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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Kinetics of Liquid-Phase Redox Reactions Involving Hydroxy- and Aminoalkanesulfinates

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Abstract—The mechanisms and kinetics of practically important redox reactions proceeding under the action of hydroxy- and aminoalkanesulfinates are analyzed. The general features allowing forecasting of the rates of reactions involving the above reducing agents are elucidated.

Hydroxy- and aminoalkanesulfinates are widely used as reducing agents in various branches of engineering and technology. The best known compounds, hydroxymethanesulfinate (HMS, technical name rongalite) and thiourea dioxide (TUDO, aminoiminomethanesulfinic acid), are used in textile industry, production of synthetic rubber, stabilizers for polymeric materials, uranium salts and salts of transuranium elements, electroless metal plating of polymeric materials, and other processes [1].

By now the experimental data on the kinetics and mechanisms of redox reactions involving the above compounds are quite extensive and, in our opinion, sufficient to generalize and elucidate the general features.

Based on an analysis of the concentration dependences of the reaction rates and the effect of various additives on the reaction rate, the reactions in hand can be divided into three groups. The reactions of the first group are characterized by the occurrence of an induction period, zero reaction order with respect to oxidizing agent for a long reaction time, first reaction order with respect to reducing agent, and abrupt decrease in the reaction rate, even to the point of complete inhibition, upon addition of formaldehyde. This group includes reduction of disodium 5,5'-indigotindisulfonate (indigocarmine) with sodium hydroxy- and aminoalkanesulfinates [2], 2-nitro-2'-hydroxy-5'-methylazobenzene (NAB) with HMS and TUDO [3, 4], Direct Red 2C azo dye with HMS and TUDO [5], uranyl acetate with TUDO [6], and iodine, bromine, and chlorite ions with HMS and TUDO [7]. Typical kinetic curves characteristic of this group of reactions are shown in Fig. 1.

The reactions of the second group have zero induction period, fractional reaction order with respect to the oxidizing agent, and first order with respect to the reducing agent. Addition of formaldehyde also inhibits the reaction, but to a lesser extent than for the reactions of the first group. The second group includes reduction of vat dye precursors with sodium hydroxy- and aminoalkanesulfinates [8], nickel and cobalt salts with HMS and TUDO [9], and ethylenediaminetetraacetatoferrate ($FeEDTA^-$) with TUDO [10].

The reactions in which formaldehyde exerts weak or practically no effect on the reduction rate belong to the third group. These reactions are first-order with respect to the oxidizing agent at moderately low temperatures, and a fractional reaction order is observed with increasing temperature; in all cases, the reaction order with respect to the reducing agent is 1. The ex-

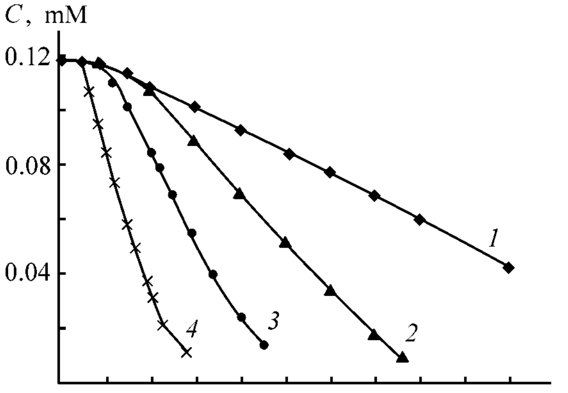

Fig. 1. Concentration of NAB C vs. time τ of its reduction with HMS. T = 298 K, C_{HMS} = 0.252 M. C_{NaOH} (M): (*1*) 0.78, (*2*) 1.74, (*3*) 2.43, and (*4*) 3.11.

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amples of these reactions are reduction of $FeEDTA^-$ [11] and 4-nitrosodiphenylamine (4NDPA) [12] with rongalite and of *p*-benzoquinone with rongalite and TUDO [2].

Studies of decomposition of HMS and TUDO showed [13, 14] that the induction period is caused by the autocatalytic decomposition of molecules of the reducing agent, proceeding with rupture of the C–S bond (with HMS molecules as an example) in neutral

$$HOCH_2SO_2^- = HSO_2^- + CH_2O \qquad (1)$$

or in alkaline medium:

$$HOCH_2SO_2^- + OH^- = SO_2^{2-} + CH_2(OH)_2. \qquad (2)$$

To pass from the induction period to a steady state, it is necessary to accumulate a sufficient amount of decomposition catalysts (“active sulfur” and sulfide), which are by-products of processes (1) and (2). When the excess of the reducing agent is sufficiently high, the reactions of the first group proceed in quasi-steady-state mode to 90% and higher conversion of the oxidizing agent. The inhibiting effect of formadehyde is caused by a shift to the left of the equilibrium of reactions (1) and (2) and the resulting decrease in the quasi-steady-state concentration of the intermediates, anions of sulfoxylic acid (HSO_2^- and SO_2^{2-}) [1, 2].

The kinetic data suggest that the reduction with derivatives of aminoalkanesulfinic acids proceeds by two concurrent pathways: with preliminary cleavage of the C–S bond, accompanied by the formation of sulfur-oxygen intermediates by reactions (1) and (2), and by direct reaction between molecules of the oxidizing and reducing agents [i.e., with stages (1) and (2) by-passed]. The first pathway is arbitrarily named the dissociative pathway, and the second, the associative pathway [15].

Thus, as regards the nature of the reducing effect, the reactions of the first group can be classed with dissociative-autocatalytic reactions.

For the second group of reactions, the absence of the induction period in the kinetic curves suggests that the reduction rather easily proceeds by the dissociative pathway without accumulation of active sulfur able to catalyze stages (1) and (2).

For the third group of reactions, along with the reduction with HSO_2^- or SO_2^- anions, there occurs direct reaction of the oxidizing agent with molecules of the initial reducing agent (associative pathway).

The relative contribution of associative and dissociative pathways to the total process can be estimated from the corresponding reaction rates r_a and r_d determined in experiments with and without addition of formaldehyde. The rate r_a for the reactions proceeding by two pathways was determined under the condition $r_d = 0$, i.e., when an increase in the concentration of added formaldehyde did not affect the reaction rate. The rate r_d was evaluated on the basis of experimental data obtained in the absence of formadehyde addition, from the difference between the apparent reaction rate r and r_a. It should be noted that the ratio $r_a : r_d$, characterizing the contribution of the individual pathways, is governed by the following factors: (a) chemical nature of the oxidizing and reducing agents; (b) reaction conditions, primarily temperature and pH; and (c) process duration.

Let us consider the effect of each factor separately. Data on the kinetics and mechanisms of reactions involving HMS and TUDO are summarized in Tables 1 and 2.

According to the experimental data, associative mechanism is of the greatest importance in reduction of $FeEDTA^-$ with HMS (at a temperature below 303 K the reaction proceeds completely by the associative pathway).

In reduction of organic compounds, the dissociative pathway is dominant. For example, the ratio $r_a : r_d$ is 1 : 6 for 4NDPA (T = 308 K, C_{NaOH} = 1 M), and 1 : 380 for NAB (T = 308 K, C_{NaOH} = 1 M). Reduction of indigocarmine proceeds completely by the dissociative autocatalytic pathway.

The $r_a : r_d$ ratio depends on the nature of the reducing agent. In reduction with TUDO, reactions with an appreciable contribution of the associative pathway are less common than in reduction with HMS. This is apparently caused by the presence of sulfoxylates, which are more readily formed under conditions of reduction with TUDO, i.e., in alkaline media.

The temperature and acidity of the medium govern the degree and rate of cleavage of the reducing agent molecules and thus affect the ratio $r_a : r_d$. The temperature effect is particularly noticeable in reaction of $FeEDTA^-$ with HMS [16]. In this process the reaction proceeds below 303 K by the associative pathway ($r_d = 0$), and by both pathways above 303 K ($r_a : r_d$ = 1 : 2.5 at T = 308 K, $C_{HMS} = 6.5 \times 10^{-3}$ M, pH 10.8).

This fact is accounted for by stronger temperature dependence of the reaction rate in the case of dissociative mechanism (Table 1), which follows from a comparison of the activation energies E^I and E^{II}. There-

Table 1. Results of kinetic studies of the reactions involving sodium hydroxymethylsulfinate*

Oxidizing agent	Mechanism of the redox process	Evaluated kinetic parameters
NAB	$HOCH_2SO_2^- + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SO_2^{2-} + CH_2(OH)_2$ $NAB + SO_2^{2-} \xrightarrow{k_2} BTANO + SO_3^{2-}$	T = 308 K, C_{NaOH} = 0.1–4 M, $k_1 = (0.32 \pm 0.07) \times 10^{-6}$ M^{-1} s^{-1}, $k_{-1} = 8 \pm 5$ M^{-1} s^{-1}, $k_2 = (1.2 \pm 0.07) \times 10^{-2}$ M^{-1} s^{-1}, $E_{app} = 40 \pm 5$ kJ mol^{-1}
4NDPA	$HOCH_2SO_2^- + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SO_2^{2-} + CH_2(OH)_2$ $4NDPA + SO_2^{2-} \xrightarrow{k_2} Int + SO_3^{2-}$ $Int + SO_2^{2-} \xrightarrow{k_3} 4ADPA + SO_3^{2-}$ $4NDPA + HOCH_2SO_2^- \xrightarrow{k_4} Int + HOCH_2SO_3^-$ $Int + HOCH_2SO_2^- \xrightarrow{k_5} 4ADPA + HOCH_2SO_3^-$	T = 308 K, C_{NaOH} = 0.1–2 M, $k_1 = (0.47 \pm 0.08) \times 10^{-6}$ M^{-1} s^{-1}, $k_1 : k_2 = (13 \pm 4) \times 10^{4-}$, $E_{app} = 54 \pm 4$ kJ mol^{-1}
FeEdta$^-$	$HOCH_2SO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HSO_2^- + CH_2O$ $FeEdta^- + HSO_2^- \xrightarrow{k_2} FeEdta^{2-} + H\dot{S}O_2$ $FeEdta^- + H\dot{S}O_2 \xrightarrow{k_3} FeEdta^{2-} + SO_2 + H^+$ $FeEdta^- + HOCH_2SO_2^- \xrightarrow{k_4} FeEdta^{2-} + H\dot{S}O_2 + CH_2O$	T = 308 K, pH 10.8 (Robinson–Britton buffer solution), $k_1 = (0.14 \pm 0.01) \times 10^{-5}$ s^{-1}, $k_1 : k_2 = (0.7 \pm 0.1) \times 10^{-5}$, $k_4 = 0.55 \pm 0.07$ M^{-1} s^{-1}, $E^{I}_{app} = 21 \pm 4$ kJ mol^{-1}, $E^{II}_{app} = 109 \pm 8$ kJ mol^{-1}
[IC(CO)$_2$]	$HOCH_2SO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HSO_2^- + CH_2O$ $IC(CO)_2 + HSO_2^- \xrightarrow{k_2} ICCOCOH^- + SO_2$	T = 333 K, pH 10.5, $k_1 = 1.03 \times 10^{-5}$ s^{-1}, $k_1 : k_2 = 24 \times 10^{-3}$, E_{app} = 114 kJ mol^{-1}
Ni^{2+}(NiCl$_2$)	$HOCH_2SO_2^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} HSO_2^- + CH_2O$ $Ni^{2+} + HSO_2^- + H_2O \xrightarrow{k_2} Ni + HSO_3^- + 2H^+$ $2HSO_2^- \xrightarrow{k_3} HS^- + HSO_4^-$ $2HSO_2^- \xrightarrow{k_4} SO_3^{2-} + S + H_2O$ $Ni^{2+} + HS^- \xrightarrow{k_5} NiS + H^+$ – fast	T = 308 K, pH 4.0, $k_1 = 10^{-3}$ s^{-1}, $k_{-1} = 8.47 \times 10^{2}$ M^{-1} s^{-1}, $k_2 = 4.9 \times 10^{-2}$ M^{-1} s^{-1}, $k_3 = 27.6$ M^{-1} s^{-1}, $k_4 = 110.9$ M^{-1} s^{-1}, $E_{app} = 134 \pm 12$ kJ mol^{-1}

* (BTANO) Benzotriazole *N*-oxide; the reaction proceeds by the dissociative mechanism, contribution of the associative mechanism is insignificant; (Int) intermediate, (4ADPA) 4-aminodiphenylamine; (E^{I}_{app}) and (E^{II}_{app}) apparent activation energies for reactions proceeding by the associative and both pathways, respectively; (IC) indigocarmine; and (ICCOCOH) leuco form of indigocarmine.

fore, in all reducing reactions involving hydroxy- and aminoalkanesulfinates, the contribution of the associative pathway must grow with increasing temperature.

An increase in pH facilitates cleavage of TUDO molecules by the scheme

$$NHC(SO_2H)NH_2 + OH^- = HSO_2^- + (NH_2)_2CO. \quad (3)$$

Thereby, the contribution of the dissociative pathway to redox processes involving TUDO increases. The acidity of the medium affects the degree of dissociation of HMS and other derivatives of sodium alkanesulfinates in two ways. On the one hand, their dissociation becomes more pronounced with decreasing pH, owing to autocatalysis by the products of decomposition of the reducing agents [13, 14] and,

Table 2. Results of the kinetic studies of the reactions involving thiourea dioxide

Oxidizing agent	Mechanism of the redox process	Evaluated kinetic parameters
NAB	$NH_2CSO_2NH_2 \xrightleftharpoons[k_{-1}]{k_1} NHC(SO_2H)NH_2$ $NHC(SO_2H)NH_2 + OH^- \xrightarrow{k_2} HSO_2^- + (NH_2)_2CO$ $NAB + HSO_2^- \xrightarrow{k_3} BTANO + HSO_3^-$ $HSO_2^- \xrightarrow{k_4}$ Decomposition products in the presence of formaldehyde additive $CH_2O + HSO_2^- \xrightleftharpoons[k_{-5}]{k_5} HOCH_2SO_2^-$	T = 281 K, C_{NaOH} = 0.18 M, $k_5 : k_3 = (9.4 \pm 0.8) \times 10^{-3}$, E_{app} = 60 ± 5 kJ mol^{-1}
FeEdta^{-*}	$NH_2CSO_2NH_2 \xrightleftharpoons[k_{-1}]{k_1} NHC(SO_2H)NH_2$ $NHC(SO_2H)NH_2 + OH^- \xrightarrow{k_2} HSO_2^- + (NH_2)_2CO$ $FeEdta^- + HSO_2^- \xrightarrow{k_3} FeEdta^{2-} + HSO_2^{\bullet}$ $FeEdta^- + HSO_2^{\bullet} \xrightarrow{k_4} FeEdta^{2-} + SO_2 + H^+$ $HSO_2^- \xrightarrow{k_5}$ Decomposition products	T = 301 K, pH 8.7, $k_5 : k_3 = (1.7 \pm 0.4) \times 10^{-4}$, E_{app} = 110 ± 10 kJ mol^{-1}
Uranyl acetate**	$NH_2CSO_2NH_2 \xrightleftharpoons[k_{-1}]{k_1} NHC(SO_2H)NH_2$ $NHC(SO_2H)NH_2 + H_2O \xrightarrow{k_2} H_2SO_2 + (NH_2)_2CO$ $UO_2^{2+} + H_2SO_2 \xrightarrow{k_3} U^{4+} + SO_2 + 2OH^-$ $H_2SO_2 \xrightarrow{k_4}$ Decomposition products in the presence of formaldehyde additive $CH_2O + H_2SO_2 \xrightleftharpoons[k_{-5}]{k_5} HOCH_2SO_2H$	T = 323 K, C_{CH_3COOH} = 2.0 M, $k_5 : k_3$ = 0.08, E_{app} = 39 ± 5 kJ mol^{-1}

* In the experiments with formaldehyde additive, the possibility of direct reaction of FeEDTA$^-$ with TUDO was found, but the contribution of the associative pathway is insignificant.

** $UO_2(CH_3COO)_2$.

on the other hand, a decrease in pH shifts the equilibrium of reaction (2) to the left, which decreases the contribution of the dissociative pathway when it is present. It is evident that the first factor plays a decisive role in this case. Previously, it has been shown [2] that in the reaction of *p*-benzoquinone with rongalite the reaction order changes from 1 to a fractional value with decreasing pH. It can be suggested that the contribution of the dissociative pathway of the reduction increases.

The following problems are very important for both elucidating the general features of the kinetics of the redox processes and solving the practical problems: (1) demonstration of the adequacy of the proposed reduction schemes, (2) goal-seeking control of the reduction rates, (3) forecasting of the rates and selectivity of the reduction depending on the nature of a reducing agent and an atom or a group of atoms to be reduced.

To prove the adequacy of the reduction schemes, we identified the intermediates of the redox reactions proceeding by the dissociative pathway, using polarography. It was found that the quasi-steady-state concentration of the intermediate active species ($S_2O_4^{2-}$, SO_2^{2-}, and SO^{2-}) varies in parallel with the reduction rate [17, 18]. As additional argument, we checked experimentally in a series of the reactions the kinetic equation obtained from the conditions of the quasi-steady-state approximaton, which demonstrated a satisfactory agreement between the experimental and calculated reaction rates.

In the general form the reaction rates in the quasi-steady-state mode of many reactions involving HMS and its analogs can be described by the following equation (in alkaline medium):

$$\frac{dC_{Ox}}{d\tau} = \frac{k_1 k_2 C_{Red} C_{Ox} C_{OH^-}}{k_{-1} k_{CH_2O} + k_2 C_{Ox}} + k_3 C_{Red} C_{Ox}, \qquad (4)$$

where k_1 is the constant of direct decomposition of the reducing agent (Red), k_{-1} is the constant of the reverse stage, k_2 is the rate constant of the reaction of the reducing agent with reduction intermediates, and k_3 is the rate constant of the associative pathway.

The first term in the right-hand side of Eq. (4) accounts for the reaction rate by the dissociative pathway, and the second, by the associative pathway.

For the reactions involving TUDO, the equations for the reaction rates have a more complicated form as a result of the presence of the stage of rearrangement and irreversible decomposition of the reducing agent molecules. However, in many cases, the experimental verification of the linear forms of the kinetic equations allows conclusion about the suitability of the quasi-steady-state approximation for reduction processes involving TUDO [4, 6, 10].

In the case of reduction of NAB, Ni^{2+},[1] and *N,N'* derivatives of binaphthylhexylcarboxylic acid diimide, we determined the kinetic parameters using the procedures of mathematic simulation with criterial selection of possible process schemes [19–21]. This approach makes it possible to determine the rate constants of individual stages or combination of these, estimate errors, and correlate the parameters with sufficient reliability.

The constants for NAB and Ni^{2+}, evaluated by the above procedures, are listed in Table 1.

It should be noted that the rate constants of the individual stages can be reliably determined only when the information content of the experimental data corresponds to the complexity of the system. When experimental data are scarce and the kinetic model is complex, a large number of parameter sets providing the same adequate description of the experimental data can be selected. Therefore, for some of reactions (Tables 1, 2) we determined not individual constants but their combinations.

Of some interest is to compare the rate constants of the same stages in different reduction reactions. It turns out that at 308 K the rate constant of the stage of HMS cleavage involving OH^- ions, k_1, determined from the kinetic data for reduction of NAB $[(0.32 \pm 0.07) \times 10^{-6}\ M^{-1}\,s^{-1}]$, is close to the k_1 value determined for reduction of 4NDPA $[(0.47 \pm 0.08) \times 10^{-6}\ M^{-1}\,s^{-1}]$. The rate constants of the stages of HMS cleavage without OH^- ions involved in the reduction of $FeEDTA^-$ and indigocarmine are also comparable: $(0.14 \pm 0.01) \times 10^{-5}$ and $(0.17 \pm 0.03) \times 10^{-5}\ s^{-1}$, respectively.

The k_1 values[2] for indigocarmine were recalculated from 333 to 308 K using the values E_{app} = 114 kJ mol^{-1} and $\ln p_{app} = 37$. The kinetic parameters of the reaction of vat dye precursors of varied structures with HMS were evaluated in [22]. It was shown that for various hydroxyalkanesulfinates the rate constants of the stages of reaction of the same vat dye precursor with sulfoxylate anions [which corresponds to constant k_2 in Eq. (4)] agree within the order of magnitude. These facts additionally prove the adequacy of the proposed reaction schemes to experimental data.

The control of the reduction rate by addition of catalysts and formadehyde is only possible when the dissociative mechanism is dominant. For example, cobalt dioximines [23] and sodium sulfide [24] accelerate the process. It was found that cobalt dioximines exhibit high catalytic activity in reduction of azo dyes with rongalite and in reductive cyclization of nitroazobenzene to give light stabilizer of polymers, benzene P. The mechanism of the effect of dioximines consists in substitution of hydroxymethanesulfinate anion for one of the axial ligands, with its subsequent inner-sphere cleavage and release of sulfoxylate anions.

The effect of sodium sulfide is caused by an increase in the steady-state concentration of SO_2^{2-} owing to the inhibition of sodium hydroxyalkanesulfinate decomposition [13].

The selectivity of the reduction effect of alkanesulfinates of various structures is well seen in reductive cyclization of binaphthylhexacarboxylic acid der-

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[1] The reduction of Ni^{2+} is arbitrarily considered homogeneous since it yields nickel in the solid state. However, owing to the irreversibility of the stage of solid nickel formation we can use the equations of homogeneous kinetics for mathematical description of the process.

[2] For reduction of Ni^{2+} ion, this rate constant is four orders of magnitude higher, which is caused by, first, the difference in pH and, second, different character of cleavage of reducing agent molecules, as mentioned above.

Table 3. Kinetic parameters of reduction of transition metal compounds

Oxidant + reductant	k_{app} (333 K), min^{-1}	E_{app}, kJ mol^{-1}	ln *p*	$\Delta_f H^0$ (298 K), kJ mol^{-1}
Co^{2+} + HMS	0.08×10^{-2}	74 ± 8	19 ± 1	–56.6
Ni^{2+} + HMS	0.11×10^{-2}	134 ± 12	42 ± 4	–53.1
$CuEdta^{2-}$ + HMS	13.3	189 ± 19	71 ± 6	1643.9
Co^{2+} + TUDO	0.52×10^{-2}	78 ± 7	22 ± 1	–56.6
Ni^{2+} + TUDO	12.5×10^{-2}	149 ± 15	51 ± 5	–53.1
$CuEdta^{2-}$ + TUDO	0.96	96 ± 10	35 ± 3	1643.9
UO_2^{2+} +TUDO	3.1×10^{-4}	39 ± 5	6 ± 2	–1024.9

ivatives. In this case, the final products of the reaction in solution are di- and tetraanions of perylenetetracarboxylic acid derivatives [25]. It was shown that the most probable process is concurrent formation of these derivatives from the corresponding initial compounds. For all of the studied derivatives of binaphthylhexacarboxylic acid, the relative yield of the product with four reduced carbonyl groups increases in the series of the reducing agents sodium dimethylaminomethanesulfinate < sodium diethylaminomethanesulfinate < sodium hydroxymethanesulfinate < sodium hydroxyethanesulfinate < sodium hydroxypropanesulfinate. It was shown [2] that the stabilities of the first three reducing agents are much the same, whereas introduction of alkyl substituent to α-carbon atom drastically decreases the stability of the reducing agent. The rise in the reducing power is due to an increase in the quasi-steady-state concentration of sulfoxylate anions, which, in turn, accelerates formation of products with four reduced groups.

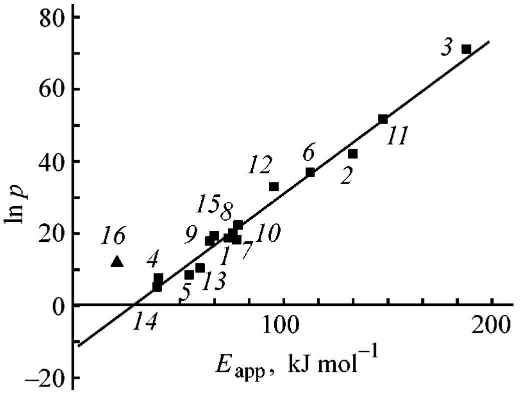

Fig. 2. Correlation between the Arrhenius parameters for reduction of various compounds with HMS and TUDO. (*p*) Pressure and (E_{app}) apparent activation energy. (*1*) Co^{2+} + HMS, (*2*) Ni^{2+} + HMS, (*3*) $CuEDTA^{2-}$ + HMS, (*4*) NAB + HMS, (*5*) 4NDPA + HMS, (*6*) $IC(CO)_2$ + HMS, (*7*) Direct Red 2C + HMS, (*8*) $CoEDTA^{2-}$ + HMS, (*9*) $NiEDTA^{2-}$ + HMS, (*10*) Co^{2+} + TUDO, (*11*) Ni^{2+} + TUDO, (*12*) $CuEDTA^{2-}$ + TUDO, (*13*) NAB + TUDO, (*14*) UO_2^{2+} + TUDO, (*15*) $IC(CO)_2$ + TUDO, and (*16*) $FeEDTA^-$ + HMS (by the associative pathway).

The correlations obtained on the basis of kinetic data for reduction of a wide variety of reducing agents may be useful for forecasting the rates of reduction of various compounds with rongalite and TUDO.

The kinetic parameters of reduction of transition metal ions and complex compounds with rongalite and TUDO are presented in Table 3. Comparison of the apparent rate constants and enthalpies of formation of oxidizing agents suggests that these parameters vary in parallel for both the reducing agents.

Figure 2 shows the compensation relation between the Arrhenius parameters, which is described by the equation

$$\ln p = 0.43E_{app} - 12.06 \quad (R = 0.987).$$

This dependence is observed for those reactions in which the dissociative mechanism of reduction is predominant. Therefore, the point with the coordinates E_{app} = 21 kJ mol^{-1} and ln *p* = 12, obtained for the reduction of $FeEDTA^-$ with rongalite proceeding at low temperatures by the associative pathway, falls out of this dependence. The observed compensation effect suggests the occurrence of the limiting stages of the reactions through transition states with similar configurations [26]. In the stages of decomposition of reducing agents, transition states are likely to form by protonation or deprotonation of hydrated molecules, as shown by quantum-chemical calculations for tautomeric conversion of TUDO as an example [2].

In conclusion, it should be noted that the data presented make it only possible to determine schemes of stoichiometric mechanisms of the processes. The existing experimental data are insufficient to come to reliable conclusions on the structure of transition states in particular stages.

REFERENCES

1. Budanov, V.V. and Makarov, S.V., *Khimiya serosoderzhashchikh vosstanovitelei* (Chemistry of Sulfur-Containing Reducing Agents), Moscow: Khimiya, 1994.
2. Makarov, S.V., Reactivity of Sulfur-Oxygen Reducing Agents with the C–S Bond, *Cand. Sci. Dissertation*, Ivanovo, 2000.
3. Sokolova, I.N., Budanov, V.V., Polenov, Yu.V., and Polyakova, I.R., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1983, vol. 26, no. 7, pp. 822–825.
4. Polenov, Yu.V. and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1988, vol. 31, no. 8, pp. 66–70.
5. Budanov, V.V., Boleslavskaya, N.F., Muratova, T.P., *et al.*, *Tr. Ivanov. Khim.-Tekhnol. Inst.*, 1975, no. 18, pp. 50–53.
6. Kolesnik, V.V., Makarov, S.V., Polenov, Yu.V., *et al.*, in *Khimiya Urana*, (Uranium Chemistry), Moscow: Nauka, 1989, pp. 296–299.
7. Makarov, S.V., Mundoma, C., Penn, J.H., *et al.*, *J. Phys. Chem., Ser. A*, 1998, vol. 102, no. 17, pp. 2915–2920.
8. Kublashvili, G.D., Polenov, Yu.V., Budanov, V.V., *et al.*, *Zh. Prikl. Khim.*, 1990, vol. 63, no. 7, pp. 1622–1625.
9. Egorova, E.V., Physicochemical Aspects of the Use of Reducing Agents, Derivatives of sulfoxylic Acid in Electroless Metal plating of Nitron Fiber, *Cand. Sci. Dissertation*, Ivanovo, 1991.
10. Polenov, Yu.V. and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1986, vol. 29, no. 5, pp. 53–56.
11. Polenov, Yu.V., Zalesova, T.S., Aleksandrova, A.N., and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*, 1981, vol. 24, no. 5, pp. 577–581.
12. Polenov, Yu.V. and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1988, vol. 31, no. 4, pp. 40–43.
13. Makarov, S.V., Polenov, Yu.V., and Budanov, V.V., *Zh. Neorg. Khim.*, 1984, vol. 29, no. 10, pp. 2456–2460.
14. Polenov, Yu.V., Makarov, S.V., and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1986, vol. 29, no. 12, pp. 30–33.
15. Budanov, V.V., Abstracts of Papers, *Mezhdunarodnyi seminar "Sernistye soedineniya i okruzhayushchaya sreda"* (Int. Seminar "Sulfur-Containing Compounds and Environment"), Ivanovo: Ivanov. Gos. Khim.-Tekhnol. Akad., 1996, pp. 10–14.
16. Polenov, Yu.V., Budanov, V.V., and Kublashvili, G.D., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1988, vol. 31, no. 3, pp. 58–61.
17. Budanov, V.V., Sokolova, I.N., and Mel'nikov, B.N., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1974, vol. 17, no. 8, pp. 1155–1160.
18. Budanov, V.V., Sokolova, I.N., and Mel'nikov, B.N., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1976, vol. 19, no. 2, pp. 240–244.
19. Polenov, Yu.V., Labutin, A.N., Tsareva, A.A., and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1987, vol. 30, no. 9, pp. 63–66.
20. Polenov, Yu.V., Labutin, A.N., Khalizov, R.L., *et al.*, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1999, vol. 42, no. 2, pp. 84–87.
21. Khalizov, R.L., Polenov, Yu.V., Labutin, A.N., and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1999, vol. 42, no. 2, pp. 79–83.
22. Polenov, Yu.V., Kublashvili, G.D., Labutin, A.N., and Budanov, V.V., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1997, vol. 40, no. 1, pp. 52–55.
23. Budanov, V.V., Sokolova, I.N., and Mel'nikov, B.N., *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1975, vol. 18, no. 3, pp. 489–491.
24. Aleksandrova A.N., Polenov, Yu.V., Zvegintseva, G.B., *et al.*, *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.*, 1983, vol. 26, no. 10, pp. 1188–1192.
25. Polenov, Yu.V., Kublashvili, G.D., Budanov, V.V., *et al.*, *Zh. Prikl. Khim.*, 1992, vol. 65, no. 11, pp. 2570–2574.
26. Basolo, F. and Pearson, R.G., *Mechanisms of Inorganic Reactions. A Study of Metal Complexes in Solution*, New York: Wiley, 1967.