REDUCTION KINETICS OF BROMATE WITH THIOCYANATE AND DYNAMICS OF THE CLOSED SYSTEM $BrO_3^-/SCN^-/HClO_4$

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The reduction kinetics of bromate ions with thiocyanate was studied polarographically and the dynamics of the BrO_3^-/SCN^- system was studied spectrophotometrically in the medium of perchloric acid in both cases. The reduction in the presence of an at least ten-fold excess of SCN^- ions is governed by the kinetic equation $-d[Br(V)]/dt = a[Br(V)][SCN^-][H^+]^2/(1 + b[SCN^-])$, where $a = 19{\cdot}2 \pm 0{\cdot}9\ mol^{-3}\ dm^9$, $b = 4{\cdot}4 \pm 0{\cdot}5\ mol^{-1}\ dm^3$ at 20°C. A mechanism was proposed, based on the transfer of oxygen atom from $HBrO_3$ to SCN^- ion. The dynamic system $BrO_3^-/SCN^-/HClO_4$ is non-monotonous in character. According to the conditions, the production of bromine has a sigmoidal course preceded by a lag phase or the bromine concentration passes through a maximum.

Chemical dynamics belongs to rapidly developing interdisciplinary research fields. Its significance consists mainly in that it is increasingly more often employed in elucidating the fascinating phenomena of life. An important role in this respect belongs to the investigation of chemical oscillators, the historical mile-stone being the discovery of the Belousov–Zhabotinskii (BZ) reaction[1]. Since then, more than thirty years elapsed and the discussion about the mechanism of the BZ reaction continues. Many modifications of this reaction have become known[2-5]; there is a tendency to replace the organic substrates by inorganic compounds[6]. There exists a number of purely inorganic oscillators based on halogens[7-10], capable of functioning in a continuously stirred tank reactor (CSTR), however not all of them can be regarded as oscillators of the BZ type.

Thiocyanate ions could be a suitable inorganic substrate for the BZ reaction. Oscillations and dynamics of the system BrO_3^-/SCN^- in CSTR was studied by Simoyi[8], oscillations in a batch reactor were not hitherto described. The present work deals with the kinetics and mechanism of the reduction of bromates with thiocyanate ions and with the dynamics of the closed system BrO_3^-/SCN^- in the medium of $HClO_4$. The redox reaction between BrO_3^- and SCN^- proceeds according to the equation[8]

$$BrO_3^- + SCN^- + H_2O \rightarrow Br^- + SO_4^{2-} + CN^- + 2\,H^+ . \qquad (A)$$

At a sufficient excess of SCN^- ions the reaction between BrO_3^- and Br^- ions may be suppressed and only reaction (*A*) proceeds to a notable extent. In the presence of excess bromate the bromide ions react with bromate to form bromine[11],

$$BrO_3^- + 5\,Br^- + 6\,H^+ \rightarrow 3\,Br_2 + 3\,H_2O \qquad (B)$$

which can react with SCN^- ions; this together with other processes causes a non-linear dynamic behaviour of the system.

EXPERIMENTAL

All chemicals were of reagent grade. Bromocyan, BrCN, was prepared by the reaction of Br_2 with NaCN (ref.[12]) and after distillation it was stored at −20°C. Water was redistilled with the addition of $KMnO_4$.

The reduction kinetics of bromate ions with thiocyanate in the medium of $HClO_4$ was followed polarographically: the limiting diffusion current of bromate ions at −1·3 V against saturated mercurous sulphate electrode (MSE) was recorded as a function of the time. Measurements were done on an OH-105 type polarograph (Radelkis, Hungary) in a Kalousek cell with a thermostated mantle piece and with a dropping mercury electrode. The temperature was kept constant by an ultrathermostat UT-12 (Horyzont, Poland) to within ±0·1°C. The reaction solution was deaerated by bubbling nitrogen. The values of rate constants are averages from 2—4 measurements.

The same reaction system was also studied spectrophotometrically: the time dependence of the absorbancy at 400 nm, corresponding to the absorption maximum of bromine ($\varepsilon = 166\ mol^{-1}\,.\,dm^3\,cm^{-1}$) was recorded on a Specord UV VIS apparatus (Carl Zeiss, Jena). The cuvettes were 2 and 5 cm thick and were tempered at 20 ± 0·1°C by water from a U 15 thermostat.

RESULTS

The Reduction Kinetics of BrO_3^- *with* SCN^- *Ions*

The initial concentration of BrO_3^- ions was $5\,.\,10^{-4}\ mol\,dm^{-3}$, SCN^- ions were at least in a ten-fold excess and $HClO_4$ in at least a hundred-fold excess. The polarographic current was due to reduction of BrO_3^- ions; the dependence of $\ln(I_0/I)$ was linear in a wide interval of initial SCN^- concentrations. Hence, the reaction was of the pseudo-first order with the kinetic equation

$$-\frac{d[Br(V)]}{dt} = k_{obs}[Br(V)]\,, \qquad (1)$$

where $[Br(V)]$ denotes concentration of bromate ions and k_{obs} is the measured rate constant, whose dependence on the concentration of SCN^- ions was determined in the medium of 0·05 and 0·1 $mol\,dm^{-3}$ $HClO_4$ at 10 and 20°C. This dependence is linear with a positive slope in the coordinates $1/k_{obs}$ against $1/[SCN^-]$.

The influence of the concentration of hydrogen ions on the reaction rate was studied at three different temperatures at ionic strength $I = 2 \text{ mol dm}^{-3}$ ($NaClO_4$); the value of k_{obs} is directly proportional to the square of the concentration of H^+ ions.

The results suggest the following form of the rate equation valid up to 0·3 mol . . dm^{-3} SCN^- and 0·5 mol dm^{-3} $HClO_4$:

$$-\frac{d[Br(V)]}{dt} = \frac{a[Br(V)]\,[SCN]^-]\,[H^+]^2}{1 + b[SCN^-]} . \tag{2}$$

The measured rate constant is given as

$$\frac{1}{k_{obs}} = \frac{1}{a}\frac{1}{[SCN^-]\,[H^+]^2} + \frac{b}{a}\frac{1}{[H^+]^2} , \tag{3}$$

where $a = 19{\cdot}2 \text{ mol}^{-3} \text{ dm}^9 \text{ s}^{-1}$, $b = 4{\cdot}4 \text{ mol}^{-1} \text{ dm}^3$ at 20°C and $a = 13{\cdot}7 \text{ mol}^{-3}$ . . $\text{dm}^9 \text{ s}^{-1}$, $b = 5{\cdot}0 \text{ mol}^{-1} \text{ dm}^3$ at 10°C. The value of a was calculated from the slope of the dependence of k_{obs} on $[H^+]^2$ or of $1/k_{obs}$ on $1/[SCN^-]$ and the value of b from the intersection of the latter dependence with the y axis.

In the medium of sulphuric acid the reaction of BrO_3^- with SCN^- proceeds by the factor of about 1·4 more rapidly.

Dynamic System $BrO_3^-/SCN^-/HClO_4$

With a decreasing ratio of $[SCN^-]/[BrO_3^-]$ the reaction of Br^- with BrO_3^- comes into play, where the bromine formed participates in other reactions, causing a complicated, non-monotonous behaviour of the whole system.

At a ten-fold excess of SCN^- ions the relatively simple reduction of bromate with thiocyanate ions still takes place (reaction *A*). At an equimolar ratio of the two species no bromine is present after the reaction is finished, but BrCN can be found. In systems with an excess of bromate, bromine is formed at a proportion of 1 mol Br_2 to 5 mol SCN^-, which is at variance with the experimental results of Simoyi[8] showing the stoichiometry of 3 : 5.

Influence of H^+ *Ions on the Production of Bromine*

The influence of H^+ ions was studied spectrophotometrically at a ten-fold excess of bromate ions (0·05 mol dm^{-3} BrO_3^- and 0·005 mol dm^{-3} SCN^-), constant temperature and ionic strength $I = 2 \text{ mol dm}^{-3}$ (maintained by addition of $NaClO_4$).

In 0·1 mol dm^{-3} $HClO_4$ the production of bromine is autocatalytic in character

(Fig. 1). However, the curve does not have a simple sigmoidal course. At the beginning there is a period (about 90 s) during which any significant amount of bromine is absent. Then the concentration of bromine increase abruptly up to a quasistationary state ($6 \,.\, 10^{-5}$ mol dm^{-3}). Afterwards the Br_2 level increases steadily and the curve takes a form characteristic for autocatalysis.

The character of the formation of bromine can be changed by increasing the concentration of H^+ ions (Fig. 2). At concentrations of $HClO_4$ lower than 0·4 mol dm^{-3} the sigmoidal course is preserved, however the initial induction period becomes shorter and the quasistationary level of Br_2 higher. At higher concentrations of H^+ ions the induction period gradually disappears and a maximum is formed corresponding to a transitorily superstoichiometric amount of Br_2, which increases if the concentration of H^+ ions rises further.

Influence of BrO_3^- *Ions on the Production of Bromine*

If the ten-fold excess of BrO_3^- ions is increased to a hundred-fold excess (in the presence of 0·005 mol dm^{-3} SCN^-), the effect on the formation of bromine is similar to that of H^+ ions. The time dependence of the absorbancy is shown in Fig. 3. The initial induction period could not be followed at the given experimental conditions. An increase of the bromate concentration has a less marked influence on the process than an equivalent increase of the concentration of H^+ ions.

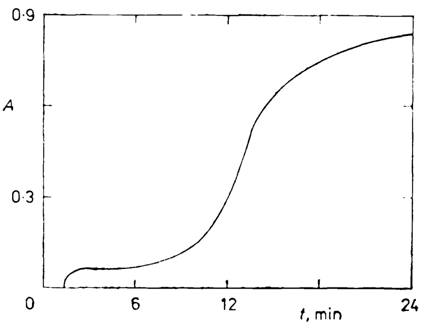

Fig. 1

Autocatalytic production of bromine in dynamic system. Initial concentrations: 0·05M-BrO_3^-, 0·005M-SCN^-, 0·1M-$HClO_4$; $I = 2$ mol dm^{-3}, 20°C

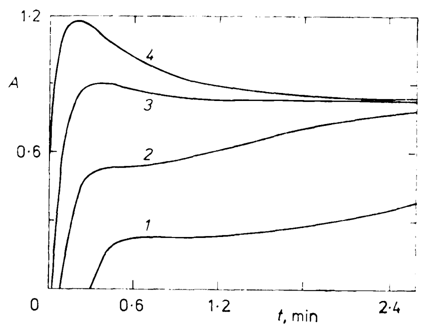

Fig. 2

Influence of H^+ ions on bromine production in dynamic system. Initial concentrations: 0·05M-BrO_3^-, 0·005M-SCN^-; *1* 0·2M-$HClO_4$; *2* 0·3M-$HClO_4$; *3* 0·4M-$HClO_4$; *4* 0·5M-$HClO_4$; $I = 2$ mol dm^{-3}, 20°C

Influence of SCN^- *Ions on the production of Bromine*

Increasing concentration of SCN^- ions in the presence of 0·05 mol dm^{-3} BrO_3^- and 0·1 mol dm^{-3} $HClO_4$ causes an increase of the quantity of bromine formed in agreement with the 1 : 5 stoichiometry. At the same time, the initial induction period becomes somewhat longer and the inflexion point of the sigmoidal curve is shifted towards a longer time interval (Fig. 4).

Influence of CN^- *Ions on the Autocatalytic* Br_2 *Production*

Cyanide ions retard the autocatalytic exponential rise of the bromine concentration (they cause a shift of the inflexion point of the sigmoidal curve). The influence of CN^- ions on the system in the quasistationary state of bromine concentration is shown in Fig. 5. Owing to the reaction of CN^- ions with bromine, the quantity of evolved Br_2 decreases. If cyanide is added into the system in the exponential phase, the autocatalytic formation of Br_2 can temporarily be stopped, or at higher CN^- concentrations even returned back to the quasitationary state (Fig. 6). Experiments with addition of CN^- ions before the start of the reaction showed that cyanide ions do not influence the length of the initial lag phase.

DISCUSSION

Mechanism of Bromate Reduction with Thiocyanate Ions

The transer of an electron from an SCN^- to a BrO_3^- ion can, in principle, take place

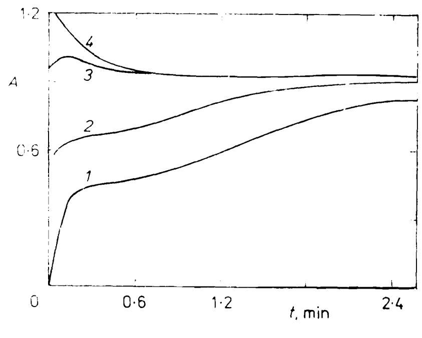

FIG. 3

Influence of BrO_3^- ions on bromine production. Initial concentrations: 0·005M-SCN^-, 0·2M-$HClO_4$; *1* 0·1M-BrO_3^-; *2* 0·15M-BrO_3^-; *3* 0·3 M-BrO_3^-; *4* 0·5M-BrO_3^-; $I = 2$ mol . . dm^{-3}, 20°C

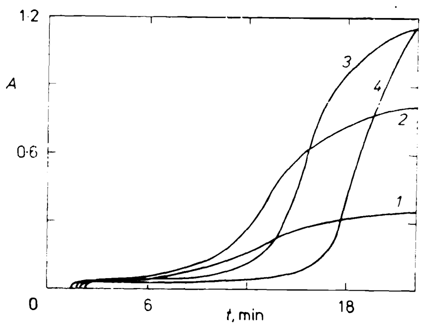

FIG. 4

Influence of SCN^- ions on bromine production. Initial concentrations: 0·05M-BrO_3^-, 0·1M-$HClO_4$; *1* 0·006M-SCN^-; *2* 0·012M-SCN^-; *3* 0·018M-SCN^-; *4* 0·025M-SCN^-; $I = 2$ mol dm^{-3}, 20°C in three ways: directly, or through an oxygen atom, or via a complex. The formation of a BrO_2SCN complex is assumed by Treindl and Kostrová[13] in the reaction of bromate with thicyanate ions in the medium of HCl, and they consider the homolytic decomposition of this complex as the slowest reaction step. According to Simoyi[14], direct electron transfer from SCN^- ion to molecular iodine can be excluded on the basis of energetic considerations (the redox potential of the $SCN^{\bullet}/SCN^-$ couple is equal to 1·62 V).

The inner-sphere electron transfer with simultaneous displacement of the O atom to the SCN^- ion seems to be the most probable initial elementary step of the reduction of bromate with SCN^-ions. This is supported by the observations that Taube proved by isotopic tracers the transfer of an O atom from BrO_3^- to SO_3^{2-} ion[15] and that most oxidations of SCN^- ions proceed via HOSCN (ref.[14]). The thoroughly studied reaction between BrO_3^- and Br^- ions[16] and the reaction between BrO_3^- and I^- ions[17] also proceed analogously.

Based on the preceding considerations and results of kinetic studies, we propose the following probable mechanism:

$$H^+ + BrO_3^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HBrO_3 \qquad (4)$$

$$BrO_2OH + SCN^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} BrO_2(OH)SCN^- \qquad (5)$$

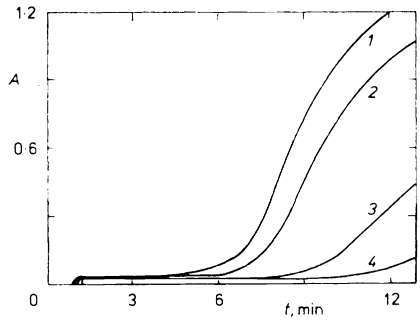

Fig. 5

Influence of CN^- ions on autocatalytic bromine production (in stationary phase). Initial concentrations: 0·075M-BrO_3^-, 0·0075M-SCN^-; 1 without addition; 2 $5 \cdot 10^{-4}$M-CN^-; 3 $2{\cdot}5 \cdot 10^{-3}$M-CN^-; 4 $3{\cdot}5 \cdot 10^{-3}$M-CN^-; 20°C

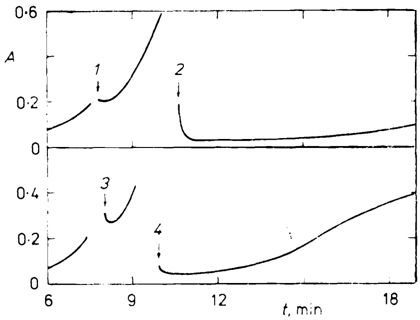

Fig. 6

Influence of CN^- ions on autocatalytic bromine production (in exponential phase). Initial concentrations: 0·075M-BrO_3^-, 0·0075M-SCN^-, 0·1M-$HClO_4$. The instant denoted by an arrow corresponds to the addition of: 1 $5 \cdot 10^{-4}$M-CN^-; 2 $3{\cdot}5 \cdot 10^{-3}$M-CN^-; 3 10^{-3}M-CN^-; 4 $2{\cdot}5 \cdot 10^{-3}$M-CN^-; 20°C

$$BrO_2(OH)SCN^- + H^+ \xrightarrow{k_3} HBrO_2 + HOSCN \qquad (6)$$

The equilibria (*4*) and (*5*) are rapid, reaction (*6*) is rate-determining. Further steps of the conversion of $HBrO_2$ and HOSCN to Br^-, SO_4^{2-} and CN^- ions are again rapid and do not influence the kinetics of the whole process. The kinetic equation based on the envisaged mechanism has the form

$$-\frac{d[Br(V)]}{dt} = \frac{K_1K_2k_3[Br(V)][SCN^-][H^+]^2}{(1 + K_1[H^+])(1 + K_2[SCN^-])} . \qquad (7)$$

In slightly acidic medium we have $K_1[H^+] \ll 1$, hence

$$-\frac{d[Br(V)]}{dt} = \frac{K_1K_2k_3[Br(V)][SCN^-][H^+]^2}{1 + K_2[SCN^-]} \qquad (8)$$

in agreement with the experimental kinetic equation (*2*), where $a = K_1K_2k_3$ and $b = K_2$.

It follows from the experiments that the parameter a is markedly influenced by the temperature, whereas the parameter b changes only little with the temperature. From their temperature dependence and the value of the dissociation constant of $HBrO_3$, $K_1 = 0{\cdot}5$ (ref.[18]) the rate constant k_3 for reaction (*6*) can be calculated as $k_3 = 5{\cdot}6 \pm 0{\cdot}5$ and 10 ± 1 $mol^{-1}\,dm^3\,s^{-1}$ at 10 and 20°C, respectively.

From the temperature dependence of k_3 we obtain according to the theory of absolute reaction rates the following activation parameters for reaction (*6*): $\Delta H^{\neq} = 37 \pm 2\,kJ\,mol^{-1}$ and $\Delta S^{\neq} = -90 \pm 10\,J\,K^{-1}\,mol^{-1}$. These are in accord with the proposed mechanism. Also the observed influence of ionic strength on the experimental rate constant can qualitatively be elucidated by interaction of oppositely charged ions.

The detailed mechanism of the reduction of BrO_3^- with SCN^- ions is complicated. Reaction (*6*) is probably followed by further steps of the transfer of O atom between oxo acids of bromine in lower oxidation states and sulfur compounds. The mechanism of the transfer of an S atom from the oxidation state +2 (HOSCN) to +6 (SO_4^{2-}) remains unclear. The products of the whole process, Br^- and CN^- ions, can participate in side reactions. As already mentioned, the concurrence between BrO_3^- and Br^- can be excluded, however reactions of Br^- ions with $HBrO_2$ and HOBr should be considered as well as the reaction of CN^- ions with HOBr leading to BrCN Naturally, many other processes may also take place (reactions of intermediate sulfur-containing products, radical reactions, etc.).

Dynamic System $BrO_3^-/SCN^-/HClO_4$

In the presence of an excess of BrO_3^- ions against SCN^-, reaction (*B*) can play a role in addition to reaction (*A*). Thiocyanate ions react rapidly with bromine solution causing decoloration, so that the bromine formed in reaction (*B*) is consumed in this process, which according to Simoyi[8] can be written as

$$3\,Br_2 + SCN^- + 4\,H_2O \rightarrow 6\,Br^- + CN^- + SO_4^{2-} + 8\,H^+ . \qquad (C)$$

According to our results, CN^- ions react very rapidly with Br_2 forming BrCN:

$$Br_2 + CN^- \rightarrow BrCN + Br^- . \qquad (D)$$

From the experiments (Fig. 6) it is possible to estimate the rate constant of the reaction of bromine with CN^- ions as $6 \,.\, 10^9\ mol^{-1}\ dm^3\ s^{-1}$ at 20°C (ref.[19]).

The four mentioned main processes (*A*)–(*D*) form probably the essence of the dynamic system under study. The reaction of BrCN with SCN^- ions plays no marked role under the experimental conditions, as follows from special experiments in which BrCN was added into the reaction solution. The process corresponding to Fig. 1 can be divided into four phases:

1) (0–90 s) – initial induction period (lag phase). Reactions (*A*) and (*B*) dominate; the bromine formed is kept at a very low quasistationary concentration by the rapid reaction (*C*) with SCN^- ions. This phase is distinguished by accumulation of Br^- ions and increasing concentration of CN^- ions.

2) (90 s – 2 min) – sudden start of the production of Br_2 (clock reaction). When the Br^- ions attain a certain critical concentration ($5 \,.\, 10^{-4}\ mol\ dm^{-3}$), rapid autocatalytic production of Br_2 (and Br^- ions) starts by combining reactions (*B*) and (*C*) in the ratio of 6 : 5; the corresponding stoichiometric equation is

$$6\,BrO_3^- + 5\,SCN^- + 2\,H_2O \rightarrow 3\,Br_2 + 5\,CN^- + 5\,SO_4^{2-} + 4\,H^+ . \qquad (E)$$

With increasing concentrations of Br_2 and CN^-, reaction (*D*) becomes significant, which is manifested by a deviation of the Br_2 production from a straight line.

3) (2–6 min) – stationary state. The rates of reactions (*E*) and (*D*) become equal and the Br_2 concentration attains a stationary value of $6 \,.\, 10^{-5}\ mol\ dm^{-3}$. The stoichiometric equation is

$$3\,BrO_3^- + 2\,SCN^- + CN^- + 2\,H^+ \rightarrow 3\,BrCN + 2\,SO_4^{2-} + H_2O . \qquad (F)$$

The concentration of CN^- decreases and the system passes fluently into the subsequent phase. The stationary phase is the longer the more cyanide ions were formed in the two preceding stages (Figs 5 and 4).

4) (more than 6 min) – autocatalytic Br_2 production. After consumption of a substantial part of CN^- ions the concentration of Br_2 rises slowly and the autocatalytic reaction (*E*) becomes dominant. However, CN^- ions formed by reaction (*E*) react immediately with bromine, resulting in retardation of the autocatalytic production of Br_2 compared to phase *2*), reaction (*E*). The resulting stoichiometric equation

$$7\,BrO_3^- + 5\,SCN^- + 2\,H^+ \rightarrow Br_2 + 5\,BrCN + 5\,SO_4^{2-} + H_2O \quad (G)$$

is in agreement with the measured ratio of the bromine formed to the thiocyanate consumed in the presence of an excess of bromate ions. The sigmoidal course of the curve is due to the decrease of thiocyanate ions as the starting substance.

The dynamic system preserves qualitatively the character described above until the initial concentrations of bromate and hydrogen ions surpass the value of the product $[BrO_3^-]_0\,[H^+]_0^2 = 5\,.\,10^{-3}$ mol^3 dm^{-9} (at $[SCN^-]_0 = 5\,.\,10^{-3}$ mol dm^{-3}, 20°C, and ionic strength 2 mol dm^{-3}). If the two initial concentrations increase above the limit indicated, reaction (*E*) (second phase) is so accelerated that most SCN^- ions are consumed already during this phase and the transitorily formed quantity of bromine approaches the stoichiometric ratio of 3 : 5 with respect to SCN^- ions. The rate of reaction (*E*) is controlled by the reaction of BrO_3^- with Br^- ions, whose rate is directly proportional to the concentration of bromate and to the square of the H^+ ions concentration[17]. After attaining the maximum (curve *4*, Fig. 2), the concentration of Br_2 decreases by reaction (*D*) to the value given by the stoichiometry of reaction (*G*).

The proposed reaction mechanism enables a rough description of the behaviour of the dynamic system $BrO_3^-/SCN^-/HClO_4$, although many details are unknown. Interactions of some intermediate products (such as $HBrO_2$, HOBr, HOSCN) and their reactions with Br^- and CN^- ions may play an important role.

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