Analytic study of the chain dark decomposition reaction of iodides – atomic iodine donors – in the active medium of a pulsed chemical oxygen – iodine laser: 1. Criteria for the development of the branching chain dark decomposition reaction of iodides

T.L. Andreeva, S.V. Kuznetsova, A.I. Maslov, V.N. Sorokin

Abstract. **The scheme of chemical processes proceeding in the active medium of a pulsed chemical oxygen – iodine laser (COIL) is analysed. Based on the analysis performed, the complete system of differential equations corresponding to this scheme is replaced by a simplified system of equations describing in dimensionless variables the chain dark decomposition of iodides – atomic iodine donors, in the COIL active medium. The procedure solving this system is described, the basic parameters determining the development of the chain reaction are found and its specific time intervals are determined. The initial stage of the reaction is analysed and criteria for the development of the branching chain decomposition reaction of iodide in the COIL active medium are determined.**

1. Introduction

In a chemical oxygen – iodine laser (COIL) operating at the $I^*(5\,^2P_{1/2}) \rightarrow I(5\,^2P_{3/2})$ transition of the iodine atom, iodine atoms are excited due to the quasi-resonance energy transfer from singlet oxygen molecules $O_2^*\,(^1\Delta_g)$ produced in a chemical singlet oxygen generator. A conventional source of iodine atoms in such a laser are I_2 molecules, which efficiently (according to the unknown mechanism) dissociate in the singlet oxygen medium. However, it is not always convenient to use molecular iodine, which has a low vapour pressure at room temperature and a high efficiency of 'adhesion' to solid surfaces. Therefore, since the creation of COILs, search for new atomic iodine donors has been under way.

Photolysis of organic and fluorine-organic iodides RI (CH_3I, CF_3I) and their homologues was used for the first time in a pulsed COIL in paper [1]. During photolysis RI molecules dissociate into the radical R and the iodine atom

T.L. Andreeva, S.V. Kuznetsova, A.I. Maslov, V.N. Sorokin
P.N. Lebedev Physics Institute, Russian Academy of Sciences, Leninsky prosp. 53, 119991 Moscow, Russia;
e-mail: amaslov@sci.lebedev.ru

I^*. Because of large absorption cross sections for UV radiation and high vapour pressures at room temperature, RI molecules turned out to be very convenient donors of iodine atoms in pulsed COILs. However, subsequent investigations showed [2] that during the transport of the laser mixture containing O_2^*, O_2, RI and Cl_2 molecules (Cl_2 is an impurity coming from the singlet oxygen generator), dark decomposition of organic iodides (CH_3I, etc.) occurs. This decomposition leads to the spontaneous emission of iodine atoms in the dark zone [3]. In the case of fluorine-organic iodides (CF_3I, etc.) dark decomposition of RI was not observed. We proposed in [4] a chain mechanism of the dark decomposition of RI (CH_3I, CF_3I) in the medium containing O_2^*, O_2 and Cl_2 and explained the experimentally observed peculiarities of these systems.

The numerical method used in [4] to solve the system of differential equations (SDE) describing the chain decomposition of RI makes it possible to calculate chemical reactions in the active medium of pulsed COILs at different initial concentrations of the laser-mixture components. However, it does not allow one to select concentrations to control purposefully the decomposition rate of RI, in particular, to suppress undesirable dark decomposition of RI or, vice versa, to use it as a chemical source of iodine atoms in a pulsed COIL.

The aim of this paper is to obtain analytic expressions for main characteristics of the chain decomposition reaction of iodides RI in the pulsed COIL active medium, which make it possible to control the behaviour of the chain decomposition of RI by directly selecting the initial concentrations of the components of the active medium.

This paper is the first part of investigations on the chain decomposition reaction of RI in the pulsed COIL active medium, which is based on the analytic solution of the corresponding SDE. We obtained expressions to calculate the basic characteristics of this reaction and analysed the initial stage of the chain reaction and determined the criteria for the development of the branching chain decomposition reaction of RI in the active medium of the pulsed COIL.

This paper consists of seven sections and six Appendices and is organised as follows. In section 2, we discuss the complete system of differential equations (SDE1) describing the chain decomposition of RI; a simplified system of differential equations (SDE3) corresponding to SDE1 has been derived using substantial approximations. In section 3, based on the characteristic features of SDE3 equations, we

select four characteristic time intervals of the chain decomposition reaction of RI and describe the procedure of the approximate analytic solution of SDE3. In section 4, we analyse the first stage of the chain decomposition and obtain the first critical condition for the development of the branching chain reaction. In section 5, the second stage of the chain decomposition is analysed and the second critical condition for the development of the branching chain reaction is determined. In section 6, we discuss the obtained results and compare them with the results of the numerical solution of SDE1. In Conclusions, we list the main results of this work. Appendices present the system of differential equations SDE1 and the dimensionless variables and constants used in the paper as well as dependences between the variables determined by SDE3.

2. System of differential equations

Let us analyse the scheme of basic processes [4, 5] describing the chain decomposition of RI:

$$I_2 + 2O_2^* \rightarrow 2I + 2O_2, \qquad (1)$$

$$I^* + O_2 \rightleftarrows I + O_2^*, \qquad (2)$$

$$I^* + Cl_2 \rightarrow ICl + Cl, \qquad (3)$$

$$Cl + RI \rightarrow ICl + R, \qquad (4)$$

$$R + Cl_2 \rightarrow RCl + Cl, \qquad (5)$$

$$R + O_2 \rightarrow RO_2, \qquad (6)$$

$$I^* + ICl \rightarrow I_2 + Cl, \qquad (7)$$

$$O_2^* + RO_2 \rightarrow O_2 + RO_2. \qquad (8)$$

The rate constants of reactions (1)–(7) are presented in Table 1 and the rate constant of reaction (8) is discussed below.

Consider first the nonbranching chain decomposition reaction of RI [reactions (1)–(6)]. To decompose RI according to this scheme, Cl atoms are required, which

Table 1. Rate constants of reactions (1)–(7) for $T = 300$ K.

Constant/ cm^3 s^{-1}	Radical	
	CF$_3$	CH$_3$
$K_1^{*)}$	6×10^{-29} [6]	6×10^{-29} [6]
K_2	2.7×10^{-11} [7]	2.7×10^{-11} [7]
K_{-2}	7.8×10^{-11} [7]	7.8×10^{-11} [7]
K_3	2×10^{-14} [8]	2×10^{-14} [8]
K_4	10^{-12} [9]	10^{-12} [9] (determined in [9] for CF$_3$I; due to the proximity of binding energies R–I for CF$_3$I and CH$_3$I, the values K_4 are assumed equal)
K_5	1.1×10^{-13} [10]	1.6×10^{-12} (estimated by analysing data [11], [12])
K_6	2.5×10^{-12} (estimated for conditions of this paper by using data [13])	2.5×10^{-13} (estimated for conditions of this paper by using data [14])
K_7	3.0×10^{-11} [8]	3.0×10^{-11} [8]

$^{*)}$ measured in cm^6 s^{-1}; K_{-2} corresponds to inverse reaction (2).

are produced in reaction (3). In turn, the latter is possible only in the presence of I* atoms. The source of iodine atoms, as was shown in [4], is the molecular iodine, which is present in the initial medium as a small impurity ($[I_2]_0$) of the initial iodide RI.

Cl atoms produced in reaction (3) initiate chain reactions (4), (5) of RI decomposition. In the absence of the loss of radicals R in reaction (6), the final degree of RI decomposition is equal to unity. The decrease in the concentration of Cl atoms at each link of chain (4)–(6) is determined by the relation

$$\alpha = K_5[Cl_2]/(K_6[O_2] + K_5[Cl_2]). \qquad (9)$$

Let N be the average number of links in chain (4)–(6) per Cl atom produced in reaction (3). It is obvious that N is equal to the sum of terms of an infinitely decreasing geometric progression with the denominator equal to α and the first term equal to unity. Simple calculations yield

$$N = 1/(1 - \alpha) = 1 + K_5[Cl_2]/K_6[O_2]. \qquad (10)$$

The parameter N is equal to the maximum number of RI molecules, which can be decomposed by one Cl atom produced in reaction (3).

In the absence of continuous supply of molecular iodine into the volume, the rate of the chain initiation [reactions (1)–(3)] tends to zero with time because the sum of concentrations of iodine atoms ($[I^*] + [I]$) decreases. Therefore, the decomposition degree of RI molecules (η_{RI}) will be small and determined by the inequality

$$\eta_{RI} = ([RI]_0 - [RI])/[RI]_0$$

$$= \Delta[RI]/[RI]_0 < 2[I_2]_0 N/[RI]_0. \qquad (11)$$

Let us supplement scheme (1)–(6) with reaction (7). This process initiates chain reaction (4)–(6) because both I$_2$ molecules and Cl atoms are produced in (7). In this case, one active centre entering into the reaction (I* atom) produces, taking into account (1) and (2), three active centres – two iodine atoms and a Cl atom. Thus, simple chain reaction (1)–(6) in the presence of reaction (7) is transformed into the branching chain reaction. Because ICl molecules (the source of branching) are accumulated during a simple chain reaction, the whole set of reactions (1)–(7) is the degenerate branching chain reaction [15]. A specific feature of these reactions is the presence of an induction period within which the critical concentration of the intermediate products (in the case under study, ICl molecules) is rather slowly accumulated, after which the rate of the chain reaction increases exponentially.

In scheme (1)–(7) singlet oxygen O$_2^*$ is required to decompose RI. Therefore, the rate of the chain reaction is very sensitive to the relative content of O$_2^*$ molecules in the mixture of O$_2^*$ and O$_2$. If there is no additional loss of O$_2^*$, $\eta_{RI} = 1$ under the condition

$$4[RI]_0/[O_2^*]_0 < 1. \qquad (12)$$

It was shown in papers [4, 16, 17] that the main loss of O$_2^*$ in the system under study occurs in reaction (8). Its action blocks processes (1), (2) [initiation of chain reaction (1)–(7)] and limits the η_{RI} quantity.

To describe quantitatively the process of RI decomposition, we will write the system of differential equations SDE1 corresponding to the scheme of reactions (1) – (8) (see Appendix 1). First, we will introduce some simplifications. The characteristic time $N/K_4[\text{RI}]$ of RI decomposition in the active medium of a pulsed COIL in scheme (4) – (6) is usually much greater than the characteristic time of I_2 dissociation, which is equal to $1/K_1[\text{O}_2^*]^2$, the lifetime of R radicals $(1/K_6[\text{O}_2] + K_5[\text{Cl}_2])$ and the characteristic time of the resonance exchange between iodine atoms and oxygen molecules $(1/K_{-2}[\text{O}_2^*])$. This makes it possible to take advantage of the conditions for quasi-stationarity (see [18]) of concentrations $[\text{I}_2]$, $[\text{R}]$ and ratio $[\text{I}^*]/([\text{I}]+[\text{I}^*])^{-1}$ and assume that $\text{d}[\text{I}_2]/\text{d}t = 0$, $\text{d}[\text{R}]/\text{d}t = 0$ and the fraction of excited iodine atoms in the mixture of I^* and I is determined by the parameter δ (see Appendix 1). By using the quasi-stationarity condition for $[\text{I}_2]$ and $[\text{R}]$ and for the ratio $[\text{I}^*]/([\text{I}] + [\text{I}^*])$ and introducing dimensionless variables we will transform the system of differential equations SDE1 to the form (SDE2):

$$\frac{\text{d}x}{\text{d}\tau} = \varepsilon y(u - 1)x, \tag{13}$$

$$\frac{\text{d}v}{\text{d}x} = \frac{u + 1}{u - 1} - \frac{A}{u - 1}\frac{v}{x}, \tag{14}$$

$$\frac{\text{d}u}{\text{d}\tau} = \frac{1}{a}\varepsilon yx(D + 1 - u), \tag{15}$$

$$\frac{\text{d}(y + b\varepsilon yx)}{\text{d}\tau} = -b\varepsilon(3u + 1)yx - By\frac{x - 1 + au}{a}. \tag{16}$$

All quantities entering SDE2, variables x, y, u, v, τ and parameters a, b, A, B, D, ε are defined in Appendix 1. The dimensionless concentration of excited iodine atoms is given by the expression

$$[\text{I}^*]/(2[\text{I}_2]_0) = xy\varepsilon. \tag{17}$$

By using (17) and assuming that $\varepsilon \approx \text{const}$ (see Appendix 1), we will write out also the expression for the derivative $\text{d}([\text{I}^*]/(2[\text{I}_2]_0))/\text{d}\tau$ necessary for the following analysis in the form

$$\varepsilon\frac{\text{d}(xy)}{\text{d}\tau} = \varepsilon x\frac{\text{d}y}{\text{d}\tau} + \varepsilon y\frac{\text{d}x}{\text{d}\tau}. \tag{18}$$

Note than SDE2 does not contain the differential equations to find $[\text{RI}](t)$, $[\text{RO}_2](t)$ and $[\text{RCl}](t)$. Due to low concentrations of $[\text{R}]$ and $[\text{I}_2]$, the concentrations $\Delta[\text{RI}]$ of decomposed molecules RI and $[\text{RO}_2]$ and $[\text{RCl}]$ were determined by the algebraic equations:

$$\Delta[\text{RI}] = [\text{I}] + [\text{I}^*] - 2[\text{I}_2]_0 + [\text{ICl}] = [\text{RO}_2] + [\text{RCl}],$$

$$[\text{RO}_2] = \Delta[\text{RI}]/N, \quad [\text{RCl}] = \Delta[\text{RI}] - [\text{RO}_2] \tag{19}$$

[see (9), (10)]. Relations (19) were used to derive expression (16), in which the factor $x - 1 + au$ is the change in the RI concentration $(\Delta[\text{RI}])$ expressed in dimensionless units.

Let us discuss briefly system (13) – (16). Equation (13) describes in dimensionless variables the time dependence of

the sum of concentrations of iodine atoms $x(\tau)$. Equation (14) gives the relation between the concentration of Cl atoms and the sums of concentrations of iodine atoms. Equation (15) describes the time dependence of $[\text{ICl}]$ $[u(\tau)]$. Equation (16) describes the time dependence of the sum of concentrations $([\text{O}_2^*] + [\text{I}^*])$, i.e. the relaxation of energy stored in the system. The first term in the right-hand side of (16) determines the losses of singlet oxygen spent to dissociate I_2 and then to excite iodine atoms I, while the second term describes the quenching of O_2^* by RO_2 radicals. The second term of the sum in the left-hand side of (16) under the derivative sign can be neglected because it is equal to the ratio $[\text{I}^*]/[\text{O}_2^*]_0$, which is much smaller than unity in the dark zone of the pulsed COIL.

Thus, expression (16) takes the form

$$\frac{\text{d}y}{\text{d}\tau} = -b\varepsilon(3u + 1)yx - By\frac{x - 1 + au}{a}. \tag{20}$$

We will consider below SDE3 containing equations (13) – (15), (20).

3. Procedure for solving SDE3

SDE3 is a complicated nonlinear system, which cannot be solved analytically. However, the equations entering it have specific features, which make it possible to select four time intervals in the development of the chain reaction of RI decomposition. These intervals differ in the range of variations in u (concentrations of ICl molecules – the main particle determining the branching). This allows one to derive approximate analytic expressions for concentrations of components of the pulsed COIL active medium at each interval of the chain decomposition of RI as well as for the time parameters characterising these intervals.

The procedure for the approximate solution of SDE3 consisted in the following:

(i) Instead of the time dependences of variables, the dependences $x(u)$, $y(x)$, and $(v/x)(u)$ in four ranges of variations in u were determined. Note that the parameters entering SDE3 are not strictly constant. Therefore, for each range of the u variations we determined the range of variations in each parameter and, if necessary, found the expression for calculating its average value.

(ii) The time characteristics of the branching chain reaction of RI decomposition were determined for each range of u by solving Eqn (13) with the help of obtained dependences $x(u)$ and $y(x)$.

Figures 1 and 2 present typical dependences, which are obtained by solving numerically SDE1 and describe the time dependences of the sum of concentrations of iodine atoms and excited iodine atoms, these time dependences illustrating the above-analysed behaviour of the chain reaction of RI decomposition. The point of the minimum of the dependence $([\text{I}^*] + [\text{I}])(t)$ (values $x_{\min}$ and $\tau_{\min}$) and points of the minimum and maximum of the dependence $[\text{I}^*](t)$ (values $[\text{I}^*]_{\min}$, $[\text{I}^*]_{\max}$ and time instants corresponding to them) are the critical points of these dependences. The determination of these quantities is the main objective of the approximate analytic solution of SDE3.

In this paper we studied the initial stage of the chain reaction of RI decomposition, which includes the first $(0 \leqslant u \leqslant 1)$ and second $(1 < u \leqslant 2)$ variation ranges of u. At the end of the first time interval, when $u = 1$, the minimal
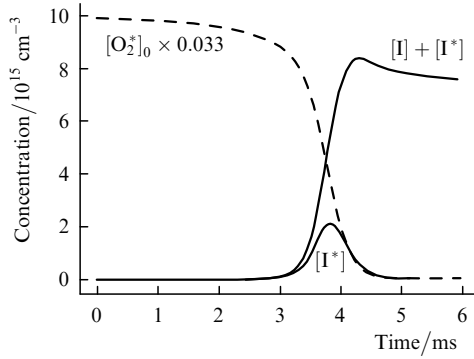
Figure 1. Time dependences of the concentrations of iodine atoms (I^* and I) and singlet oxygen obtained by solving numerically SDE1 during the dark decomposition of CH_3I in the mixture $[CH_3I]_0 = 10^{16}$ cm^{-3}, $[O_2^*]_0 = [O_2]_0 = 3 \times 10^{17}$ cm^{-3}, $[Cl_2]_0 = 5 \times 10^{16}$ cm^{-3} and $[I_2]_0 = 10^{13}$ cm^{-3} at $K_8 = 10^{-12}$ cm^3 s^{-1}.
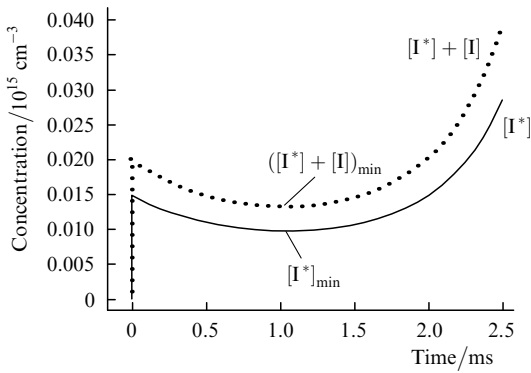
Figure 2. Parts of two dependences in Fig. 1 in an enlarged scale with respect to the y axis.

value x_{min} of the sum of concentrations of iodine atoms is achieved, while in the range $1 < u \leqslant 2$ the minimum value $[I^*]_{min}$ of concentrations of excited iodine atoms is achieved. The presence of minima in the dependences $x(\tau)$ and $[I^*](\tau)(2[I_2]_0)^{-1}$ can be treated as a criterion for the existence of the branching chain reaction of RI decomposition. Indeed, in the case of simple chain reaction (1)–(6), decomposition of RI molecules leads to an increase only in concentrations [ICl], [RCl] and [RO$_2$] and only in the case of effective reaction (7) the increase in the concentrations of iodine atoms is possible. In this paper we obtained the criteria for achieving x_{min} and $[I^*]_{min}$, which are criteria for the transformation of simple chain reaction (1)–(6) of RI decomposition into branching chain reaction (1)–(8).

The approximate solution of SDE3 is quite complicated and mainly presented in Appendices 2–6, while in the main text we present the characteristic of the analysed time interval, the basic expressions determining the development of the branching chain reaction of RI decomposition and discuss the obtained results.

4. Analysis of the first stage of the development of the chain reaction ($0 \leqslant u \leqslant 1$)

4.1 Determination of basic characteristics

Consider the first stage of the chain reaction called the induction period, which is determined using the peculiarities

of expression (13). In this time interval ($0 \leqslant \tau \leqslant \tau_{min}$), the derivative is $dx/d\tau \leqslant 0$ and, hence, the sum of concentrations of iodine atoms decreases from the initial value $2[I_2]_0$ ($x = 1$) to some minimal value x_{min} achieved for $u = 1$ at the time instant τ_{min}. The concentration $[I^*]$ proportional to x and y [see (18)] also decreases at the first stage because x and y decrease. The concentration of ICl molecules, on the contrary, increases from zero to the critical value $[ICl]_{cr}$ ($u = 1$). When this critical value is achieved, the rates of reactions (3) and (7) become equal and the chain reaction of RI decomposition becomes branching.

Note that due to smallness of $[ICl]_{cr}$, the degrees of [RI] and [Cl$_2$] (η_{RI} and η_{Cl_2}) decomposition at the first stage are also small and determined by the inequalities

$$\eta_{RI} < [ICl]_{cr}/[RI]_0 \ll 1, \quad \eta_{Cl_2} < [ICl]_{cr}/(2[Cl_2]) \ll 1 \quad (21)$$

[see (19), Appendix 1 and Table 1]. Thus, we can assume that $[RI] = [RI]_0$ and $[Cl_2] = [Cl_2]_0$ for $0 \leqslant \tau \leqslant \tau_{min}$.

Expressions for calculating x_{min} and τ_{min} derived in Appendices 2, 5, 6 have the forms:

$$x_{min} = 1 - a\left[1 + D_1 \ln\left(1 - \frac{1}{D_1 + 1}\right)\right], \quad (22)$$

$$\tau_{min} = 2\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2} \arctan\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2} \frac{1}{\delta_1}, \quad (23)$$

where

$$D_1 = \frac{3}{2} \frac{N\varphi(\tau_{min})}{1 - 1/(2A)} \quad (24)$$

and δ_1 are the average values of these parameters at the first stage of the development of the chain reaction and $\varphi(\tau_{min}) < 1$ [determined from (A4.6), (A5.3)]. Parameters entering expressions (22)–(24) were calculated for the initial concentrations of RI and Cl$_2$. At low η_{RI} [see (21)] due to smallness of [RO$_2$] we can neglect in the first approximation the decrease in $[O_2^*]$ and assume that $y_1 = y(\tau_{min}) \sim 1$. Therefore, the average value of δ at the first stage (δ_1) will coincide with its initial value: $\delta_1 = \varepsilon y_1 = \delta_0 = \text{const} = \varepsilon_0$. This conclusion is confirmed by calculations of y_1 with the help of Eqn (A3.7) and by the numerical solution of SDE1.

Quantities x_{min}, τ_{min}, D_1 because of their mutual dependence are simultaneously determined by solving expressions (22)–(24) with the help of the method of successive approximations. In the case of very strong quenching, when $y_1 = y(\tau_{min})$ is noticeably lower than unity [see (A3.7)], the above procedure for the combined solution of the system of equations (22)–(24) and (A3.7) is employed.

4.2 First critical condition for existence of the branching chain reaction of RI decomposition

Let us discuss the derived expressions. The inequality $x_{min} < 0$ yields the first critical condition for the development of the branching chain reaction of RI decomposition. Indeed, if a and D_1 are such that $x_{min} < 0$, the derivative $dx/d\tau < 0$ for any τ [i.e. $x(\tau) \to 0$ for $\tau \to \infty$], the critical concentration $[ICl]_{cr}$ is not achieved, branching is absent and, therefore, the rate of the chain reaction of RI decomposition tends to zero.

Using the condition $x_{\min} \leqslant 0$, we determine the limiting initial concentration of molecular iodine $[I_2]_0^{\min}$, whose excess is required for the development of the branching chain reaction. Two parameters, namely, a and D_1, enter the expression for $x_{\min}$. For $x_{\min} \to 0$, the parameter $D_1 \to \frac{3}{2}N$, because $\tau_{\min} \to \infty$ and $\varphi(\tau) \to 1$ [see (24), (A4.6) and (A5.3)]]. By substituting into (22) the expression for a, $D_1 = \frac{3}{2}N$ and corresponding constants, we obtain

$$\frac{[I_2]_0}{[Cl_2]_0} \leqslant \frac{1}{3}\, 10^{-3}\left\{1 + \frac{3}{2}N\ln\left[1 - \left(\frac{3}{2}N + 1\right)^{-1}\right]\right\} \quad (25)$$

from the condition $x_{\min} \leqslant 0$. Let us estimate $[I_2]_0^{\min}$ using expression (25) first for small N, which are realised, for example, for the following composition of the pulsed COIL active medium: $[RI]_0 = 10^{16}$ cm^{-3}, $[Cl_2]_0 = 5 \times 10^{16}$ cm^{-3}, $[O_2]_0 = [O_2^*]_0 = 3 \times 10^{17}$ cm^{-3}. Under these conditions, in the case of CH_3I we have $K_6 = 2.5 \times 10^{-13}$ cm^3 s^{-1}, $K_5/K_6 = 6.4$ (see Table 1), $N \simeq 2.1$, and from (25) we obtain $[I_2]_0^{\min}/[Cl_2]_0 = 4.4 \times 10^{-5}$ (5.2×10^{-5}). In the case of CF_3I, the ratio $K_5/K_6 = 0.044 \ll 1$ (see Table 1), $N = 1$, and from (25) we obtain $[I_2]_0^{\min}/[Cl_2]_0 = 7.8 \times 10^{-5}$ (8.4×10^{-5}). In braces we present values obtained by solving numerically SDE1. The analytic estimates with the help of Eqn (25) agree well with the results of numerical calculations.

Note that for CF_3I the value of N is close to unity almost for any active medium composition of the pulsed COIL because $K_5/K_6 \ll 1$ in a broad range of pressures (see [13]) and $[Cl_2]_0/[O_2]_0 < 1$.

Consider now the case of large N, which is realised only for CH_3I and anly at low pressures of the initial medium (small values of K_6, see [14]). By using two terms in the logarithm expansion in (22) and taking into account that at large N the equality $N \approx K_5[Cl_2]/K_6[O_2]$ holds true, we transform (25) to the form valid for CH_3I at $N \gg 1$ and obtain

$$[I_2]_0^{\min}/[O_2]_0 = K_3 K_6/(6K_7 K_5). \quad (26)$$

The constant K_6 depends on the pressure. By substituting $K_6 = 2.5 \times 10^{-14}$ cm^3 s^{-1} into (26), we obtain

$$[I_2]_0^{\min}/[O_2]_0 = 1.7 \times 10^{-6}. \quad (27)$$

The presented estimates show that at small N (which is always valid for CF_3I and only at large K_6 for CH_3I) the limiting value $[I_2]_0^{\min}$ depends on the initial concentration Cl_2 and in the case of large N, which is realised only for CH_3I (small K_6), the limiting concentration $[I_2]_0^{\min}$ is determined by the initial concentration of O_2.

5. Analysis of the second stage of the development of the chain reaction $(1 < u \leqslant 2)$

5.1 Second critical condition for existence of the branching chain reaction of RI decomposition

Consider the second stage of the chain decomposition of RI according to the scheme of reactions (1)–(8). This stage determines the further behaviour of the chain reaction because in this range of the u variations the concentration of I^* becomes minimal: $I^* = [I^*]_{\min}$. At $\tau > \tau_{\min}$ the sum of the concentrations of iodine atoms begins to increase slowly

($dx/d\tau > 0$), but the concentration of excited iodine atoms still continues to decrease for some time. Indeed, the first term in the right-hand side of (18) is always less than zero because $dy/d\tau < 0$ always, and the second term changes its sign at $u = 1$. At $u < 1$ the derivative $dx/d\tau < 0$ and $[I^*]$ decreases. At $u > 1$ the derivative $dx/d\tau > 0$, therefore, at some x (in the vicinity of $x_{\min}$) the right-hand side of (18) can vanish and, hence, $[I^*]_{\min}$ is achieved. However, this minimum can be and cannot be achieved.

Let us determine the criterion for the presence of the minimum in the dependence $[I^*](t)$ in the range $1 < u \leqslant 2$. Dividing (18) by $dx/d\tau$ and using expression (A3.5) for dy/dx, we derive

$$\varepsilon\, \frac{d(xy)}{dx} = \varepsilon y(x) - \varepsilon\, \frac{B}{\varepsilon}\, a\, \frac{x - 1 + au}{u - 1}, \quad (28)$$

where $y(x)$ is a monotonically decreasing function of x and the second term is strongly changed in the vicinity of $u \gtrsim 1$ (for $x \gtrsim x_{\min}$). Thus, $[I^*]_{\min}$ is achieved only in the case when $1 < u \leqslant 2$. The concentration of I^* reaches $[I^*]_{\min}$ if the right-hand side of (28) is nonnegative. Then, using expressions (A3.8) and (A2.7) for $y(x)$ and $u - 1$, respectively, and assuming that $u - 1 \ll 1$, we obtain from (28)

$$(y_1\varepsilon/B - 1)(u - 1) - (x_{\min} - 1 + a)/a$$
$$-(1 - x_{\min})(3x_{\min} + 2a - 2)(u - 1)^2/(ax_{\min}) \geqslant 0. \quad (29)$$

The last two terms in the left-hand side of (29) are negative, because $a > 0$, $x_{\min} < 1$ and $x_{\min} - 1 + a > 0$, where $x_{\min} - 1 + a$ is the concentration of decomposed RI molecules at $u = 1$ ($\tau = \tau_{\min}$) [see (19)]. Therefore, the solution of inequality (29) at $u - 1 > 0$ exists only if $y_1\varepsilon/B - 1 > 0$ and the discriminant of the quadratic trinomial in the left-hand side of the inequality is nonnegative. This makes it possible to obtain the condition for the presence of the minimum in the dependence $[I^*](t)$:

$$y_1\varepsilon/B - 1 \geqslant 2[(1 - x_{\min})/x_{\min}]^{1/2}$$
$$\times [(x_{\min} - 1 + a)(3x_{\min} + 2a - 2)]^{1/2}/a, \quad (30)$$

where y_1 is defined by expression (A3.7).

Expression (22) for $x_{\min}$ and inequality (30) allow one to formulate two criteria for the development of the branching chain reaction of RI decomposition in the general case: for $x_{\min} < 0$ [see (22)] branching is impossible and for $x_{\min} > 0$ branching is possible only if inequality (30) is fulfilled.

Therefore, for specified $x_{\min}$ there exists a critical value B_{cr} and, hence, K_{8cr} defined by (30), after the excess of which the development of the branching chain reaction of RI decomposition becomes impossible. By substituting expression (A3.7) for y_1 into (30), we obtain the expression to derive K_{8cr}:

$$K_{8cr} = K_7 N\varepsilon\big\{1 + 2(1 - x_{\min})/a + \ln x_{\min} + 2(a - 1)/a$$
$$\times [(1 - x_{\min})/x_{\min}]^{1/2} \arctan\, [(1 - x_{\min})/x_{\min}]^{1/2} + (2/a) \quad (31)$$
$$\times [(1 - x_{\min})/x_{\min}]^{1/2}[(x_{\min} - 1 + a)(3x_{\min} + 2a - 2)]^{1/2}\big\}^{-1}.$$

6. Discussion of the results

To confirm the validity of the analytic expressions derived in this paper for describing processes proceeding in the active medium of a pulsed COIL, we compared the cal-

culation results of parameters of the chain decomposition of CH_3I obtained with the help of analytic expressions and in the numerical solution of SDE1. For the typical composition of the pulsed COIL active medium ($[CH_3I]_0 = 10^{16}$ cm^{-3}, $[O_2^*]_0 = [O_2]_0 = 3 \times 10^{17}$ cm^{-3}, $[I_2]_0 = 10^{13}$ cm^{-3}, $[Cl_2] = 5 \times 10^{16}$ cm^{-3} and $K_8 = 10^{-12}$ cm^3 s^{-1}) the parameters entering system (22)–(24) take the following values: $N = 2.07$, $a = 5/3$, $A = 6.44$, $\varepsilon = 3/4$, $B = 0.021$. Then, for the first stage of the chain reaction development ($0 \leqslant u \leqslant 1$) we obtain from system (22)–(24) and (A3.7) that $D_1 = 2.5$, $x_{min} = 0.73$ (0.67), $\tau_{min} = 0.89$ (1.02) and $y_1 = 0.99$ (0.99). For the second stage ($1 < u \leqslant 2$), from expressions (A2.2) at $u = 2$, $u_0 = 1$, $x_0 = x_{min}$, $x = x_2$ and from (A3.9), (A5.5) and (A6.2) we have $D_2 = 4.8$, $x_2 = 0.88$ (0.86), $\tau_2 = 1.76$ (1.82) and $y_2 = 0.988$ (0.98). The values of the parameters obtained during the numerical solution of SDE1 are presented in braces. One can see that these results coincide fairly well with the corresponding values obtained analytically. Note also that the value of $x_2 = 0.88$ calculated with (A2.2) is close to $x_2 = 1$ calculated with approximate expression (A2.5), which is used in this paper to find the dependence $y(x)$.

Figure 3 presents the dependences $([I^*] + [I])(t)$ obtained by solving numerically SDE1 at $K_8 = 0$ for two variants of initial conditions for the dark decomposition of CH_3I, which differ only in initial concentrations of molecular iodine. On the curve corresponding to $[I_2]_0 = 2.55 \times 10^{12}$ cm^{-3} the minimum is absent, while on the curve corresponding to $[I_2]_0 = 2.60 \times 10^{12}$ cm^{-3}, the minimum is present. Calculations with the help of (25) yield close limiting value of $[I_2]_0^{min}$ (2.2×10^{12} cm^{-3}). Figure 3 also shows the dependences $[ICl](t)$ corresponding to the same initial conditions. These dependences confirm that the absence of the minimum in the dependence $([I^*] + [I])(t)$ is caused by the fact that the critical concentration $[ICl]_{cr}$ is not achieved in the system.

Note that in the case of CF_3I, at the same initial concentrations of RI, Cl_2, O_2 and O_2^* curves similar to those in Fig. 3 are plotted but at larger initial concentrations of molecular iodine: $[I_2]_0 = 4.2 \times 10^{12}$ cm^{-3} (minimum is absent), 4.3×10^{12} cm^{-3} (minimum is present). The limiting (critical) initial concentration of molecular iodine calculated under these conditions with expression (25) was 3.9×10^{12} cm^{-3}.

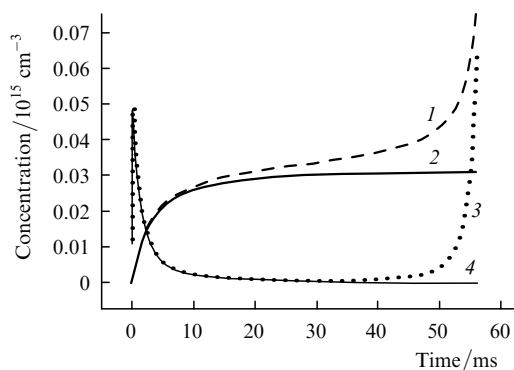Before confirming the validity of second condition (31) for the development of the branching chain reaction of RI decomposition we will analyse the dependence of $K_{8\,cr}$ on x_{min} with the help of expression (31). At $x_{min} \to 1$ the denominator of fraction in (31) tends to its minimum value equal to unity for which the quantity $K_{8cr} = K_7 N\varepsilon$ will be maximal. To obtain $x_{min} \sim 1$, it is necessary to select such initial concentration $[I_2]_0$ so that the inequality $a = ([ICl]_{cr}/[I_2]_0) \ll 1$ should be fulfilled, the parameter D_1 taking any values [see (21)]. At $a > 1$ (small concentrations $[I_2]_0$) $x_{min} < 1$ and K_{8cr} is smaller than its maximum value.

The validity of condition (31) was verified for two iodides (CH_3I and CF_3I) at equal initial concentrations of RI, Cl_2, O_2 and O_2^* but different concentrations of molecular iodine $[I_2]_0$. In the case of CF_3I (Fig. 4) the most favourable conditions were selected for the development of the chain reaction – high initial concentration of molecular iodine ($[I_2]_0 = 10^{14}$ cm^{-3}) for which $x_{min} = 0.937 \approx 1$. For CH_3I (Fig. 5) the concentration $[I_2]_0 = 3.5 \times 10^{12}$ cm^{-3} was used for which $x_{min} = 0.31$. This allows us to verify expression (31) for small x_{min}.

It follows from the dependences presented in Fig. 5 for CH_3I that the results of the numerical solution of SDE1 are
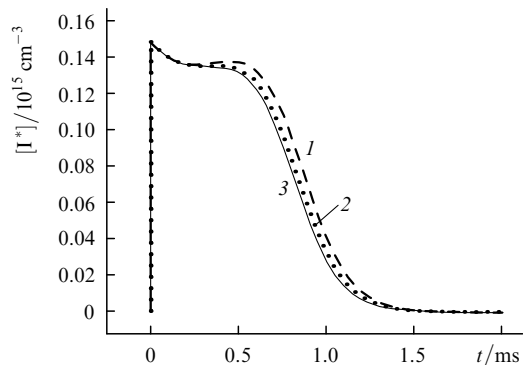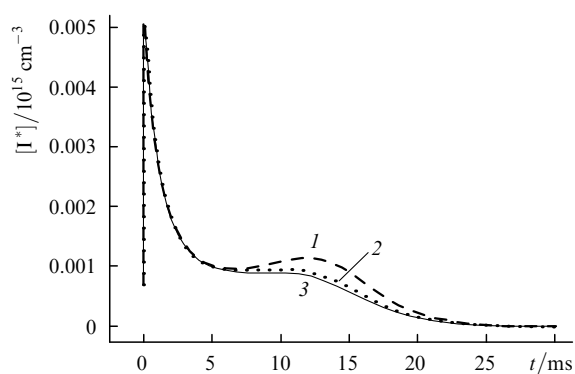
Figure 4. Time dependences $[I^*](t)$ obtained by solving numerically SDE1 during the dark decomposition of CF_3I in the mixture $[CF_3I]_0 = 10^{16}$ cm^{-3}, $[O_2^*]_0 = [O_2]_0 = 3 \times 10^{17}$ cm^{-3}, $[Cl_2]_0 = 5 \times 10^{16}$ cm^{-3} and $[I_2]_0 = 10^{14}$ cm^{-3}; $K_8 = 1.7 \times 10^{-11}$ (*1*), 1.9×10^{-11} (*2*), 2.0×10^{-11} cm^3 s^{-1} (*3*).

Figure 3. Time dependences of the concentrations [ICl] (*1*, *2*) and ($[I^*] + [I]$) (*3*, *4*) obtained by solving numerically SDE1 at $K_8 = 0$ during the dark decomposition of CH_3I in mixtures $[CH_3I]_0 = 10^{16}$ cm^{-3}, $[O_2^*]_0 = [O_2]_0 = 3 \times 10^{17}$ cm^{-3}, $[Cl_2]_0 = 5 \times 10^{16}$ cm^{-3} with initial concentrations of iodine $[I_2]_0 = 2.60 \times 10^{12}$ (*1*, *3*) and 2.55×10^{12} cm^{-3} (*2*, *4*).

Figure 5. Time dependences $[I^*](t)$ obtained by solving numerically SDE1 during the dark decomposition of CH_3I in the mixture $[CF_3I]_0 = 10^{16}$ cm^{-3}, $[O_2^*]_0 = [O_2]_0 = 3 \times 10^{17}$ cm^{-3}, $[Cl_2]_0 = 5 \times 10^{16}$ cm^{-3} and $[I_2]_0 = 3.5 \times 10^{12}$ cm^{-3}; $K_8 = 8 \times 10^{-12}$ (*1*), 8.7×10^{-12} (*2*), 9×10^{-12} cm^3 s^{-1} (*3*).

close to the values $K_{8\,cr} \approx 8.0(8.7) \times 10^{-12}$ cm^3 s^{-1} estimated using expression (31). (The value of $K_{8\,cr}$ obtained by solving numerically SDE1 is presented in braces.)

For CF$_3$I, the value $K_{8\,cr} \approx 2 \times 10^{-11}$ cm^3 s^{-1} (see Fig. 4) obtained by solving numerically SDE1 is close to the maximum one, $K_{8\,cr}^{max} = \varepsilon K_7 \approx 2.25 \times 10^{-11}$ cm^3 s^{-1}, determined from (31) at $N = 1$, $x_{min} = 1$ and $\varepsilon = 3/4$. For $x_{min} = 0.937$ (see above), expression (31) gives a somewhat lower value of $K_{8\,cr}$ equal to $\sim 1.1 \times 10^{-11}$ cm^3 s^{-1}. The observed discrepancy is explained by the fact that in deriving expressions (29)–(31) we used the approximate dependence $x(u)$ (A2.5) derived by expanding the logarithm in (A2.2) existing at $D_1 > 1$, while for CF$_3$I at $x_{min} = 0.937$ we have $D_1 \approx 0.67$. Thus, in the case of large initial concentrations of molecular iodine ($a < 1$) for which $x_{min} \approx 1$ and $D_1 < 1$, expression (31) gives a more exact estimate of $K_{8\,cr}$ when substituting $x_{min} = 1$.

Note that calculated dependences $[I^*](t)$ in Figs 4 and 5 both quantitatively and qualitatively confirm the second critical condition for the development of the branching chain reaction of RI decomposition. It follows from (29)–(31) that for $K_8 > K_{8\,cr}$ the derivative $d[I^*]/d\tau$ twice (at minimum and maximum points) vanishes and for $K_8 < K_{8\,cr}$ extreme points are absent. Therefore, for $K_8 \to K_{8\,cr}$ the time interval between the minimum and maximum points for $[I^*]$ as well as the difference $([I^*]_{max} - [I^*]_{min})$ tend to zero, which is shown by the curves in Figs 4 and 5.

Analysis of the obtained results allows one to explain the absence of dark decomposition of CF$_3$I observed experimentally by two factors – low efficiency of the primary chain ($N = 1$) and high efficiency of O$_2^*$ quenching by CF$_3$O$_2$ radicals ($K_8 \gtrsim 2 \times 10^{-11}$ cm^3 s^{-1}). In addition, because of lower boiling temperatures the initial admixture of molecular iodine in fluorine-organic iodides is usually significantly lower than in organic. For CH$_3$I the primary chain under typical conditions of the active medium of pulsed COILs is always effective ($N > 1$) while the value of K_8 for CH$_3$O$_2$ radicals should be lower than 10^{-11} cm^3 s^{-1}. Otherwise, the dark decomposition of CH$_3$I observed in numerous experiments should be absent.

7. Conclusions

The main results of the paper are:
(i) Scheme of basic reactions describing the chain reaction of RI decomposition in the dark zone of a pulsed COIL is analysed.

(ii) A simplified system of differential equations (SDE3) is derived, which describes in dimensionless variables the chain decomposition of RI in the active medium of a pulsed COIL.

(iii) The procedure for solving SDE3 is described.

(iv) The main parameters determining the development of the chain decomposition reaction of RI are found and the characteristic time intervals of the chain development are defined.

(v) The first ($0 \leqslant u \leqslant 1$) and second ($1 < u \leqslant 2$) stages of the development of the chain reaction of RI decomposition are studied and expressions for calculating the concentrations of basic components of the active medium are derived at these stages.

(vi) Criteria for the development of the branching chain reaction of RI decomposition in the active medium of a pulsed COIL are determined.

Appendix 1

System of differential equations SDE1

$$\frac{d[I]}{dt} = 2K_1[I_2][O_2^*]^2 + K_2[I^*][O_2] - K_{-2}[I][O_2^*], \quad (A1.1)$$

$$\frac{d[I^*]}{dt} = K_{-2}[I][O_2^*] - K_2[I^*][O_2]$$
$$- K_3[I^*][Cl_2] - K_7[I^*][ICl], \quad (A1.2)$$

$$\frac{d[O_2^*]}{dt} = -2K_1[I_2][O_2^*]^2 + K_2[I^*][O_2] - K_{-2}[I][O_2^*]$$
$$- K_8[O_2^*][RO_2], \quad (A1.3)$$

$$\frac{d[O_2]}{dt} = 2K_1[I_2][O_2^*]^2 - K_2[I^*][O_2] + K_{-2}[I][O_2^*]$$
$$+ K_8[O_2^*][RO_2] - K_6[R][O_2], \quad (A1.4)$$

$$\frac{d[Cl]}{dt} = K_3[I^*][Cl_2] + K_7[I^*][ICl] + K_5[R][Cl_2]$$
$$- K_4[Cl][RI], \quad (A1.5)$$

$$\frac{d[ICl]}{dt} = K_3[I^*][Cl_2] + K_4[Cl][RI] - K_7[I^*][ICl], \quad (A1.6)$$

$$\frac{d[I_2]}{dt} = -K_1[I_2][O_2^*]^2 + K_7[I^*][ICl], \quad (A1.7)$$

$$\frac{d[R]}{dt} = K_4[Cl][RI] - K_5[R][Cl_2] - K_6[R][O_2], \quad (A1.8)$$

$$\frac{d[RI]}{dt} = -K_4[Cl][RI], \quad (A1.9)$$

$$\frac{d[RCl]}{dt} = K_5[R][Cl_2], \quad (A1.10)$$

$$\frac{d[RO_2]}{dt} = K_6[R][O_2]. \quad (A1.11)$$

Dimensionless variables

$$\tau = \gamma t; \quad x = \frac{[I] + [I^*]}{2[I_2]_0}; \quad v = \frac{[Cl]}{2[I_2]_0}; \quad u = \frac{[ICl]}{[ICl]_{cr}}; \quad y = \frac{[O_2^*]}{[O_2^*]_0}.$$

Parameters

$$[ICl]_{cr} = \frac{K_3[Cl_2]}{K_7}; \quad \gamma = K_3[Cl_2]; \quad a = \frac{K_3[Cl_2]}{K_7 2[I_2]_0} = \frac{[ICl]_{cr}}{2[I_2]_0};$$

$$N = 1 + \frac{K_5[Cl_2]}{K_6[O_2]}; \quad \varepsilon = \frac{K_{eq}(K_{eq} - 1)^{-1}}{y + ([1 + [O_2]_0/[O_2^*]_0)(K_{eq} - 1)^{-1}},$$

where $K_{eq} = K_{-2}/K_2$ (the parameter ε is a slowly varying

function of y; thus, at $[O_2^*]_0 = [O_2]_0$ for $T = 300$ K ($K_{eq} \approx$ 2.9) $\varepsilon = 3/4$ for $y = 1$ and $\varepsilon \leqslant 3/2$ for $y = 0$, i.e. $\varepsilon \sim 1$);

$$\delta = \frac{[I^*]}{[I^*] + [I]} = \varepsilon y; \quad A = \frac{K_4[RI]/K_3[Cl_2]}{N\varepsilon y}; \quad D = \frac{K_4[RI][Cl]}{K_3[Cl_2][I^*]}$$

$$= \frac{K_4[RI]}{K_3[Cl_2]} \frac{v/x}{\varepsilon y} = AN(v/x); \quad B = \frac{K_8}{K_7 N}; \quad b = \frac{2[I_2]_0}{[O_2^*]_0};$$

$$\theta = \frac{K_8}{K_4 N(v/x)}.$$

In Appendices 2–4 dependences $x(u)$, $y(u)$, $(v/x)(u)$ are determined under assumption that in the given range of the u variations all the parameters – a, A, N, D, ε, B – are constant quantities.

Appendix 2

Dependence $x(u)$. General expression
To find $x(u)$ we divide equation (15) by equation (13). As a result, we have

$$\frac{du}{dx} = \frac{1}{a} \frac{D + 1 - u}{u - 1}. \tag{A2.1}$$

Solving this equation at $D = \text{const}$ and $a = \text{const}$ we derive the expression establishing a relation of concentrations of ICl molecules (u) and the sum of concentrations of iodine atoms (x):

$$u - u_0 + D \ln\left(1 - \frac{u - u_0}{D + 1 - u_0}\right) = \frac{1}{a}(x_0 - x). \tag{A2.2}$$

Expression (A2.2) is valid at $u - u_0 < (D + 1 - u_0)$.

The first stage: $0 \leqslant u \leqslant 1$
For the first stage $u_0 = 0$, $x_0 = 1$, $x(\tau_{min}) = x_{min}$, $u(\tau_{min}) = 1$. Using (A2.2) we derive an expression for x_{min}:

$$x_{min} = 1 - a\left[1 + D_1 \ln\left(1 - \frac{1}{D_1 + 1}\right)\right], \tag{A2.3}$$

where D_1 is defined by expression (A5.4).

The range $0 < u \leqslant 2$
In this range of u variations at $D_1 > 1$ the expression in the logarithm in (A2.2) is smaller than $1/2$ and the logarithm can be expanded. Using two terms of expansion and assuming that $x_0 = x_{min}$, $u_0 = 1$, we will rewrite (A2.2) in the form

$$x(u) \approx \frac{a}{2D}(u - 1)^2 + x_{min}. \tag{A2.4}$$

Expression (A2.4) is a quadratic function of u, which taking (A2.3) into account with good approximation can be represented in the form:

$$x(u) \approx (1 - x_{min})(u - 1)^2 + x_{min}. \tag{A2.5}$$

At the first stage $u - 1 \leqslant 0$, and, hence, solving (A2.5), we obtain

$$u - 1 = -\left(\frac{x - x_{min}}{1 - x_{min}}\right)^{1/2}. \tag{A2.6}$$

Similarly for the range $1 < u \leqslant 2$ at $u - 1 > 0$, we have

$$u - 1 = \left(\frac{x - x_{min}}{1 - x_{min}}\right)^{1/2}. \tag{A2.7}$$

Appendix 3

Dependence $y(x)$
We will establish the dependence $y(x)$ for the range of u variations under study. Dividing equation (20) by equation (13), we obtain

$$\frac{dy}{dx} = -\frac{b(3u + 1)}{u - 1} - \frac{B}{\varepsilon} \frac{x - 1 + au}{a(u - 1)x}. \tag{A3.1}$$

By simplifying (A3.1), it can be represented in the form

$$\frac{dy}{dx} = -3b - \frac{B}{a\varepsilon(u - 1)}\left(1 + \frac{4ba\varepsilon}{B}\right) - \frac{B}{\varepsilon} \frac{1}{x}$$

$$- \frac{B(a - 1)}{a\varepsilon} \frac{1}{(u - 1)x}. \tag{A3.2}$$

Let us evaluate K_8 for which the ratio $4ba\varepsilon/B = 4K_3[Cl_2]N/(K_8[O_2^*]_0) \ll 1$. Consider the case of large N (low pressures), when $K_6 \sim K_{6\,min} \sim 10^{-14}$ cm^3 s^{-1} and $N \approx K_5[Cl_2]/(K_6[O_2])$ [see (10) and Table 1]. Using this expression for N and taking into account that the concentration of chlorine in the active medium of a pulsed COIL usually does not exceed $\sim 20\%$ of the oxygen concentration, we obtain

$$K_8 \gg N \times 10^{-14} \text{ cm}^3 \text{ s}^{-1} \text{ (for } N \leqslant 20). \tag{A3.3}$$

For the values of K_8 satisfying (A3.3), we can neglect the ratio $4ba\varepsilon/B$ in the second term of the right-hand side of (A3.2) and rewrite this equation in the form

$$\frac{dy}{dx} = -3b - \frac{B}{a\varepsilon(u - 1)} - \frac{B}{\varepsilon} \frac{1}{x} - \frac{B(a - 1)}{a\varepsilon} \frac{1}{(u - 1)x}. \tag{A3.4}$$

One can see that for the range of the u variations ($0 \leqslant u \leqslant 2$) considered in this paper, the first term in the right-hand side of (A3.4) can be excluded and written in the form

$$\frac{dy}{dx} = -\frac{B}{a\varepsilon(u - 1)} - \frac{B}{\varepsilon} \frac{1}{x} - \frac{B(a - 1)}{a\varepsilon} \frac{1}{(u - 1)x}. \tag{A3.5}$$

Let us determine the dependence $y(x)$ for the first stage ($0 \leqslant u \leqslant 1$). Using (A2.6) and (A3.5), we obtain

$$y(x) = 1 - \frac{B}{\varepsilon}\left\{\ln x + \frac{2(1 - x_{min})}{a} - \frac{2[(1 - x_{min})(x - x_{min})]^{1/2}}{a}\right.$$

$$+ \frac{2(a - 1)}{a}\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\left[\arctan\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\right.$$

$$\left.\left. - \arctan\left(\frac{x - x_{min}}{x_{min}}\right)^{1/2}\right]\right\}. \tag{A3.6}$$

By substituting $x = x_{min}$ in this expression, we will determine y at the end of the first stage (at $u = 1$):

$$y_1 = y(x_{min}) = 1 - \frac{B}{\varepsilon}\left[\ln x_{min} + \frac{2(1 - x_{min})}{a} + \frac{2(a-1)}{a}\right.$$

$$\left. \times \left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\arctan\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\right]. \quad (A3.7)$$

Let us find the dependence $y(x)$ for the second stage ($1 < u \leqslant 2$). By substituting (A2.7) into (A3.5) and solving it, we obtain

$$y(x) = y_1 - \frac{B}{\varepsilon}\left[\ln\frac{x}{x_{min}} + \frac{2[(1 - x_{min})(x - x_{min})]^{1/2}}{a} +\right.$$

$$\left. + \frac{2(a-1)}{a}\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\arctan\left(\frac{x - x_{min}}{x_{min}}\right)^{1/2}\right]. (A3.8)$$

By substituting $x = x_2 \approx 1$ [see (A2.5)] and y_1 into this expression, we will determine the value of y at the end of the second stage (at $u = 2$):

$$y_2 \approx 1 - \frac{4B}{\varepsilon}\left[\frac{1 - x_{min}}{a} + \frac{a - 1}{a}\right.$$

$$\left. \times \left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\arctan\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\right]. \quad (A3.9)$$

Appendix 4

Dependence $(v/x)(u)$
First, we estimate qualitatively how the ratio $[Cl]/([I^*] + [I]) = v/x$ changes with changing u. The source of Cl atoms are reactions (3) and (7). First, the increase in $[Cl]$ mainly occurs due to reaction (3) but the role of reaction (7) increases with increasing $[ICl]$. It is obvious that in the limit, when reaction (7) becomes the main 'supplier' of chlorine and iodine atoms, the ratio $v/x = (v/x)_{max} \sim 1$.

We will solve expression (14) to determine the dependence $(v/x)(\tau)$. The parameter A characterises the efficiency of the development of nonranching chain (1)–(6) because it is equal to the ratio of the characteristic time of chain initiation [reaction (3)] to the characteristic time of chain continuation [reactions (4)–(6)]. At $A \geqslant 1$ the rate of chain process (1)–(6) is determined by the rate of reaction (3). The parameter A depends on $[RI]$, $[Cl_2]$, $[O_2^*]$, $[O_2]$ and in the case of their small change (see below) can be considered constant. By solving equation (14) and treating the variable u as a parameter, we obtain

$$v/x = [\overline{(u+1)/(A+u-1)}](1 - x^{-\overline{(A+u-1)/(u-1)}}). \quad (A4.1)$$

Here, the bar implies averaging over the entire variation range of u. Consider equation (13). Assuming $[RI]$, $[Cl_2]$, $[O_2^*]$, $[O_2]$ to be constants and u to be a parameter, we will solve equation (13) and determine the time dependence $x(\tau)$:

$$x(\tau) = \exp[\overline{\varepsilon y(u-1)}\tau]. \quad (A4.2)$$

By substituting (A4.2) into (A4.1) we obtain

$$(v/x)(\tau) = [\overline{(u+1)/(A+u-1)}]\varphi(\tau),$$
$$(A4.3)$$

$$\varphi(\tau) = 1 - \exp[-\overline{(A+u-1)\varepsilon y}\tau].$$

Let us analyse the obtained dependence $(v/x)(\tau)$. At small τ, the ratio v/x linearly depends on time:

$$v/x \approx \overline{(u+1)\varepsilon y}\tau. \quad (A4.4)$$

When time increases $\varphi(\tau) \to 1$, the ratio v/x is determined by the expression, which is explicitly independent of time:

$$(v/x)_{stat} = \overline{(u+1)/(A+u-1)}. \quad (A4.5)$$

The time of achieving $(v/x)_{stat}$ is determined by the exponential factor in (A4.3) and in the case of efficient development of the chain reaction (when $A \geqslant 2$) even at $0 < u < 1$ does not exceed the characteristic time of reaction (3). Therefore, $\varphi(\tau) \sim 1$. Note that to average the dependence $\varphi(\tau)$ in the given time interval, we can take advantage of the expression

$$\overline{\varphi(\tau)} = 1 - [1 - \exp(-\xi)]/\xi, \quad (A4.6)$$

where $\xi = (A + u - 1)\varepsilon y\tau$.

In this case, the average value $(v/x)_{av}$ is calculated using expression

$$(v/x)_{av} = (v/x)_{stat}\overline{\varphi(\tau)}. \quad (A4.7)$$

It follows from (A4.5) that at $A = 2$ the ratio $(v/x)_{stat} = 1$ for any u and at $A \neq 2$ this ratio is a slowly varying function of u tending to unity with increasing $[ICl](u)$. This allows one to use the arithmetic mean value of u for calculating $(v/x)_{stat}$ in the given range of the u variations ($u_1 \leqslant u \leqslant u_2$).

Appendix 5

Estimate of parameters a and D. The first stage: $0 \leqslant u \leqslant 1$
The parameter $a = [ICl]_{cr}/(2[I_2]_0)$ contains only one variable, i.e. the concentration of Cl_2. The parameter D equal to the ratio of rates of reactions (4) and (3) depends on the ratios $[RI]/[Cl_2]$, v/x on the parameter $\delta = \varepsilon y$ and is also a variable quantity (see Table 1).

Note that the degree of RI and Cl_2 decomposition (η_{RI} и η_{Cl_2}) at the first stage are small and determined by inequalities (21). In the case of small decomposition of RI due to the smallness of $[RO_2]$, we can also neglect in the first approximation the decrease in $[O_2^*]$ and assume that $y_1 = y(\tau_{min}) \sim 1$ and the average value of δ at the first stage (δ_1) coincides with its initial value: $\delta_1 = (\varepsilon y)_1 = \delta_0 = const = \varepsilon_0$ [see (A3.7)] and Appendix 1]. Therefore, for $0 \leqslant \tau \leqslant \tau_{min}$, the parameter $a = const$ and the time dependence $D(\tau)$ is determined by the dependence $(v/x)(\tau)$ [see (A4.3)].

Calculation of D_1 – the average value D at the first stage ($0 \leqslant u \leqslant 1$)
The parameter D is equal to the ratio of the decomposition rate of RI to the rate of production of chlorine atoms in reaction (3). At $t = 0$ the concentration of Cl is equal to zero and, hence, $D_{1\,min} = 0$. Let us estimate $D_{1\,max}$. The number of RI molecules decomposed by one Cl atom can vary from 1 to the maximum possible value N [see (10)]. Thus, if Cl atoms are produced only in reaction (3) the

maximum possible value of D_1 is equal to N. If the chain is initiated by reactions (7), (1), (2), two Cl atoms are produced: one – directly in reaction (7) and the other – by replacing the I^* atom by the Cl atom in reaction (3) or (7). Because at the first stage the rate of reaction (3) surpasses that of reaction (7), the maximum possible value of D_1 in this case is equal to $2N$ and is achieved at the end of the first stage. Thus, at the first stage the relation

$$0 < D_1 < 2N \tag{A5.1}$$

is valid.

To obtain a more precise estimate of D_1, we will represent the parameter D in the form

$$D = AN(v/x)_{av} = \overline{N(u+1)/[1 + (u-1)A^{-1}]\varphi(\tau)}. \tag{A5.2}$$

At the first stage $u = u_{av} \approx 1/2$ and $\overline{\varphi(\tau)} = \overline{\varphi(\tau_{min})}$ is determined by expression (A4.6) at

$$\xi = A\tau_{min}\delta_1[1 - 1/(2A)]. \tag{A5.3}$$

By substituting $\overline{\varphi(\tau_{min})}$ and $u = 1/2$ in (A5.2), we obtain

$$D_1 = {}^3\!/_2\, N\overline{\varphi(\tau_{min})}/[1 - 1/(2A)] \tag{A5.4}$$

for the range $0 \leqslant u \leqslant 1$.

Calculation of D_2 – the average value D at the second stage $(1 < u \leqslant 2)$
By substituting $\varphi(\tau) = 1$ and $u = 3/2$ in (A5.2), we obtain

$$D_2 = {}^5\!/_2\, N/[1 + 1/(2A)] \tag{A5.5}$$

for the range $1 < u \leqslant 2$.

Appendix 6

Determination of the time characteristics of the chain reaction of RI decomposition. The first stage: $0 \leqslant u \leqslant 1$
The second main characteristic of the first stage of the chain decomposition of RI, i.e. its duration τ_{min}, is determined by using equations (13) and (A2.6).

By substituting (A2.6) into (13) and integrating it, we derive the expression to find τ_{min}:

$$\tau_{min} = 2\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2} \arctan\left(\frac{1 - x_{min}}{x_{min}}\right)^{1/2}\frac{1}{\delta_1}. \tag{A6.1}$$

The second stage: $1 < u \leqslant 2$
It follows from (A2.5) that the function $x(u)$ is symmetric with respect to the point $u = 1$. Therefore, we can set

$$\tau_2(u = 2) \approx 2\tau_{min}. \tag{A6.2}$$

References

1. Basov N.G., Vagin N.P., et al. *Kvantovaya Elektron.*, **11**, 1893 (1984) [*Sov. J. Quantum Electron.*, **14**, 1275 (1984)].
2. Vagin N.P., Zolotarev V.A., et al. *Kvantovaya Elektron.*, **18**, 840 (1991) [*Sov. J. Quantum Electron.*, **21**, 760 (1991)].
3. Suzuki K., Minoshima K., Sugimoto D., et al. *Proc. SPIE Int. Soc. Opt. Eng.*, **4184**, 124 (2001).
4. Andreeva T.L., Kuznetsova S.V., Maslov A.I., Sorokin V.N. *Kvantovaya Elektron.*, **32**, 485 (2002) [*Quantum Electron.*, **32**, 485 (2002)].
5. Andreeva T.L., Kuznetsova S.V., Maslov A.I., Sorokin V.N. *Kvantovaya Elektron.*, **34**, 1004 (2004) [*Quantum Electron.*, **34**, 1004 (2004)].
6. Hays G.N., Fisk G.A. *Appl. Phys. Lett.*, **42**, 3 (1983).
7. Dervent R.G., Thrush B.A. *Faraday Discuss. Chem. Soc.*, **53**, 162 (1972).
8. Burrows M.D. *J. Chem. Phys.*, **81**, 3546 (1984).
9. Kuznetsova S.V., Maslov A.I. *Khim. Fiz.*, **6**, 1554 (1987).
10. Kuznetsova S.V., Maslov A.I. *Khim. Vysok. Energ.*, **13**, 448 (1979).
11. Kovalenko L.J., Leone S.R. *J. Chem Phys.*, **80**, 3656 (1984).
12. Timonen R.S., Gutman D. *J. Phys. Chem.*, **90**, 2987 (1986).
13. Forst W., Caralp F. *J. Chem. Soc. Faraday Trans.*, **87**, 2307 (1991).
14. Kaiser E.W. *J. Phys. Chem.*, **97**, 11681 (1993).
15. Kondrat'ev V.N., Nikitin E.E. *Khimicheskie protsessy v gazakh* (Chemical Processes in Gases) (Moscow: Nauka, 1981) p. 210.
16. Vagin N.P., Zolotarev V.A., et al. *Kvantovaya Elektron.*, **18**, 33 (1991) [*Sov. J. Quantum Electron.*, **21**, 28 (1991)].
17. Andreeva T.L., Kuznetsova S.V., Maslov A.I., Sorokin V.N. *Kvantovaya Elektron.*, **24**, 511 (1997) [*Quantum Electron.*, **27**, 497 (1997)].
18. Kondrat'ev V.N., Nikitin E.E. *Khimicheskie protsessy v gazakh* (Chemical Processes in Gases) (Moscow: Nauka, 1981) p. 15.