

Analytic study of the chain dark decomposition reaction of iodides – atomic iodine donors – in the active medium of a pulsed chemical oxygen – iodine laser:

2. Limiting parameters of the branching chain dark decomposition reaction of iodides

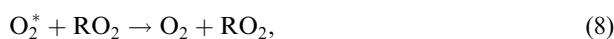
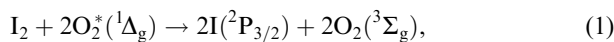
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Abstract. The final stages in the development of a branching chain decomposition reaction of iodide in the active medium of a pulsed chemical oxygen–iodine laser (COIL) are analysed. Approximate expressions are derived to calculate the limiting parameters of the chain reaction: the final degree of iodide decomposition, the maximum concentration of excited iodine atoms, the time of its achievement, and concentrations of singlet oxygen and iodide at that moment. The limiting parameters, calculated by using these expressions for a typical composition of the active medium of a pulsed COIL, well coincide with the results of numerical calculations.

Keywords: chemical oxygen–iodine laser, singlet oxygen, iodide, chain reaction.

1. Introduction

This work is the continuation of paper [1], in which we analysed the scheme of basic processes describing the chain decomposition reaction of RI iodides in the active medium of a pulsed chemical oxygen–iodine laser (COIL),



and instead of the complete system of differential equations (SDE1) constructed using the scheme of reactions (1)–(8), we derived a simplified system of nonlinear differential equations in dimensionless variables (SDE3), which corresponded to this scheme:

$$\frac{dx}{d\tau} = \varepsilon y(u - 1)x, \quad (9)$$

$$\frac{dv}{dx} = \frac{u + 1}{u - 1} - \frac{A}{u - 1} \frac{v}{x}, \quad (10)$$

$$\frac{du}{d\tau} = \frac{1}{a} \varepsilon y x (D + 1 - u), \quad (11)$$

$$\frac{dy}{d\tau} = -b\varepsilon(3u + 1)yx - By \frac{x - 1 + au}{a}, \quad (12)$$

as well as found the main parameters determining the development of the branching chain reaction and briefly discussed the scheme of the approximate solution of SDE3. (Table 1 presents the rate constants of reactions (1)–(7) and Appendix 1 – dimensionless variables and parameters entering SDE3.)

Table 1. Rate constants of reactions (1)–(7) at $T \approx 300$ K.

| Constant/ $cm^3 s^{-1}$ | Radical | |
|----------------------------|--|--|
| | CF_3 | CH_3 |
| $K_1^{(*)}$ | 6×10^{-29} [2] | 6×10^{-29} [2] |
| K_2 | 2.7×10^{-11} [3] | 2.7×10^{-11} [3] |
| $K_{-2}^{(**)}$ | 7.8×10^{-11} [3] | 7.8×10^{-11} [3] |
| K_3 | 2×10^{-14} [4] | 2×10^{-14} [4] |
| K_4 | 10^{-12} | 10^{-12} (determined in [5] for CF_3I ; due to the proximity of binding energies R–I for CF_3I and CH_3I , the values K_4 are assumed equal) |
| K_5 | 1.1×10^{-13} [6] | 1.6×10^{-12} (estimated by analysing data [7, 8]) |
| K_6 | 2.5×10^{-12} (estimated for conditions of this paper by using data [9]) | 2.5×10^{-13} (estimated for conditions of this paper by using data [10]) |
| K_7 | 3.0×10^{-11} [4] | 3.0×10^{-11} [4] |

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

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The specific features of SDE3 equations make it possible to divide the chain reaction of RI decomposition into four stages differing by the range of changes in the concentration of ICl molecules (the dimensionless variable $u = [\text{ICl}]/[\text{ICl}]_{\text{cr}}$) – the main particles determining branching, i.e. transformation of a simple chain reaction into a branching one [1]. In paper [1], we analysed the first two time intervals corresponding to two ranges of u variations: $0 \leq u \leq 1$ and $1 < u \leq 2$. By solving approximately SDE3 for these ranges of u variations, we obtained the criteria for the development of the branching chain reaction of RI decomposition in the dark zone of a pulsed COIL.

In this paper, we studied the further development of the branching chain reaction of RI decomposition and derived approximate expressions for calculating the limiting parameters of this reaction. These parameters include the final degree of RI decomposition, the maximum concentration of excited iodine atoms, the time of its achievement, and the concentration of singlet oxygen and iodide at that moment. The obtained expressions make it possible to predict the course of the chain reaction and, by selecting the starting concentrations of initial substances, to control the rate of RI decomposition, for example, to suppress the undesirable dark decomposition of RI or use it as a chemical source of iodine atoms in a pulsed COIL.

2. Analysis of the third stage of the development of the chain reaction ($2 \leq u \leq u^*$)

2.1 Brief description

Consider how the sum of concentrations of iodine atoms changes at the third stage. At $u = 2$, the quantity $x = ([\text{I}^*] + [\text{I}])/(2[\text{I}_2]_0)$ is still small and close to its initial value $x = x_2 \sim 1$ [see (A2.2) in [1]], but at $u > 2$, the value of x increases with increasing the rate. In this case, the ratio of the concentration of Cl atoms ($v = [\text{Cl}]/(2[\text{I}_2]_0)$) and the sum $([\text{I}^*] + [\text{I}])$ also increases: $v/x \simeq (v/x)_{\text{stat}} \rightarrow (v/x)_{\text{max}} \lesssim 1$ [see (A3.1), (A3.4)]. At $\tau > \tau_2$ ($u > 2$), according to (11), the concentration $[\text{ICl}]$ continues to increase. However, the derivative du/dt decreases with increasing u , and at $\tau = \tau_3$, the concentration $[\text{ICl}]$ achieves its maximum $u_{\text{max}} = D_{\text{max}} + 1$ determined from equation (11) at $du/d\tau = 0$. The peculiarities of the dependence $u(\tau)$ allows one to restrict the following (third) time interval of the chain decomposition of RI by the inequality $\tau_2 \leq \tau \leq \tau_3$, where τ_3 is the time of achievement of u_{max} . The dependence $x(u)$ at the third time interval is determined by expression (A2.2) from [1] at $u_0 = 2$ and $x_0 = x_2$:

$$u - 2 + D \ln \left(1 - \frac{u - 2}{D - 1} \right) = -\frac{x - x_2}{a}, \quad (13)$$

which does not allow the values of $x(\tau_3)$ to be determined, because at $u_{\text{max}} = D_{\text{max}} + 1$, the expression under the logarithm sign is equal to zero. Thus, as an upper time boundary of the third stage we will conventionally take the instant τ^* ($\tau^* \lesssim \tau_3$), when

$$x^* - 1 = au^*, \quad (14)$$

i.e. when the sum of concentrations of iodine atoms minus $2[\text{I}_2]_0$ becomes equal to the concentration $[\text{ICl}]$ [in expression (14), $x^* = x(\tau^*)$, $u^* = u(\tau^*)$]. By solving equa-

tion (13) under conditions (14), we obtain that the ratio $(u^* - 1)/D^*$, equal to ~ 0.8 at $D \gg 1$ and ~ 0.9 at $D = 3$, is close to unity in a wide range of variations in D . Because $u^* \lesssim (D^* + 1)$ and $D^* \lesssim D_{\text{max}}$, $u^* \lesssim u_{\text{max}}$. By substituting these estimates into the equality $x^* - 1 = au^*$, we obtain

$$x^* \approx aD^* \lesssim aD_{\text{max}}. \quad (15)$$

(The expression for calculating D_{max} is presented in Appendix 3.) Using (15) and assuming in expression (A3.4) for D_{max} that $(v/x)_{\text{max}} \sim 1$, $[\text{RI}] = [\text{RI}]_0$, $[\text{Cl}_2] = [\text{Cl}_2]_0$, $y \approx 1$ (weak quenching), we obtain the upper estimate for D_{max} , x^* and the decomposition degree η_{RI}^* at $\tau = \tau^*$ for the case of weak quenching [hereafter, ‘weak quenching’ and ‘strong quenching’ are used to characterise the efficiency of O_2^* quenching by RO_2 radicals in reaction (8)]:

$$D_{\text{max}} \lesssim \frac{K_4}{K_3 \varepsilon} \frac{[\text{RI}]_0}{[\text{Cl}_2]_0},$$

$$x^* < \frac{K_4}{K_7 \varepsilon} \frac{[\text{RI}]_0}{2[\text{I}_2]_0}, \quad (16)$$

$$\eta_{\text{RI}}^* < \frac{2K_4}{K_7 \varepsilon} \ll 1.$$

At $[\text{O}_2^*]/[\text{O}_2] \sim 1$ ($\varepsilon \approx 0.75$), it follows from (16) that $\eta_{\text{RI}}^* < 0.09 \ll 1$. Thus, despite a considerable increase in the RI decomposition rate at the third stage, the concentration of RI and Cl_2 still weakly differs from the initial.

In the presence of quenching (8), the RI decomposition rate decreases, because the concentration of singlet oxygen decreases and, hence, the rate of initiation of the branching chain reaction also decreases. It is obvious that in the case of strong quenching, condition (14) will not be fulfilled, i.e. the following (fourth) stage, which is characterised by a drastic increase in the RI decomposition rate (see below), is not realised. As a critical value of K_8 determining the development of the fourth stage, we will use K_8^* for which the maximum of the concentration of excited iodine atoms $[\text{I}^*]_{\text{max}} = [\text{I}^*](\tau_{\text{max}})$ is achieved at $\tau_{\text{max}} = \tau^*$. Thus, to determine the basic parameters of the third stage, we will consider two cases: $K_8 < K_8^*$ (weak and moderate quenching) and $K_8 \gtrsim K_8^*$ (strong quenching).

2.2 Determination of characteristics of the third stage in the case of weak quenching ($\tau_{\text{max}} > \tau^*$)

In the case of weak quenching, the maximum of the concentration $[\text{I}^*]_{\text{max}}$ is achieved at $\tau_{\text{max}} > \tau^*$, and, hence, the main parameters of the third stage are the quantities x^* , u^* , y^* , τ^* .

The value of $x^* = au^* + 1$ is unambiguously determined by the known value of u^* . By substituting this expression into (13), we obtain an expression containing two variables (u^* and D^*),

$$\frac{2(u^* - 1)}{D^*} + \ln \left(1 - \frac{u^* - 2}{D^* - 1} \right) = -\frac{1 - x_2}{aD^*}, \quad (17)$$

where D^* is the average value of the parameter D during the variation in u in the range $2 \leq u \leq u^*$. Note that $x_2 \approx 1$,

and the product $aD^* > 1$, therefore, the right-hand side of equation (17) is close to zero.

In Appendix 3 we obtained general expression (A3.3) to calculate D_{av} – the average value of D for the given range $u_1 \leq u \leq u_2$. By assuming in (A3.3) that $u_{av} = \frac{1}{2}(u^* + 2)$, $D = D^*$, we have the second equation for determining u^* , D^* :

$$D^* = N_{av} \left(\frac{u^*}{2} + 2 \right) \left\{ 1 + \frac{u^*}{2} (\varepsilon y N)_{av} \frac{K_3 [Cl_2]_0}{K_4 [RI]_0} \right\}^{-1}. \quad (18)$$

The right-hand side of (18) includes the average values of N and $\varepsilon y N$ when varying u in the range $2 \leq u \leq u^*$, which weakly depend on the variable y ($y_2 \leq y \leq y^*$) [see Appendix 1 and (A4.2)]. The estimates by expression (18) taking into account the dependences of $\varepsilon(y)$ and $N(y)$ show that D^* rather weakly depends on y . Nevertheless, the values of u^* , D^* , and y^* were found by solving together the system of equations (17), (18), and (A2.4), respectively. While solving this system, we used the method of successive approximations. The value of x^* was determined by expression (14).

Let us estimate τ^* with the help of equation (9). Assuming $x_0 = x_2$, $\tau_0 = \tau_2 \approx 2\tau_{min}$ to be initial conditions [see A6.1 in [1]], we derive the expression for calculating τ^* – the time characteristic of the third stage,

$$\tau^* \approx 2\tau_{min} + \frac{\ln(x^*/x_2)}{(\varepsilon y)_{av}(u-1)_{av}}, \quad (19)$$

in which $(u-1)_{av} = [(u^* + 2)/2 - 1] = u^*/2$ and the product $(\varepsilon y)_{av}$ is calculated using the values of y_2 , y^* [see (A3.9) in [1] and (A2.4)]. Because the ratio $(u^*/u_{max}) \lesssim 1$ and at $\tau > \tau^*$ the rate of RI decomposition is large, we can assume that $\tau_3 \approx \tau^*$. The validity of this approximation is confirmed by numerical calculations. The calculated values of x^* , u^* , D^* , y^* and τ^* are presented in Table 2.

2.3 Determination of limiting parameters of the chain decomposition of RI at the third stage in the case of strong quenching ($\tau_2 < \tau_{max} < \tau^*$)

Consider the case of strong quenching when the concentration of excited atoms has a maximum which is achieved at $\tau = \tau_{max}$, so that $\tau_2 < \tau_{max} < \tau^*$. Let us determine first the condition for the achievement of the maximum $[I^*]_{max}$. The dimensionless concentration I^* is given by the expression

$$[I^*]/(2[I_2]_0) = \varepsilon xy \quad (20)$$

{see (17) from paper [1] and determination of the parameter δ in Appendix 1}. $[I^*]_{max}$ can be found by solving the equation $d[I^*]/dt = 0$, which, taking into account (20), at $\varepsilon \approx const$ has the form

$$y + x \frac{dy}{dx} = 0. \quad (21)$$

By using expression (A2.5) for dy/dx , the dependence $y(x)$ [see (A2.2)] and the expression for calculating y_2 [see (A3.9) in [1]], we represent (21) in the form

$$\begin{aligned} \frac{\varepsilon}{B} \{1 - 3b[2x(\tau_{max}) - x_2]\} &= 1 + 4 \left[\frac{1 - x_{min}}{a} + \frac{a - 1}{a} \right. \\ &\times \left. \left(\frac{1 - x_{min}}{x_{min}} \right)^{1/2} \arctan \left(\frac{1 - x_{min}}{x_{min}} \right)^{1/2} \right] + \frac{x(\tau_{max}) - x_2}{aD_{av}} \\ &+ \frac{u(\tau_{max}) - 2}{D_{av}} + \frac{x(\tau_{max}) - 1}{a[u(\tau_{max}) - 1]} + \frac{1}{u(\tau_{max}) - 1} \\ &+ \left[1 + \frac{2(a - 1)}{au(\tau_{max})} \right] \ln \frac{x(\tau_{max})}{x_2}. \end{aligned} \quad (22)$$

Note that $3b[2x(\tau_{max}) - x_2] < 3\eta_{RI}^*[RI]_0/[O_2]_0 \ll 1$, and we

Table 2. The values of the main parameters and characteristics of the chain reaction of dark decomposition of CH_3I at different values of K_8 , calculated by using analytic expressions from this paper and paper [1] (I) and by solving numerically SDE1 (II) ($[CH_3I]_0 = 10^{16} \text{ cm}^{-3}$, $[Cl_2]_0 = 5 \times 10^{16} \text{ cm}^{-3}$, $[O_2]_0 = [O_2^*]_0 = 3 \times 10^{17} \text{ cm}^{-3}$, $[I_2]_0 = 10^{13} \text{ cm}^{-3}$).

| Parameters and characteristics | $K_8 = 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ | | $K_8 = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ | | $K_8 = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ | |
|--------------------------------|--|-------|---|--------|--|--------------|
| | I | II | I | II | I | II |
| D_2 | 4.8 | 5.0 | 4.7 | 4.9 | 4.6 | 5.0 |
| x_2 | 0.88 | 0.86 | 0.93 | 0.88 | 0.94 | 0.88 |
| y_2 | 0.98 | 0.98 | 0.87 | 0.89 | 0.75 | 0.78 |
| τ_2 | 1.8 | 1.8 | 1.85 | 1.85 | 2.0 | 1.9 |
| u^* | 7.1 | 7.4 | 7.1 | 8.3 | not achieved | not achieved |
| D^* | 7.3 | – | 7.3 | – | – | – |
| x^* | 12.8 | 13.2 | 12.8 | 14.9 | – | – |
| y^* | 0.88 | 0.87 | 0.40 | 0.39 | – | – |
| η_{RI}^* | 0.048 | 0.049 | 0.048 | 0.056 | – | – |
| τ^* | 2.8 | 3.2 | 3.0 | 3.5 | – | – |
| $\theta(\tau_{max})$ | 1.08 | 1.02 | 6.6 (7.9) | 7.5 | – | – |
| $\eta_{RI}(\tau_{max})$ | 0.48 | 0.56 | 0.13 (0.11) | 0.11 | 0.026 | 0.028 |
| $x(\tau_{max})$ | 230 | 264 | 53 (41) | 32.5 | 4.0 | 5.2 |
| $y(\tau_{max})$ | 0.40 | 0.37 | 0.21 (0.23) | 0.21 | 0.24 | 0.24 |
| $[I^*]_{max}/[RI]_0$ | 0.18 | 0.21 | 0.028 (0.023) | 0.0165 | 0.0027 | 0.0029 |
| τ_{max} | 3.6 | 3.8 | 3.3 (3.3) | 3.7 | 2.9 | 3.5 |
| η_{RI}^∞ | 1 | 1 | 0.45 (0.42) | 0.285 | 0.052 | 0.06 |

Note: the values of D_2 , x_2 , y_2 , τ_2 are calculated by using expressions from paper [1]; the value of $\theta(\tau_{max})$ in brackets is obtained under the assumption that $\theta = \theta(\tau_{max})D^*/(u^* - 1)$ (see section 4); other values in brackets are calculated at $\theta = \theta(\tau_{max})D^*/(u^* - 1) = 1.2\theta(\tau_{max})$.

can replace the multiplier $\{1 - 3b[2x(\tau_{\max}) - x_2]\}$ in the left-hand side of equation (22) by unity. The value of x_{\min} is determined by the expressions (22), (24) from [1]. The right-hand side of (22) contains three unknown quantities: $x(\tau_{\max})$, $u(\tau_{\max})$ and D_{av} , where D_{av} is the average value of D upon varying u in the range $2 \leq u \leq u(\tau_{\max})$. By combining together (22), (13) and expression (A3.3) for D_{av} , we obtain a system of three equations for determining $x(\tau_{\max})$, $u(\tau_{\max})$ and D_{av} . This system should be supplemented with the dependence $y(x)$ (A2.2) because the parameters ε and N entering equations (22), (A3.3) depend on y . The results of calculations of the limiting parameters of the dark decomposition of RI in the case of strong quenching ($K_8 = 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) are presented in Table 2.

K_8^* can be found by solving the system of equations (17), (18), (A2.4) and equation (22), in which the following changes should be made: $x(\tau_{\max}) \rightarrow x^* = au^* + 1$, $D_{\text{av}} \rightarrow D^*$, $u(\tau_{\max}) \rightarrow u^*$. Taking into account the $(1 - x_2)/aD^* \ll 1$ and $1 - 3b[2x(\tau_{\max}) - x_2] \approx 1$, we transform equation (22) to the form

$$\begin{aligned} \frac{\varepsilon}{B} = & 2 + 4 \left[\frac{1 - x_{\min}}{a} + \frac{a - 1}{a} \left(\frac{1 - x_{\min}}{x_{\min}} \right)^{1/2} \right. \\ & \times \arctan \left(\frac{1 - x_{\min}}{x_{\min}} \right)^{1/2} \left. \right] + \frac{2(u^* - 1)}{D^*} + \frac{2}{u^* - 1} \\ & + \left[1 + \frac{2(a - 1)}{au^*} \right] \ln \frac{au^* + 1}{x_2}. \end{aligned} \quad (23)$$

The value of K_8^* ($\sim 6.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) calculated in this way is close to K_8^* ($6.5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$) obtained by solving numerically SDE1 for the initial conditions specified in this paper.

To determine η_{RI}^∞ under conditions of strong quenching, we can use the above-described procedure by replacing equation (22) by equation (A2.2) and setting $y(x) = 0$.

However, there exists a simpler way to estimate η_{RI}^∞ . Degenerate branching chain reactions belong to the class of autocatalytic reactions. The characteristic feature of the kinetics of such reactions consists in the fact that the decomposition rate of the initial substance in them is proportional to the product $(1 - \eta)\eta$, where η is the degree of decomposition of the initial substance. This dependence leads to the fact that the decomposition rate has a maximum and the degree of decomposition η at this instant of time τ_{\max} is approximately half the final degree of decomposition η^∞ , i.e. $\eta(\tau_{\max}) \approx \frac{1}{2}\eta^\infty$ [11]. The data of Table 2 confirm this result.

3. Analysis of the fourth stage of the development of the chain reaction ($\tau^* < \tau < \tau_4$)

The fourth stage of the chain decomposition of RI is realised in the case of weak quenching, i.e. at $K_8 < K_8^*$. At this stage $d[\text{ICI}]/dt \approx 0$ and the RI decomposition rate is equal to the rate of production of iodine atoms, which results in a rapid growth in the sum of concentrations of iodine atoms. Note that the concentration $[\text{ICI}]$ and the parameter D at $\tau > \tau^*$ can change, however, the approximate equality

$$u - 1 \approx D \quad (24)$$

is preserved, i.e. the condition of $[\text{ICI}]$ quasi-stationarity is fulfilled. The concentration $[\text{I}^*]$ increases and at $\tau = \tau_{\max}$ achieves a maximum $[\text{I}^*]_{\text{max}}$. The presence of the maximum in the dependence $[\text{I}^*](t)$ is caused by the relaxation of singlet oxygen [reaction (8)]. Indeed, in the case of rapid decomposition of RI, concentrations of not only iodine and chlorine atoms, but also of radicals RO_2 increase, and, hence, the concentration $[\text{O}_2^*]$ decreases, which in turn restricts the growth of $[\text{I}^*]$ during reaction (1) and (2). At $\tau > \tau_{\max}$, the concentrations $[\text{O}_2^*]$ and $[\text{I}^*]$ drastically decrease and tend to zero. In this case, the RI decomposition rate also decreases and the concentration $[\text{RI}]$ tends to its final value $[\text{RI}]^\infty$. The temporal width of the peak on the curve $[\text{I}^*](t)$ at $\tau \sim \tau_{\max}$ is usually smaller than τ_{\max} . Because of this, we will restrict our further analysis to the interval $\tau^* < \tau \leq \tau_4$, where $\tau_4 = \tau_{\max}$.

The quantities $\eta_{\text{RI}}(\tau_{\max})$, $y(\tau_{\max})$, $x(\tau_{\max})$ and $[\text{I}^*]_{\text{max}}/(2[\text{I}_2]_0)$ can be determined by solving equation (21) under the conditions of the fourth stage. By introducing a new variable η_{RI} and using (A2.9), we will write equation (21) for $\tau = \tau_{\max}$ in the form

$$\begin{aligned} y(\tau_{\max}) = & \frac{3[\text{RI}]_0}{[\text{O}_2^*]_0} \left[\eta_{\text{RI}}(\tau_{\max}) - \frac{\eta_{\text{RI}}^*}{2} \right] \\ & + \frac{\theta(\tau_{\max})\eta_{\text{RI}}(\tau_{\max})y(\tau_{\max})}{1 - \eta_{\text{RI}}(\tau_{\max})}. \end{aligned} \quad (25)$$

The parameter $\theta = K_8/[K_4N(v/x)]$ determines the efficiency of the influence of quenching (8) on the RI decomposition rate. Note that the value of $\theta(\tau_{\max})$ entering expression (25) is calculated for $N(v/x) = [N(v/x)](\tau_{\max})$, which weakly depends on $\eta_{\text{RI}}(\tau_{\max})$ and $y(\tau_{\max})$ [see (A4.4)].

By combining equation (25), expression (A2.9) for the dependence $y(\eta_{\text{RI}})$ and expression (A4.4) (see above), we obtain a system of three equations for determining $\eta_{\text{RI}}(\tau_{\max})$, $y(\tau_{\max})$ and $\theta(\tau_{\max})$. Equation (25) can be simplified if the inequality $3[\text{RI}]_0/[\text{O}_2^*]_0 \ll 1$, which is usually fulfilled for typical compositions of the active media of a pulsed COIL, is valid. This allows one to neglect the first term in the right-hand side of (25) and derive directly the equation

$$\frac{\theta(\tau_{\max})\eta_{\text{RI}}(\tau_{\max})}{1 - \eta_{\text{RI}}^{\text{max}}} = 1 \quad (26)$$

for finding $\eta_{\text{RI}}^{\text{max}}$. We obtain from (26)

$$\eta_{\text{RI}}(\tau_{\max}) = [1 + \theta(\tau_{\max})]^{-1}. \quad (27)$$

Thus, $\eta_{\text{RI}}(\tau_{\max})$, $y(\tau_{\max})$ and $\theta(\tau_{\max})$ can be found by solving in the first approximation expressions (27), (A4.4) and equation (A2.9) and in the general case, when it is impossible to use approximation (26), they are found by solving the system of equations (25), (A2.9), (A4.4).

To determine $x(\tau_{\max})$ and $[\text{I}^*]_{\text{max}}/(2[\text{I}_2]_0)$ we will use the expressions

$$x(\tau_{\max}) = \frac{[\text{RI}]_0}{2[\text{I}_2]_0} \left[\eta_{\text{RI}}(\tau_{\max}) - \frac{\eta_{\text{RI}}^*}{2} \right], \quad (28)$$

$$\frac{[\text{I}^*]_{\text{max}}}{2[\text{I}_2]_0} = \varepsilon(\tau_{\max})x(\tau_{\max})y(\tau_{\max}).$$

They are valid at $\eta_{\text{RI}}(\tau_{\max}) \gg \frac{1}{2}\eta_{\text{RI}}^*$. By substituting the

values of $\eta_{\text{RI}}(\tau_{\text{max}})$ and $y(\tau_{\text{max}})$ into (28), we determine $x(\tau_{\text{max}})$ and $[I^*]_{\text{max}}/(2[I_2]_0)$. The quantity of ε weakly depends on y (see Appendix 1). The value of $\varepsilon(\tau_{\text{max}})$ is calculated for $y(\tau_{\text{max}})$.

Let us estimate τ_{max} by solving equation (9). By assuming $x_0 = x^*$, $\tau_0 = \tau^*$ to be initial conditions [see (19)], we obtain the expression for calculating the temporal characteristic of the fourth stage:

$$\tau_{\text{max}} \approx \tau^* + \frac{\ln[x(\tau_{\text{max}})/x^*]}{(u-1)_{\text{av}}(\varepsilon y)_{\text{av}}}, \quad (29)$$

in which $(u-1)_{\text{av}} \approx u^* - 1$, and the product $(\varepsilon y)_{\text{av}}$ is calculated by using the values of $y(\tau_{\text{max}})$ and y^* [see (A2.9), (A2.4)].

The dependence $y(x)$ makes it possible to determine η_{RI}^∞ . For this purpose, it is necessary to compare successively the quantities y_1, y_2, y^* with zero, i.e. to find the time interval at the end of which the rate of the chain reaction becomes equal to zero, and after this, to solve the equation $y(x) = 0$ for the interval specified. Consider the case of weak quenching, when the fourth stage of the chain decomposition of RI is realised and the values of η_{RI}^∞ , close to unity, can be achieved. By assuming in (A2.9) that $y(\eta_{\text{RI}}^\infty) = 0$, we find η_{RI}^∞ from the equation

$$(1 - \eta_{\text{RI}}^\infty) \left\{ 1 - \left[1 + \frac{(\theta - 1)y^*[O_2^*]_0}{3[RI]_0(1 - \eta_{\text{RI}}^*)} \right] \left(\frac{1 - \eta_{\text{RI}}^\infty}{1 - \eta_{\text{RI}}^*} \right)^{\theta - 1} \right\} = 0. \quad (30)$$

Equation (30) is decomposed into two equations:

$$\eta_{\text{RI}}^\infty = 1, \quad (31)$$

$$\left(\frac{1 - \eta_{\text{RI}}^\infty}{1 - \eta_{\text{RI}}^*} \right)^{\theta - 1} = \left[1 + \frac{(\theta - 1)y^*[O_2^*]_0}{3[RI]_0(1 - \eta_{\text{RI}}^*)} \right]^{-1}. \quad (32)$$

The solution of equation (32) exists if its right-hand side is more than zero, i.e. at $\theta \geq \theta_{\text{cr}} = 1 - 3[RI]_0(1 - \eta_{\text{RI}}^*) \times (y^*[O_2^*]_0)^{-1}$. If $\theta \leq \theta_{\text{cr}} < 1$ (weak quenching, $K_8 \lesssim K_4$), equation (32) does not have solutions and, hence, expression (31) is valid, i.e. $\eta_{\text{RI}}^\infty = 1$. At $\theta > \theta_{\text{cr}}$, η_{RI}^∞ is smaller than unity and is determined from equation (32). Let us estimate θ_{cr} . Under typical conditions of the active media of a pulsed COIL, the inequality $3[RI]_0/[O_2^*]_0 \ll 1$ is valid. Because $\eta_{\text{RI}}^* \ll 1$, we have $1 - \eta_{\text{RI}}^* \sim 1$. By assuming that during weak quenching $y^* \sim 1$, we obtain the upper estimate $\theta_{\text{cr}} \approx 1$. Using this estimate we will write the final expression for determining η_{RI}^∞ :

$$\eta_{\text{RI}}^\infty = 1 \text{ at } \theta \leq 1, \quad (33)$$

$$\ln \frac{1 - \eta_{\text{RI}}^\infty}{1 - \eta_{\text{RI}}^*} = - \left\{ \ln \left[1 + \frac{(\theta - 1)y^*[O_2^*]_0}{3[RI]_0(1 - \eta_{\text{RI}}^*)} \right] \right\} \frac{1}{\theta - 1} \text{ at } \theta > 1.$$

4. Discussion of the results

Figure 1 presents the time dependences of relative concentrations of CH_3I , I^* and O_2^* during the dark decomposition of CH_3I at different K_8 under the same starting concentrations of initial substances of the active medium. The data of Table 2 and Fig. 1 demonstrate a satisfactory coincidence of the results obtained by using expression of the

paper with the results of the numerical solution of SDE1. Let us analyse the effect of K_8 on the limiting parameters of the dark decomposition of CH_3I . In the case of weak quenching, when $\theta \leq 1$ ($K_8 = 10^{-12} \text{ cm}^3 \text{ s}^{-1} < K_8^*$) complete decomposition of RI takes place ($\eta_{\text{RI}}^\infty = 1$). Note that at the moment when the maximum concentration of excited iodine atoms ($\tau = \tau_{\text{max}}$) is achieved, the degree of decomposition is $\eta_{\text{RI}}(\tau_{\text{max}}) \sim 0.5$ and the concentration of singlet oxygen is $\sim 40\%$ of the initial value. Therefore, the maximum concentration of the excited iodine atoms is very large ($\sim 20\%$ of the initial concentration $[RI]_0$).

In another limiting situation – in the case of strong quenching, when $\theta > 10 \gg 1$ ($K_8 = 10^{-11} \text{ cm}^3 \text{ s}^{-1} > K_8^*$), – the final degree of RI decomposition is very small: $\eta_{\text{RI}}^\infty \approx 0.05 < \eta_{\text{RI}}^*$ [see (16)]. The degree of RI decomposition at $\tau = \tau_{\text{max}}$, as in the case of weak quenching, is approximately half the limiting degree of RI decomposition: $\eta_{\text{RI}}(\tau_{\text{max}}) \sim \frac{1}{2} \eta_{\text{RI}}^\infty$. The concentration $[O_2^*]$ at $\tau = \tau_{\text{max}}$

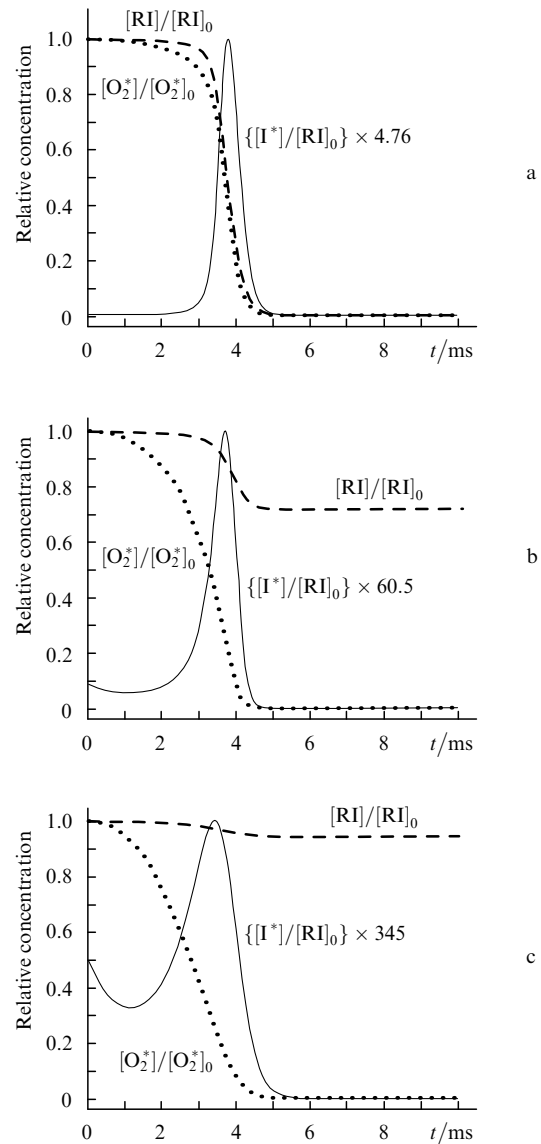


Figure 1. Time dependences of relative concentrations of CH_3I , I^* and O_2^* during the dark decomposition of CH_3I obtained by solving numerically SDE1 at $K_8 = 10^{-12}$ (a), 5×10^{-12} (b) and $10^{-11} \text{ cm}^3 \text{ s}^{-1}$ (c) ($[\text{CH}_3\text{I}]_0 = 10^{16}$, $[\text{Cl}_2]_0 = 5 \times 10^{16}$, $[\text{O}_2]_0 = [\text{O}_2^*]_0 = 3 \times 10^{17}$, and $[\text{I}_2]_0 = 10^{15} \text{ cm}^{-3}$).

decreased but not drastically compared to the case of weak quenching [$y(\tau_{\max}) \sim 0.24$] and the concentration of excited atoms $[I^*]_{\max}$ decreased by more than 70 times and only slightly exceeded the initial concentration of iodine atoms ($2[I_2]_0$).

In the intermediate case of moderate quenching ($\theta \approx 6.6$, $K_8 = 5 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1} \leq K_8^*$), when the degree of RI decomposition at $\tau = \tau_{\max}$ slightly exceeds the degree of RI decomposition at $\tau = \tau^*$, the condition $\eta_{\text{RI}}(\tau_{\max}) \gg \eta_{\text{RI}}^*$ is not fulfilled. Table 2 presents the results of calculations for this case obtained by expressions for weak quenching. The observed small discrepancy with the results of numerical calculations is explained by the fact that the main condition for realisation of the fourth stage ($u - 1 = D$) is not fulfilled and the inequality $(u^* - 1)/D^* \lesssim (u - 1)/D < 1$ is valid, which results in the increase in the parameter θ_{\max} . The results of calculations performed for $\theta = \theta(\tau_{\max})[D^*/(u^* - 1)] \approx 1.2\theta(\tau_{\max})$ demonstrate a satisfactory coincidence with the results of numerical calculations (see Table 2).

The obtained results make it possible to assert that the limiting parameters of the branching chain reaction of dark decomposition of RI are determined mainly by two dimensionless parameters: $\theta = K_8/[K_4N(v/x)]$ in the case of weak and moderate quenching and by $B/\varepsilon = K_8/(K_7N\varepsilon)$ in the case of strong quenching. Both these parameters contain the characteristic of three stages of the branching chain reaction: initiation of the chain, its continuation and break.

The parameter N is the main characteristic of the stage of the chain continuation [reactions (4)–(6)] because it is equal to the number of chain links. The constant K_8 determines the relaxation rate of singlet oxygen, i.e. the disappearance rate of I^* atoms – active centres responsible for branching. The rate of the chain initiation is the rate of reaction (7). In the case of weak quenching, the rate reaction (7) is maximal and equal to the RI decomposition rate, i.e. to the rate of reaction (4) and, hence, the parameter θ depends on K_4 . In the case of strong quenching, the rate reaction (7) does not achieve its maximum and, hence, this reaction is a limiting stage of the chain decomposition of RI and its main characteristic (the parameter B) depends on K_7 .

5. Conclusions

We have analysed the scheme of basic reactions describing the chain reaction of RI decomposition in the dark zone of a pulsed COIL. Based on this analysis and the approximate solution of SDE3, we studied the third and the fourth stages of the development of the chain reaction of RI decomposition. We have established that the fourth stage is realised only in the case of weak quenching of singlet oxygen by peroxide radicals, which is determined by the condition $K_8 < K_8^*$, and only in this case the effective decomposition of RI iodide ($\eta_{\text{RI}} = 0.2 - 1.0$) takes place and a considerable concentration of I^* atoms ($[I^*]_{\max}/[RI]_0 \approx 0.2$) is produced.

We have obtained approximate expressions to calculate the limiting parameters of the chain reaction: the final degree of RI decomposition, the maximum concentration of excited iodine atoms, the time of its achievement, the concentration of singlet oxygen and iodide at that moment. These parameters calculated for a typical composition of the active medium of a pulsed COIL show good coincidence with the results of numerical calculations.

The results obtained in this paper make it possible to predict the development of dark processes in the active medium of a pulsed COIL and to control them by selecting directly the composition of this medium. A detailed discussion of the results of this paper and paper [1] for optimisation of operation of a pulsed COIL will be presented elsewhere.

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Appendix 1

Dimensionless variables

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

$$\eta_{\text{RI}} = \frac{[RI]_0 - [RI]}{[RI]_0} = (x - 1 + au) \frac{2[I_2]_0}{[RI]_0}.$$

Parameters

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

$$N = 1 + \frac{K_5[Cl_2]}{K_6[O_2]}; \quad \delta = \frac{[I^*]}{[I^*] + [I]} = \varepsilon y;$$

$$\varepsilon = \frac{K_{\text{eq}}(K_{\text{eq}} - 1)^{-1}}{y + (1 + [O_2]_0/[O_2^*]_0)(K_{\text{eq}} - 1)^{-1}},$$

where $K_{\text{eq}} = K_{-2}/K_2$ {the parameter ε is a slowly varying function of y ; thus, at $[O_2^*]_0 = [O_2]_0$ for $T = 300 \text{ K}$ ($K_{\text{eq}} \approx 2.9$) $\varepsilon \approx 0.75$ for $y = 1$ and $\varepsilon \approx 1.5$ for $y = 0$, i.e. $\varepsilon \approx 1$ };

$$A = \frac{K_4[RI]}{K_3[Cl_2]} \frac{1}{N\varepsilon y}; \quad D = \frac{K_4[RI][Cl]}{K_3[Cl_2][I^*]} = \frac{K_4[RI]}{K_3[Cl_2]} \frac{v}{x} \frac{1}{\varepsilon y} = AN \frac{v}{x};$$

$$B = \frac{K_8}{K_7 N}; \quad b = \frac{2[I_2]_0}{[O_2^*]_0}; \quad \theta = \frac{K_8}{K_4 N(v/x)}.$$

Appendix 2

The third stage: $2 \leq u \leq u^$*

Let us write equation (A3.5) from paper [1] in the form

$$dy = -3bdx - \frac{B}{a\varepsilon(u-1)} dx - \frac{B}{\varepsilon} \left[1 + \frac{a-1}{a(u-1)} \right] \frac{dx}{x} \quad (\text{A2.1})$$

and analyse its last term. The multiplier $\{1 + (a-1) \times [a(u-1)]^{-1}\}$ satisfying the inequality $1 < \{1 + (a-1) \times [a(u-1)]^{-1}\} < 2$ at $a > 1$ is a weakly changing function of u . Assuming it to be a parameter and replacing dx by $(dx/du)du$ {see (A2.1) from [1]} in the second term in the right-hand side of (A2.1), we will integrate equation (A2.1) at the following initial conditions: $u_0 = 2$, $x_0 = x_2$, $y_0 = y_2$. By using (13), we will represent the obtained dependence $y(x)$ in the form

$$y(x) = y_2 - 3b(x - x_2) - \frac{B}{\varepsilon} \left\{ \frac{x - x_2}{aD} + \frac{u - 2}{D} + \left[1 + \frac{a - 1}{a(u - 1)} \right] \ln \frac{x}{x_2} \right\}. \tag{A2.2}$$

By setting $D = D^*$, $x^* = au^* - 1$ and taking into account that the equality $(a - 1)/[a(u - 1)] = 2(a - 1)/(au^*)$ is fulfilled at $2 \leq u \leq u^*$, we obtain

$$y^* = y_2 - 3bau^* - \frac{B}{\varepsilon} \left\{ \frac{2(u^* - 1)}{D^*} + \left[1 + \frac{2(a - 1)}{au^*} \right] \times \ln \frac{au^* + 1}{x_2} \right\}. \tag{A2.3}$$

When deriving equation (A2.3) we took into account that $x_2 \approx 1$, $aD^* \gg 1$, $u^*/D^* \sim 1$. By substituting the expression for y_2 {see (A3.9) from [1]} into (A2.3), we derive the final expression for calculating y^* :

$$y^* \simeq 1 - 3bau^* - \frac{B}{\varepsilon} \left\{ 4 \left[\frac{1 - x_{\min}}{a} + \frac{a - 1}{a} \left(\frac{1 - x_{\min}}{x_{\min}} \right)^{1/2} \times \arctan \left(\frac{1 - x_{\min}}{x_{\min}} \right)^{1/2} \right] + \frac{2(u^* - 1)}{D^*} + \left[1 + \frac{2(a - 1)}{au^*} \right] \ln \frac{au^* + 1}{x_2} \right\}. \tag{A2.4}$$

The fourth stage: $\tau^* \leq \tau \leq \tau_4$

Let us write expression (A3.5) from paper [1] in the form

$$\frac{dy}{dx} = -3b - \frac{B(x - 1 + au)}{\varepsilon a(u - 1)x}. \tag{A2.5}$$

Then, assuming that

$$u - 1 = D = \frac{K_4[\text{RI}]}{K_3[\text{Cl}_2]} \frac{v}{x} \frac{1}{\varepsilon y},$$

and using expressions for a and B , we obtain

$$\frac{dy}{dx} = -3b - \theta(x - 1 + au) \frac{2[\text{I}_2]_0}{[\text{RI}]} \frac{y}{x}, \tag{A2.6}$$

where $\theta = K_8/[K_4 N(v/x)]$. By introducing the variable $\eta_{\text{RI}} = 1 - [\text{RI}]/[\text{RI}]_0^{-1}$ and taking into account that

$$x - 1 + au = \frac{\eta_{\text{RI}}[\text{RI}]_0}{2[\text{I}_2]_0}, \quad x \simeq \frac{[\text{RI}]_0}{2[\text{I}_2]_0} \left(\eta_{\text{RI}} - \frac{\eta_{\text{RI}}^*}{2} \right), \tag{A2.7}$$

we obtain

$$\frac{dy}{d\eta_{\text{RI}}} = -\frac{3[\text{RI}]_0}{[\text{O}_2^*]_0} - \theta y \eta_{\text{RI}} \left[(1 - \eta_{\text{RI}}) \left(\eta_{\text{RI}} - \frac{\eta_{\text{RI}}^*}{2} \right) \right]^{-1}, \tag{A2.8}$$

where $\eta_{\text{RI}}^* \ll 1$ is the degree of RI decomposition at the end of the third stage [see (16)]. At $\eta_{\text{RI}}/\eta_{\text{RI}}^* \gg 1$, we have the ratio $\eta_{\text{RI}}/(\eta_{\text{RI}} - \frac{1}{2}\eta_{\text{RI}}^*) \sim 1$, and hence, the solution of equation (A2.8) has the form

$$y = \frac{3[\text{RI}]_0}{[\text{O}_2^*]_0} \frac{1 - \eta_{\text{RI}}}{1 - \theta} + \left[y^* - \frac{3[\text{RI}]_0}{[\text{O}_2^*]_0} \frac{1 - \eta_{\text{RI}}^*}{1 - \theta} \right] \left(\frac{1 - \eta_{\text{RI}}}{1 - \eta_{\text{RI}}^*} \right)^\theta.$$

At $\theta \approx 1$, equation (A2.9) is transformed to the form

$$y \approx y^* \left(\frac{1 - \eta_{\text{RI}}}{1 - \eta_{\text{RI}}^*} \right)^\theta - \frac{3[\text{RI}]_0}{[\text{O}_2^*]_0} (1 - \eta_{\text{RI}}) \eta_{\text{RI}}. \tag{A2.10}$$

Appendix 3

Determination of the dependence $D(u)$

By using expressions of Appendix 4 from paper [1], we represent the expression for calculating the parameter D in the form

$$D = AN \frac{v}{x} = AN \left(\frac{v}{x} \right)_{\text{stat}} \varphi(\tau) = AN \frac{u + 1}{A + u - 1} \varphi(\tau), \tag{A3.1}$$

where $(v/x)_{\text{stat}} = (u + 1)/(A + u - 1)$ is a weakly changing function of u and the explicitly time-dependent function $\varphi(\tau) \approx \text{const} = 1$ already at $u \gtrsim 2$. By setting $\varphi(\tau) = 1$ in (A3.1), we obtain at $u \gtrsim 2$

$$D(u) = \frac{N(u + 1)}{1 + (u - 1)/A}. \tag{A3.2}$$

Determination of D_{av} – the average value of the parameter D in the given range $u_1 \leq u \leq u_2$ ($u_1 \geq 2$, $u_2 \leq u^*$)

We will use expression (A3.2) to determine D_{av} . At the third stage the degrees of RI and Cl_2 decomposition are small [see (16)], and, hence, we can assume that the concentrations of RI and Cl_2 molecules entering into the expression for A (see Appendix 1) are equal to their initial concentrations. Taking this into account and setting in (A3.2) $u = u_{\text{av}} = \frac{1}{2}(u_1 + u_2)$, we obtain an expression to calculate the average value of the parameter D in the given range of u variations

$$D_{\text{av}} = N_{\text{av}}(u_{\text{av}} + 1) \left[1 + (u_{\text{av}} - 1)(\varepsilon y N)_{\text{av}} \frac{K_3[\text{Cl}_2]_0}{K_4[\text{RI}]_0} \right]^{-1}. \tag{A3.3}$$

Determination of D_{max}

Solving equation (A3.2) at $u = u_{\text{max}} = D_{\text{max}} + 1$, we obtain

$$D_{\text{max}} = AN \left(\frac{v}{x} \right)_{\text{max}}, \tag{A3.4}$$

$$\left(\frac{v}{x} \right)_{\text{max}} = \frac{N - 1}{N} \frac{1}{2} \left\{ 1 + \left[1 + \frac{8}{AN} \left(\frac{N}{N - 1} \right)^2 \right]^{1/2} \right\}.$$

At the third stage (see above),

$$AN \approx \frac{(AN)_0}{\varepsilon y}, \quad (AN)_0 = \frac{K_4[\text{RI}]_0}{K_3[\text{Cl}_2]_0}. \tag{A3.5}$$

By substituting A3.5) into (A3.4) we obtain

$$D_{\text{max}} = \frac{(AN)_0}{\varepsilon y} \frac{N - 1}{N} \times \frac{1}{2} \left\{ 1 + \left[1 + \frac{8}{(AN)_0} \varepsilon y \left(\frac{N}{N - 1} \right)^2 \right]^{1/2} \right\}. \tag{A3.6}$$

Appendix 4

Let us analyse the dependence of the product $N(v/x)$ on y (the concentration $[O_2^*]$ for the fourth stage ($\tau^* \leq \tau \leq \tau_{\max}$). At the fourth stage, condition (24) is fulfilled, and hence, using expression for $(v/x)_{\max}$ from (A3.4), we obtain

$$N\left(\frac{v}{x}\right) = (N-1) \frac{1}{2} \left\{ 1 + \left[1 + \frac{8}{AN} \left(\frac{N}{N-1} \right)^2 \right]^{1/2} \right\}. \quad (\text{A4.1})$$

Let us estimate the dependence of $N(v/x)$ on $y(\tau_{\max})$. Note that the large degrees of RI decomposition can be achieved in the case if the ratio $[Cl_2]_0/[RI]_0$ exceeds unity at least by several times. Thus, we can assume that at the fourth stage $[Cl_2] = [Cl_2]_0$. By setting in the expression for N (see Appendix 1) $\{[Cl_2] = [Cl_2]_0$ and taking into account that $[O_2] = [O_2]_0(1 + ([O_2^*]_0/[O_2]_0)(1-y))\}$, we obtain

$$N = 1 + (N_0 - 1) \left[1 + \frac{[O_2^*]_0}{[O_2]_0} (1-y) \right]^{-1}, \quad (\text{A4.2})$$

where

$$N_0 = 1 + \frac{K_5[Cl_2]_0}{K_6[O_2]_0}.$$

Expression (A4.2) reflects a weak decrease in the parameter N when changing y from 1 to 0. It is obvious that the difference $N-1$ and the ratio $(N-1)/N$ also weakly depend on y . Let us represent the product AN in the form

$$AN = (AN)_0 \frac{1 - \eta_{RI}}{\varepsilon y}, \quad (\text{A4.3})$$

where $(AN)_0$ is determined by expression (A3.5). By substituting (A4.3) into (A4.1), we obtain

$$N\left(\frac{v}{x}\right)(\tau_{\max}) = (N-1) \frac{1}{2} \left\{ 1 + \left[1 + \frac{8}{(AN)_0} \times \varepsilon \left(\frac{y(\tau_{\max})}{1 - \eta_{RI}(\tau_{\max})} \right) \left(\frac{N}{N-1} \right)^2 \right]^{1/2} \right\}. \quad (\text{A4.4})$$

The value of N entering into (A4.4) is calculated at $\tau = \tau_{\max}$. Let us analyse the dependence of the quantity $[N(v/x)](\tau_{\max})$ on $y(\tau_{\max})$ and $\eta_{RI}(\tau_{\max})$. In the case of strong or moderate quenching ($\theta > 1$), $\eta_{RI}(\tau_{\max}) \ll 1$, and, hence, $1 - \eta_{RI}(\tau_{\max}) \approx 1$ and the value $[N(v/x)](\tau_{\max})$ depends only on $y(\tau_{\max})$. In the case of weak quenching ($\theta \lesssim 1$), the ratio $y(\tau_{\max})/[1 - \eta_{RI}(\tau_{\max})] \approx y^*$ [see (A2.10)], and hence, the dependence of $[N(v/x)](\tau_{\max})$ on $\eta_{RI}(\tau_{\max})$ can be neglected. Thus, the values of $[N(v/x)](\tau_{\max})$ and $\theta(\tau_{\max})$ mainly depend on $y(\tau_{\max})$, this dependence being weak.

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