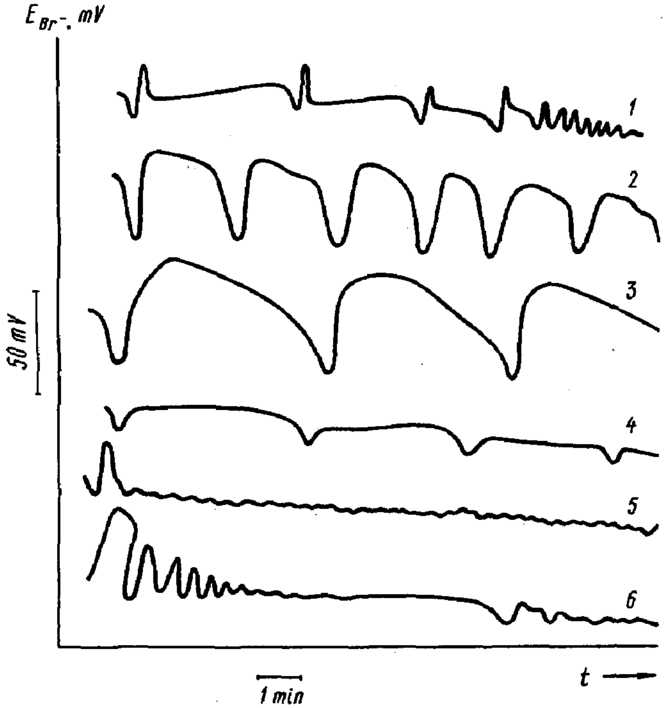


Fig. 8. Plots of the Br^--selective electrode potential vs. time for $KBrO_3$–Ni(Me$_6$[14]4,14 diene $N_4)^{2+}$ –$CH_2(COOH)_2$ system under different concentration conditions [80].

extremely low redox potential for the MeL^{2+}/MeL^{+} couple (Table 2); nevertheless a tetraazamacrocyclic nickel(I) complex is rather stable under special conditions [82].

Thus, these reactions have some features in common with classic Belousov–Zhabotinskii reactions (the key role of bromide ions) but also significant distinctions (there are no oscillations when bromomalonic acid is used instead of malonic acid). Oscillating reactions catalyzed by tetraazamacrocyclic copper(II) and nickel(II) complexes also occur in H_2SO_4 solutions, as do most oscillation reactions. A complex–sulfate ion adduct is known to be formed in H_2SO_4 solution. The binding of mineral acid anions is typical of tetraazamacrocyclic copper(II) and nickel(III) complexes [83–86]. In the latter case sulphate ion can additionally stabilize the nickel(III) oxidation state.

G. OSCILLATING REACTIONS OF THE OXIDATION OF TRANSITION METAL COORDINATION COMPOUNDS

An oscillating reaction between bromate ion and a transition metal coordination compound in the absence of an additional reductant was first reported for a bromate–ferroin system [9]. Oscillations in the potentials of platinum and bromide selective electrodes are found to occur in H_2SO_4 solutions containing comparable amounts of ferroin and bromate ions with the constant removal of molecular bromine by a flow of nitrogen. The system is heterogeneous not only because of the presence of gaseous free bromine but also a precipitate which forms and accumulates in the course of the reaction. The precipitate is thought to consist of the products of bromination and oxidation of free and coordinated 1,10-phenanthroline. It may contain a polymeric product of ferroin oxidation [56]. Free 1,10-phenanthroline cannot be regarded to be the organic substrate in this reaction; the oscillating process takes place only with its iron(II) complex. Free bromine is likely to play the key substance role similar to that of bromide ions in other reactions: when free bromine is completely removed or is present in great excess, the oscillations stop.

Some tetraazamacrocyclic copper(II) and nickel(II) complexes also periodically interact with bromate ion in H_2SO_4 solutions [10, 78–80,86]. The removal of free bromine was found to be necessary for these reactions.

Not all copper(II) and nickel(II) coordination compounds which catalyze the Belousov–Zhabotinskii reactions, can interact with bromate ion in the absence of an organic substrate. Among three copper(II) complexes studied, only $Cu(Me_6[14]\text{-}4,14\ diene\ N_4)^{2+}$ is capable of interacting periodically with bromate ion. Oscillating reactions between bromate ion and NiL^{2+} with four Ni(II) complexes (where L is $Me_6[14]ane\ N_4$, $Me_6[14]\text{-}4,14$ diene N_4,

Me_6[14]-4,11-diene N_4, Me_6[14]1,3,7,11 tetraene N_4) have been studied. The Belousov–Zhabotinskii reaction is not observed, in the presence of a $Ni(Me_6[14]ane\ N_4)^{2+}$ complex whereas in the absence of malonic acid this complex interacts periodically with bromate ion.

In reactions involving the constant removal of molecular bromine by a flow of nitrogen, changes in the potentials of platinum and bromide-selective electrodes are detected, as are changes in the optical density, at wavelengths corresponding to the absorption of MeL^{2+} and MeL^{3+} complexes. Moreover, periodic changes in the intensity characteristic of copper(II) complexes were observed [86]. All the data obtained indicate periodic oscillations in the $[MeL^{3+}]/[MeL^{2+}]$ ratio together with oscillations in the concentration of bromide ions.

Oscillating reactions of this type in the presence of copper complexes differ appreciably from those involving nickel complexes. In the former, some damped oscillations were observed [86], in the latter, oscillations last for 1.5–2 hours (Fig. 9). In similar fashion to the Belousov–Zhabotinskii reactions, the addition of bromide-ions to the reaction mixture at a concentration of 10^{-5} M switches the oscillation phase on and off and an increase in bromide concentration inhibits the oscillations. This is evidence for the key role of bromide ions in this reaction. On the other hand, the free bromine concentration is also important, as is the case with the oscillating reaction between bromate and ferroin [9]. Thus, both high and low concentrations of free bromine stop the reaction. Free bromine together with bromide ions are important controlling intermediates in all oscillating reac-

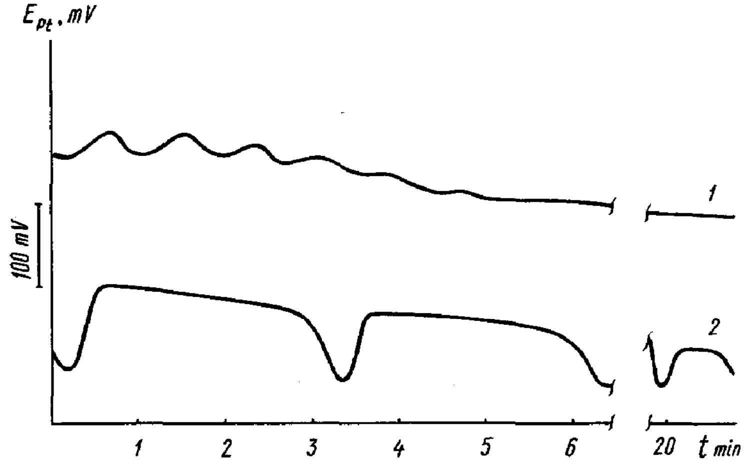


Fig. 9. Plots of the platinum electrode potential vs. time for $KBrO_3$–$Cu(Me_6[14]4,14\ diene\ N_4)^{2+}$ (1) and $KBrO_3$–$Ni(Me_6[14]4,14\ diene\ N_4)^{2+}$ (2) systems under optimal concentration conditions. Concentrations: (1) 0.167 mol l^{-1} $KBrO_3$; 1.5 mol l^{-1} H_2SO_4; 0.004 mol l^{-1} $Cu(Me_6[14]4,14\ diene\ N_4)(ClO_4)_2$. (2) 0.11 mol l^{-1} $KBrO_3$; 0.6 mol l^{-1} H_2SO_4; 0.005 mol l^{-1} $Ni(Me_6[14]4,14\ diene\ N_4)(ClO_4)_2$.

tions with tetraazamacrocyclic copper(II) and nickel(II) complexes. However, the permissible limiting concentrations for free bromine in the bromate–transition metal complex–organic substrate systems are different from those in reactions occurring in the absence of an organic substrate. The oxidation of malonic acid with bromate ion catalyzed by a nickel(II) complex, operating in a nitrogen flow, exhibits complicated oscillations involving both "micro" and "macro" oscillations (Fig. 10). Such changes in the concentrations of components suggest two simultaneous oscillating reactions.

The interaction of bromate ions with ferroin and with macrocyclic copper or nickel coordination compounds requires further detailed investigation. Periodic changes in the ratio of the concentrations of the oxidized and reduced forms of the transition metal complexes involved in these reactions may be interpreted only in terms of an alternate accumulation and consumption of the oxidant (BrO_2^-, $^{\cdot}BrO$ and $^{\cdot}Br$ radicals or hypobromous acid) and the possibility of an intracomplex reduction of the metal ion. Considering the data available in the literature [42,87,89] multiple reduction of the metal ion may take place in tetraazamacrocyclic copper(III) and nickel(III) complexes due to the removal of protons and appearance of double bonds in the ligand ring.

In the oxidation of a macrocyclic–transition metal complex, not only is the oxidation state of the central metal atom altered, but the macrocyclic ligand may also be oxidized. The oxidation proceeds in several steps. Ligand

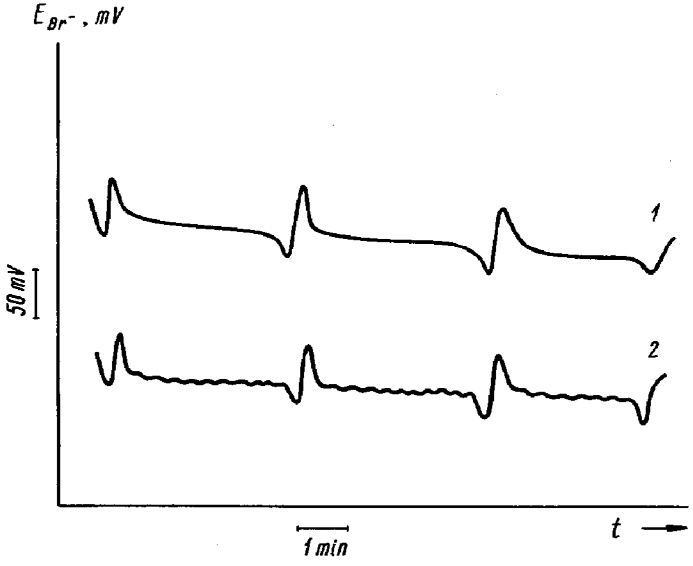
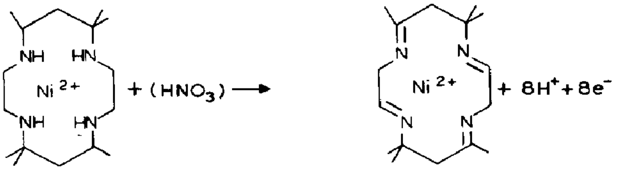


Fig. 10. Plots of Br^--selective electrode potential vs. time for $KBrO_3$–Ni(Me_6[14]4,14 diene N_4)$^{2+}$ –$CH_2(COOH)_2$ system in a nitrogen flow (1) and in its absence (2) [80].

oxidation requires a considerable amount of oxidant, e.g., eight electrons are involved in the first steps:



(32)

This fact may explain the choice of a coordinated macrocyclic ligand as a substrate in the oscillating reaction. The duration of the overall oscillating process is determined by the rate of the complete oxidation and destruction of a macrocyclic ligand to yield metal aquo- or sulfate complex.

H. CONCLUSIONS

The complexation of transition metal ions with nitrogen-containing chelate and macrocyclic ligands allows one to increase the number of catalysts suitable for the oscillating oxidation reactions of organic substrates (malonic acid) with bromate ion. The redox couplex Fe^{2+}/Fe^{3+}, Ru^{2+}/Ru^{3+}, Os^{2+}/Os^{3+} with the d^6–d^5 central ion electron configuration have been studied in some detail. The Cr^{2+}/Cr^{3+}, Co^{2+}/Co^{3+}, and Ag^+/Ag^{2+} redox couples with d^4–d^3, d^7–d^6 and d^{10}–d^9 central ion electron configurations have also been described. Macrocyclic complexes with the Cu^{2+}/Cu^{3+} (d^9–d^8) and Ni^{2+}/Ni^{3+} (d^8–d^7) couples also proved to be useful as catalysts for oscillating reactions.

The participation of coordination compound ligands in redox processes facilitates the occurrence of oscillations in the bromate–transition metal system in the absence of an additional oxidant, as illustrated by the reactions involving tris(1,10-phenanthroline) iron(II), and tetraazamacrocyclic copper(II) and nickel(II) complexes.

The nature of the ligand affects, to a certain extent, the occurrence of an oscillating reaction and its parameters. For instance, the presence of an extended π-system in the ligand ensures a high rate for reactions involving electron transfer at individual steps of the oscillating process.

REFERENCES

1 B.P. Belousov, Sb. Ref. Radiats. Med., Medgiz, Moscow, 1958, p.145.
2 A.M. Zhabotinskii, Concentration Autooscillations, Nauka, Moscow, 1974.
3 A.M. Zhabotinskii, Dokl. Akad. Nauk SSSR, 157 (1964) 392.
4 T.S. Briggs and W.C. Rauscher, J. Chem. Educ., 30 (1973) 496.
5 W.C. Bray, J. Am. Chem. Soc., 43 (1921) 1262.

6 H.A. Liebhafsky, J. Am. Chem. Soc., 53 (1931) 896.
7 D.O. Cooke, J. Chem. Soc. Chem. Commun., (1976) 27.
8 M. Orban, C. Dateo, P. De Kepper and J.R. Epstein, J. Am. Chem. Soc., 104 (1982) 5911.
9 M.T. Beck, Gy. Bazsa and K. Hauck, Kinetics of Phys.-Chem. Oscillations, Proc. Int. Conf., Aachen, 1979, p. 123.
10 K.B. Yatsimirskii, L.P. Tikhonova, L.N. Zakrevskaya, Ya.D. Lampeka and A.G. Kolchinskii, React. Kinet. Catal. Lett., 21 (1982) 381.
11 K.B. Yatsimirskii, L.P. Tikhonova and A.S. Kovalenko, Theor. Exp. Chem. (USSR), 14 (1977) 824.
12 K.B. Yatsimirskii, M.L. Kazakevich, L.I. Budarin and L.S. Degtyarev, Dokl. Akad. Nauk SSSR, 270 (1983) 108.
13 M. Orban and J.R. Epstein, J. Am. Chem. Soc., 104 (1982) 5818.
14 T.J. Kemp and W.A. Waters, J. Chem. Soc., (1964) 1489.
15 I. Tkac and L. Treindl, Collect. Czech. Chem. Commun., 48 (1983) 13.
16 K.J. Field, E. Körös and R.M. Noyes, J. Am. Chem. Soc., 94 (1972) 8649.
17 R.M. Noyes, J. Am. Chem. Soc., 102 (1980) 4644.
18 R.P. Rastogi, P. Rastogi and A. Kumar, Indian J. Chem., 15a (1977) 163.
19 G. Schmitz, Can. J. Chem., 55 (1977) 3147.
20 K.B. Yatsimirskii, L.P. Tikhonova and L.N. Zakrevskaya, Dokl. Akad. Nauk SSSR, 216 (1974) 1372.
21 L.P. Tikhonova, Biological Aspects of Coordination Chemistry (Russ.), Naukova Dumka, Kiev, 1979, p. 121.
22 A.S. Kovalenko and L.P. Tikhonova, Theor. Experim. Chem. (U.S.S.R.), 19 (1983) 108.
23 J.J. Jwo and R.M. Noyes, J. Am. Chem. Soc., 97 (1975) 5422.
24 L.P. Tikhonova, A.S. Kovalenko and K.B. Yatsimirskii, Theor. Exp. Chem. (USSR), 17 (1981) 348.
25 F. Basolo and R. Pearson, Mechanisms of Inorganic Reactions, J. Wiley, New York–London–Sydney, 1967.
26 R.D. Gillard, Coord. Chem. Rev., 16 (1975) 67.
27 L.P. Tikhonova and T.S. Ivashchenko, Theor. Exp. Chem. (USSR), 19 (1983) 693.
28 L. Kuhnert and K.W. Pehl, Chem. Phys. Lett., 84 (1981) 159.
29 L. Kuhnert and K.W. Pehl, Chem. Phys. Lett., 84 (1981) 155.
30 M. Handlířová and A. Tockstein, Collect. Czech. Chem. Commun., 45 (1980) 2621.
31 M. Orban and E. Körös, React. Kinet. Catal. Lett., 8 (1978) 273.
32 G.F. Smith and F.R. Richter, Ind. Eng. Chem. Anal. Ed., 16 (1944) 580.
33 F.P. Dwyer, J.E. Humpletz and R.S. Nyholm, J. Proc. R. Soc. N.S. Wales, 80 (1947) 212.
34 I.M. Kolthoff and D.P. Hume, J. Am. Chem. Soc., 65 (1943) 1895.
35 W.R. Mcwhinnie and J.D. Miller, Adv. Inorg. Chem. Radiochem., 12 (1969) 1135.
36 E. König and S. Herzog, J. Inorg. Nucl. Chem., 32 (1970) 585.
37 G.A. Melson (Ed.) Coordination Chemistry of Macrocyclic Compounds, Plenum Press, New York–London, 1979.
38 F.V. Loveccio, E.S. Gore and D.H. Busch, J. Am. Chem. Soc., 96 (1974) 3109.
39 D.C. Olson and J. Vasilevskis, Inorg. Chem., 8 (1968) 1611.
40 D.H. Busch, Acc. Chem. Res., 11 (1978) 392.
41 J.M. Palmer and Papaconstatinou, Inorg. Chem., 6 (1967) 1516.
42 D.C. Olson and J. Vasilevskis, Inorg. Chem., 10 (1971) 463.
43 D.H. Busch, D.G. Pillsbury, F.V. Loveccio, A.M. Tait, Y. Hang, S. Jackels, M.C. Rakowsky, W.P. Schammel and Y.L. Martin, Am. Chem. Soc. Symp. Ser., 30 (1977) 32.

44 J.N. Demas and D. Diemente, J. Chem. Educ., 50 (1973) 357.
45 L.P. Tikhonova and V.Ya. Zayats, Theor. Exp. Chem. (USSR), 16 (1980) 546.
46 A.S. Kovalenko, L.P. Tikhonova, O.M. Roizman and E.V. Protopopov, Theor. Exp. Chem. (USSR), 16 (1980) 46.
47 V.A. Vavilin, T.V. Ghulak, A.M. Zhabotinskii and A.N. Zaikin, Izv. Akad. Nauk SSSR, Ser. Khim., (1969) 2618.
48 M.L. Smoes, J. Chem. Phys., 79 (1979) 4669.
49 A.M. Zhabotinskii and A.B. Rovinskii, Theor. Exp. Chem. (USSR), 15 (1979) 25.
50 E. Körös, M. Burger, V. Friedrich, L. Ladânyi, Zs. Nagy and M. Orban, Faraday Symp. Soc., (1974) 28.
51 C.M. Singh, H.C. Mishra and R.N. Upadnyay, J. Indian Chem. Soc., 56 (1979) 835.
52 E. Körös, M. Burger and A. Kis, React. Kinet. Catal. Lett., 1 (1974) 475.
53 K. Prasad, G.S.P. Verma and M.S. Prasad, Indian J. Chem., 19a (1980) 695.
54 N. Ganathisubramanian and R.M. Noyes, J. Phys. Chem., 86 (1982) 5158.
55 K.B. Yatsimirskii, L.P. Tikhonova and L.N. Zakrevskaya, Theor. Exp. Chem. (USSR), 12 (1976) 343.
56 B.Z. Shakhashiri and B.Z. Gordon, J. Am. Chem. Soc., 91 (1969) 1103.
57 Ya.D. Tiginyanu and V.I. Oprya, Kinetics and Catalysis (Russ.), 19 (1978) 114.
58 V.I. Oprya and Ya.D. Tiginyanu, Chemical Kinetics and Catalysis (Russ.), Nauka, Moscow, 1979, p. 117.
59 A. Bartetski and T. Talachala, Kinetics and Catalysis (U.S.S.R.), 18 (1979) 2375.
60 E. Körös, M. Orbân and Zs. Nagy, J. Phys. Chem., 26 (1973) 3122.
61 J.R. Birk and S.G. Kozub, Inorg. Chem., 17 (1978) 1186.
62 S. Livingston, The Chemistry of Ruthenium, Rhodium, Iridium, Palladium, Osmium and Platinum. Compr. Inorg. Chemistry, Pergamon Press, Oxford, 1973.
62(a) N. Serpone, G. Panterini, M.A. Jamieson, F. Bolletta and M. Maestri, Coord. Chem. Rev., 50 (1983) 209.
63 R.R. Miller, W.W. Brandt and S.M. Puke, J. Am. Chem. Soc., 77 (1955) 3178.
64 F. Boiletta and V. Balzani, J. Am. Chem. Soc., 104 (1982) 4250.
65 M.S. Henry and M.Z. Hoffman, J. Am. Chem. Soc., 99 (1977) 5201.
66 V.Ya. Shafirovich, and V.V. Strelets, Izv. Akad. Nauk, Ser. Khim. (Russ.), 17 (1980) 493.
67 A.S. Kovalenko, L.P. Tikhonova and K.B. Yatsimirskii, Theor. Exp. Chem. (USSR), 17 (1981) 493.
68 E. Körös, M. Orban and I. Habon, J. Phys. Chem., 84 (1980) 559.
69 K.B. Yatsimirskii, L.P. Tikhonova and L.N. Zakrevskaya, Theor. Exp. Chem. (USSR), 9 (1973) 805.
70 K.B. Yatsimirskii, L.P. Tikhonova and L.N. Zakrevskaya, Theor. Exp. Chem. (USSR), 12 (1976) 343.
71 L.P. Tikhonova, L.N. Zakrevskaya and K.B. Yatsimirskii, J. Anal. Chem. (Russ.), 33 (1978) 1991.
72 P. Herbin and R.J. Field, J. Phys. Chem., 84 (1980) 1330.
73 V.K. Gupta, P.K.R. Nair and Srinivasulu, React. Kinet. Catal. Lett., 18 (1981) 45.
74 A. Mittal, P.K.R. Nair and Srinivasulu, React. Kinet. Catal. Lett., 13 (1980) 259.
75 P.K.R. Nair, A. Mittal and Srinivasulu, React. Kinet. Catal. Lett., 16 (1981) 399.
76 V.K. Gupta and K. Srinivasulu, React. Kinet. Catal. Lett., 19 (1982) 193.
77 V.L. Goedken, P.H. Merrel and D.H. Busch, J. Am. Soc., 94 (1972) 3397.
78 K.B. Yatsimirskii, L.N. Zakrevskaya, A.G. Kolchinskii and L.P. Tikhonova, Dokl. Akad. Nauk SSSR, 251 (1980) 132.

79 K.B. Yatsimirskii, L.P. Tikhonova, L.N. Zakrevskaya and Ya.D. Lampeka, Dokl. Akad. Nauk SSSR, 261 (1982) 647.
80 K.B. Yatsimirskii, L.P. Tikhonova, L.N. Zakrevskaya and Ya.D. Lampeka, Theor. Exp. Chem. (USSR), 18 (1982) 439.
81 K.B. Yatsimirskii and Ya.D. Lampeka, Usp. Khim., 49 (1980) 2032.
82 N. Jurbah, G. Ginzburg, H. Cohen and D. Meyerstein, J. Chem. Soc., Chem. Commun., (1982) 517.
83 B.F. Liang and C.S. Chung, Inorg. Chem., 19 (1980) 572.
84 B.F. Liang and C.S. Chung, Inorg. Chem., 19 (1980) 1867.
85 H. Kohen, L.J. Kirschenbaum, E. Zeigerson, M. Jaakobi, E. Fuchs, G. Ginzburg and D. Meyerstein, Inorg. Chem., 18 (1979) 2763.
86 E. Zeigerson, I. Bar, J. Bernstein, L.J. Kirschenbaum and D. Meyerstein, Inorg. Chem., 21 (1982) 73.
87 A.G. Kolchinskii and K.B. Yatsimirskii, Theor. Exp. Chem. (USSR), 16 (1980) 525.
88 K.E. Barefield and M.T. Mocella, J. Am. Chem. Soc., 97 (1975) 4238.
89 K.D. Whiteburn and G.S. Laurence, J. Chem. Soc., Dalton Trans., (1979) 139.
90 Z. Váradi and M.T. Beck, J. Chem. Soc., Chem. Commun., (1973) 30.