Mendeleev Commun., 2001, 11(2), 59–63

On the nature of the upper limit of isothermal flame propagation in the branching-chain decomposition of nitrogen trichloride

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10.1070/MC2001v011n02ABEH001410

The deactivation $Cl_2\ {}^3\Pi^+_{ou} + M \rightarrow Cl_2\ {}^1\Sigma^-_g + M$ is an important step giving rise to the upper limit of isothermal flame propagation in dilute gaseous mixtures of nitrogen trichloride.

Thermal decomposition of nitrogen trichloride (NCl_3) is an example of branching-chain (BC) low temperature process of the decomposition of an individual substance in a gaseous phase. In contrast to the model BC reaction of H_2 oxidation, nonlinear chain branching plays an important role in NCl_3 decomposition,[1–3] leading to the phenomena of structural organization peculiar to nonlinear dynamical systems, namely, isothermal flame propagation[2,4] and chemical oscillations.[5] The revealing of common trends in nonlinear BC processes is of interest with respect to the theory of chemical transformation. The practical utility of NCl_3 decomposition lies in laserochemical applications[6] and explosion safety.[7]

Isothermal flames comprise the traveling stationary front of chemical reaction in which the heat evaluation is very small, so that the temperature may be considered constant. The velocity of these flames is determined by the diffusion of active intermediates into an unreacted mixture.[8] In spite of BC processes of this sort are rare in occurrence, these represent a convenient object for kinetic investigations: the warming-up is negligible and diffusion may be considered binary.[9] Azatyan *et al.*[9] numerically treated experimental data[8] on isothermal flame propagation in dilute mixtures of CS_2 with O_2. The simulation showed that the most likely nonlinear branching step is $CS + O \rightarrow S + CO$ rather than $SO + SO \rightarrow S + SO_2$. The reactions of termolecular chain termination $O + O_2 + M$ and $SO + O_2 + M$ were found to be responsible for the occurrence of the upper limit of isothermal flame propagation. As for NCl_3 decomposition, the elementary steps responsible for this phenomenon, as well as for the occurrence of the upper self-ignition limit, have not been yet discussed. Our experimental data on NCl_3 decomposition[2] were examined[10] in terms of the simplified reaction scheme only for low pressures close to the first limit of isothermal flame propagation:

$NCl_3 \rightarrow NCl_2 + Cl$, chain initiation;
$Cl + NCl_3 \rightarrow NCl_2 + Cl_2$, chain propagation;
$NCl_2 + NCl_3 \rightarrow N_2 + Cl_2 + 3Cl$, linear chain branching;
$NCl_2 \rightarrow$ reactor wall;
$NCl_2 + NCl_2 \rightarrow N_2 + (2 - n/2)Cl_2 + nCl$, nonlinear chain branching.

Calculations gave the values of the flame velocity close to the experimental values near the limit. The discrepancy between calculated and experimental values evidently increased with an increase in total pressure since no chain termination reaction effective at higher pressures was included in the scheme. It was shown that n depends on the chemical nature of the diluent in agreement with the previous assumption[2] that energy branching plays an important role in the process. A consideration of the extended kinetic mechanism of NCl_3 decomposition,[3] where the process of energy branching was presented in more detail, offered a clearer view of the nature of chemical oscillations. Our interest is in describing the isothermal flame propagation using this mechanism[3] in the pressure range involving also the upper limit of nonthermal flame propagation.

This work is aimed at an establishment of the chemical nature of some elementary processes, which may give rise to the upper limit of the propagation of isothermal flame in the branching-chain process of decomposition of nitrogen trichloride in a gaseous phase.

The kinetic mechanism of the chemical decomposition of NCl_3 can be represented as follows:[3]

$NCl_3 \rightarrow NCl_2 + Cl$, $k_0 = 10^{-3}$– 10^{-5} s^{-1} (ref. 11), chain initiation;
$Cl + NCl_3 \rightarrow NCl_2 + Cl_2$, $k_1 = (1.6\pm0.2)\times10^{-12}$ $cm^3\ s^{-1}$ (ref. 11), chain propagation;
$NCl_2 + NCl_3 \rightarrow N_2 + Cl_2 + 3Cl$, $k_2 = 1.6\times10^{-16}$ (ref. 12), linear chain branching;
$NCl_2 + NCl_2 \rightarrow N_2 + Cl_2\ {}^3\Pi^+_{ou} + 2Cl$, $k_3 = (6.5\pm3.0)\times10^{-13}$ $cm^3\ s^{-1}$ (refs. 1, 10), nonlinear chain branching;
$Cl_2\ {}^3\Pi^+_{ou} \rightarrow 2Cl$, $k_4 < 10^4$ s^{-1} (ref. 13), this value accounts for the radiation lifetime of $Cl_2\ {}^3\Pi^+_{ou}$; the probability of its decomposition to the Cl atoms due to predissociation[13] is evidently less than this estimate;
$Cl_2\ {}^3\Pi^+_{ou} + NCl_3 \rightarrow NCl_2 + Cl_2 + 2Cl$, $k_5 = 1.6\times10^{-12}$ $cm^3\ s^{-1}$ (ref. 3);
$Cl_2\ {}^3\Pi^+_{ou} + Cl \rightarrow Cl_2\ {}^1\Sigma^-_g + Cl$, $k_6 = (2.5\pm1.5)\times10^{-10}$ $cm^3\ s^{-1}$ (refs. 13, 14), nonlinear chain termination;
$NCl_2 \rightarrow$ reactor wall, k_7, chain termination in diffusive area;
$Cl \rightarrow$ reactor wall, k_8, chain termination in diffusive area (see below);
$Cl_2\ {}^3\Pi^+_{ou} + M \rightarrow Cl_2\ {}^1\Sigma^-_g + M$, $k_9 = 8\times10^{-13}$–10^{-13} $cm^3\ s^{-1}$ (ref. 14), deactivation;

It has been shown previously[3] that the results of the numerical simulation are consistent with experimental data on the kinetics of NCl_3 decomposition in the vicinity of the lower limit of self-ignition. Therefore, the goal of this investigation is to clarify whether the mechanism proposed is in position to describe the isothermal flame propagation, in particular, the existence of its upper limit. Note that the steady-state isothermal propagation of a flame (wave regime) must be considered with no regard for chain initiation reaction.[15] It was also shown[10] that the role of linear chain branching is negligible (in view of a small value of k_2 as compared with k_1 and k_3) to take it into account. However, it is evident that the rate of a linear chain branching reaction cannot be neglected in the self-ignition area.

First, the characteristic scale of the process was chosen: $t_0 = 1/(k_1[NCl_3]_0)$, $x_0 = (D_3/k_1[NCl_3]_0)^{1/2}$, $U_0 = x_0/t_0 = (D_3k_1[NCl_3]_0)^{1/2}$ (time, length and velocity scales, respectively; D_3 is the diffusivity of nitrogen trichloride). The dimensionless variables were determined as $\tau = t/t_0$, $\xi = x/t_0$, $\varpi = U/U_0$, Y_i = [concentration of i-th component]/$[NCl_3]_0$, $\delta_i = D_i/D_3$ (D_i are the diffusivities). Therefore, we obtain $\tau = k_1[NCl_3]_0t$, $Y_0 = [Cl]/[NCl_3]_0$, $Y_1 = [Cl_2\ {}^3\Pi^+_{ou}]/[NCl_3]_0$, $Y_2 = [NCl_2]/[NCl_3]_0$, $Y_3 = [NCl_3]/[NCl_3]_0$. The dimensionless velocity and coordinate are $\varpi = U/(D_3k_1\times[NCl_3]_0)^{1/2}$ and $\xi = x/(D_3/k_1[NCl_3]_0)^{1/2}$, where U and x are the corresponding dimensional values of the velocity and the coordinate of the reaction wave, respectively. Dimensionless parameters are $\beta = k_2/k_1$, $\phi = k_3/k_1$, $\gamma = k_8/(k_1[NCl_3]_0)$, $\lambda = k_4/(k_1[NCl_3]_0)$, $\psi = k_5/k_1$, $\rho = k_7/(k_1[NCl_3]_0)$, $\mu = k_6/k_1$ and $\chi = k_9/(k_1[NCl_3]_0)$. The total pressure (Torr) is designated as P, *i.e.* $[NCl_3]_0 = sP$,

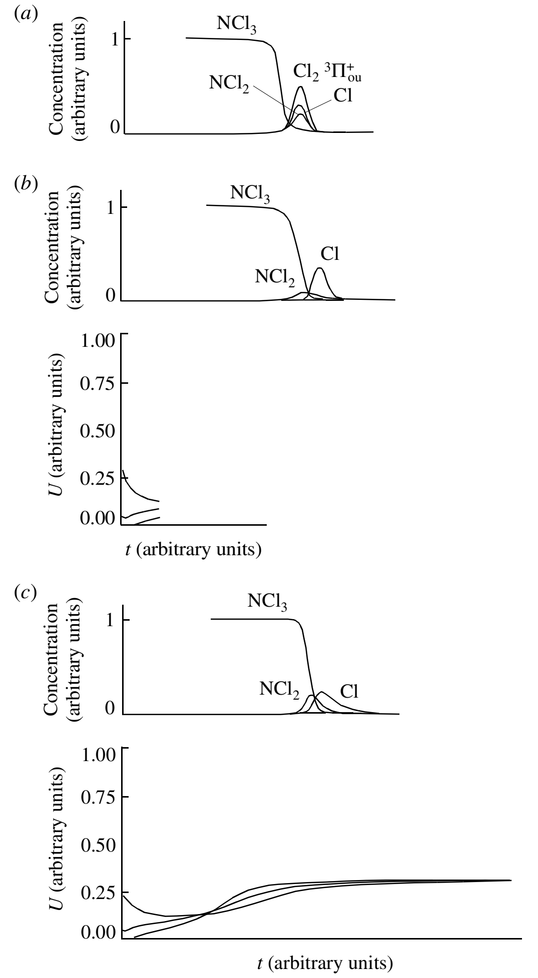

Figure 1 Evolution of system (1) upon calculation. The wave regime of propagation of isothermal flame exists; 0.4% NCl_3 in He, 10 Torr. (*a*) Initial shapes of concentrations; (*b*) transition state in 100 time steps of integrating; (*c*) establishment of the constant value of the flame velocity (0.779 m s^{-1}) and the shapes of the concentrations of the initial substance and intermediates in the front of isothermal flame in wave regime.

where *s* is the mole fraction of NCl_3 in the initial mixture. The dimensionless diffusivities δ_0, δ_1 and δ_2 are expressed in terms of diffusivities of chlorine atoms (D_0), $Cl_2\ {}^3\Pi^+_{ou}$ (D_1) and NCl_2 radicals (D_2). It is evident that the equation $x = Ut$ corresponds to wave propagation.

The corresponding system of nonlinear second-order partial differential equations for the above kinetic mechanism is the following:

$$\begin{aligned}
\partial Y_0/\partial\tau &= \delta_0\partial^2 Y_0/\partial\xi^2 + 2\phi(Y_2)^2 + \psi Y_1Y_3 + 2\lambda Y_1 - Y_0Y_3 - \gamma Y_0\\
\partial Y_1/\partial\tau &= \delta_1\partial^2 Y_1/\partial\xi^2 + 2\phi(Y_2)^2 - \psi Y_1Y_3 - \lambda Y_1 - \chi PY_1 - \mu Y_0Y_1\\
\partial Y_2/\partial\tau &= \delta_2\partial^2 Y_2/\partial\xi^2 - 2\phi(Y_2)^2 + \psi Y_1Y_3 - \rho Y_2 + Y_0Y_3\\
\partial Y_3/\partial\tau &= \partial^2 Y_3/\partial\xi^2 - \psi Y_1Y_3 - Y_0Y_3
\end{aligned} \tag{1}$$

The solutions of system (1) satisfy the following boundary conditions for flame propagation from right to left:

$$\begin{aligned}
&Y_0, Y_1, Y_2 \to 0,\ \xi \to \pm\infty\\
&Y_3 \to 1,\ \xi \to -\infty;\ Y_3 \to 0,\ \xi \to +\infty
\end{aligned} \tag{2}$$

In accordance with the foregoing, the reactions of chain initiation and linear chain branching are not included into system (1). At a given distribution of Y_i at the initial point in time [see Figure 1(*a*)], the further evolution of Y_i is determined by system (1) with boundary conditions (2). The set of equations (1) was solved numerically using the explicit second-order difference scheme on a uniform fixed ξ–τ grid. The two-step implicit scheme provides the second order of approximation of system (1) over both spatial and time variables.[16] The results of work were obtained for 500 cells in the ξ direction. The course of computation was shown graphically in the display, so the computation was monitored in an interactive regime. This allowed us to change parameters during the computation if needed and to determine the moment at which the calculation would be interrupted (for instance, when the wave regime was attained). This procedure differs from the method,[9,10] which was based on the solution of the implicit second-order difference scheme corresponding to the set of equations of form (1), where each time step was performed in converted coordinates. In this case, a new value of the velocity of the propagating flame, calculated at the previous step, was substituted into this set. As this takes place, until the stationary value of the flame velocity (that is defined as the eigenvalue of this set of equations) has been attained, the intermediate steps upon solving are not consistent with any real process.

Table 1 Diffusivities D_i in various gases ($cm^2\ s^{-1}$, 293 K, 760 Torr).

	He	CO_2	Cl_2
Cl	0.73	0.14	0.12
NCl_2	0.44	0.09	0.08
$Cl_2\ {}^3\Pi$	0.55	0.11	0.1
NCl_3	0.41	0.09	0.07

When solving set (1), the initial front of starting component Y_3 at the time origin over coordinate was defined so that $Y_3 = 1$. The shape of this front was approximated with $Y_3 = {}^1/_2 - {}^1/\pi[\arctan(b_3\xi)]$, the initial fronts of intermediates were specified as $Y_i = a_i\exp(-b_i\xi^2)$ [Figure 1(*a*)], where a_i and b_i are scale coefficients. These initial shapes correspond essentially to the initiation of nonthermal flame propagation with an external source, as in described experiments.[2,8] The chosen shapes of Y_i have no influence on the steady-state values of the velocity of isothermal flame propagation: if the set of equations (1) admits of wave solution, the system seeks it from given initial conditions. Therefore, upon solving (1), the velocities of initial fronts change [Figure 1(*b*)] as long as either a steady state is attained [for the existence of auto wave solution of (1), Figure 1(*c*)] or a trivial solution corresponding to zero velocity takes place. The velocity of the reaction wave was found from the velocities of points $Y_3 = 0.2$, 0.5 and 0.8, as can be seen from Figures 1(*b*),(*c*). It was assumed that the wave regime was attained if the average value of the velocity did not change within 20 characteristic sizes of the calculated flame front. The wave regime (if exists) is attained rather quickly in the middle of the flame propagation area and slower near the limits of flame propagation. In the latter case, the following procedure was used. When the wave approached the left border of the calculated area so that $Y_i = 0$ in the right half of the grid (the characteristic size of the wave was about 25 grid cells over ξ) then all Y_i from the left half of the grid were transferred into the right part of the grid and then the calculation was continued until either wave or trivial solution was attained.

The method was tested by the example of solving the set of nonlinear second-order differential equations, which represents a simplified kinetic model of the decomposition of NCl_3. This simplified set of equations was solved earlier using other calculational techniques.[10] Calculated[10] dependences of the dimensionless velocity of isothermal flame on the rate of heterogeneous chain termination was quantitatively reproduced. It has been also shown that as theory holds[15] our method gives nonzero velocities at the lower and upper limits of isothermal flame propagation.

Thus, the result obtained suggests that our method is applicable for the examination of isothermal flame propagation. The following parameters were chosen for solving (1): $k_1 = 1.6\times10^{-12}\ cm^3\ s^{-1}$, $k_3 = 6\times10^{-13}\ cm^3\ s^{-1}$, $k_6 = 1.6\times10^{-10}\ cm^3\ s^{-1}$ and $k_9 = 4\times10^{-13}$–$10^{-13}\ cm^3\ s^{-1}$. The reactions of chain termination (steps 7 and 8) were considered to occur on the diffusion area; therefore, k_7 and k_8 were calculated from the equation $k = 23.2D_i/(d^2P)$, where *d* is the reactor diameter and D_i is the diffusivity. The values of diffusivity D_i in various gases ($cm^2\ s^{-1}$, 293 K, 760 Torr) were taken from refs. 10, 17 and 18 (Table 1).

Both the results of numerical calculations and the experi-

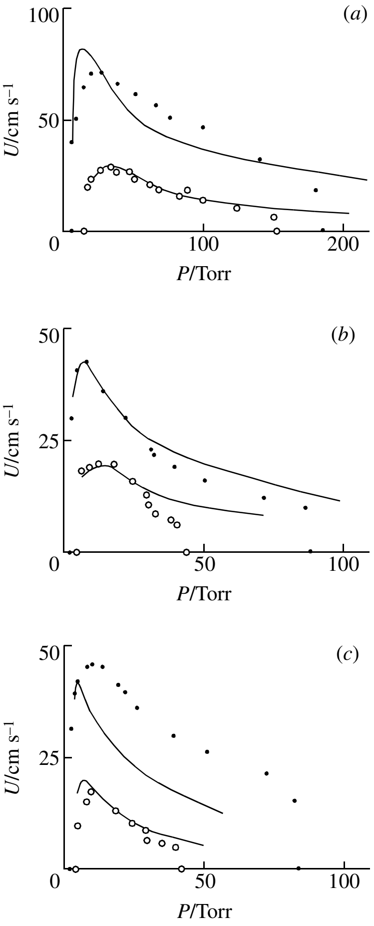

Figure 2 Dependences of the velocity of the isothermal flame propagation on the total pressure in the mixtures of NCl_3 with diluents. Points refer to experimental data,[2,15] and curves refer to numerical simulation. (*a*) Diluent He, points: NCl_3, 0.38%; upper curve: simulation for 0.38% NCl_3 in He; circles: NCl_3, 0.11%; lower curve: simulation for 0.11% NCl_3 in He; (*b*) diluent CO_2, points: NCl_3, 0.4%; upper curve: simulation for 0.4% NCl_3 in CO_2; circles: NCl_3, 0.14%; lower curve: simulation for 0.14% NCl_3 in CO_2; (*c*) diluent Cl_2, points: NCl_3, 0.76%; upper curve: simulation for 0.76% NCl_3 in Cl_2; circles: NCl_3, 0.3%; lower curve: simulation for 0.3% NCl_3 in Cl_2.

mental data on isothermal flame propagation in dilute mixtures of NCl_3 with He, CO_2 and Cl_2[2,17] are shown in Figure 2(*a*)–(*c*). The fact that elementary step 9 (deactivation of electronically excited molecular chlorine $^{3}\Pi^{+}_{\mathrm{ou}}$) was included into the reaction scheme provided a way of describing the dependence of the velocity of isothermal flame on total pressure in all diluents near the upper limit of the flame propagation. As is seen in Figure 2, the slower the diffusion of active intermediates to the reactor wall, the smaller value of the lower limit of isothermal flame propagation. In addition, if the rate of deactivation of excited molecular chlorine decreases, the value of the upper limit of isothermal flame propagation increases. One can also see from Figure 2 that the calculated values of the velocities of isothermal flame and the total pressures at the upper limit are in good agreement with experimental data. The rate constants of deactivation k_9 make up 10^{-13} $cm^3\,s^{-1}$ for He, 1.9×10^{-13} $cm^3\,s^{-1}$ for CO_2 and 3.6×10^{-13} $cm^3\,s^{-1}$ for Cl_2. The values of k_9 are in agreement with experimental data.[13,14] The value of k_4 was taken as $100\,s^{-1}$. It means that approximately one Cl_2 $^{3}\Pi^{+}_{\mathrm{ou}}$ molecule in a hundred takes part in chain branching. Therefore, the deactivation of intermediates capable of decomposition to atoms is the most probable reason for the occurrence of an upper limit of isothermal flame propagation in dilute mixtures of NCl_3 with inert diluents. As this takes place, numerical calculation of the dependences of the velocities of isothermal flame is performed by a consideration of different efficiencies of deactivation of Cl_2 $^{3}\Pi^{+}_{\mathrm{ou}}$ by diluent molecules.

The lack of experimental data gives no way of allowance for other reactions of termolecular chain termination. Actually, the upper limit of self-ignition was experimentally detected.[12] It means that a supplementary reaction of chain termination other than step 9 occurs, because the termination of only Cl_2 $^{3}\Pi^{+}_{\mathrm{ou}}$ in linear branching step (step 2) cannot give rise to the upper limit of self-ignition. Really, if step 2 gives rise even to two molecules of Cl_2 $^{3}\Pi^{+}_{\mathrm{ou}}$ and all these are deactivated, step 2 is not completely terminated because one chlorine atom remains. By this means step 2 becomes the chain propagation reaction. Thus, reactions like those are expected:

$$Cl + NCl_3 + M \rightarrow \text{termination;}$$
$$NCl_2 + NCl_3 + M \rightarrow \text{termination.}$$

Unfortunately, no experimental evidence has been found for the existence of the possible products of the reactions (NCl_4, N_2Cl_3 or N_2Cl_5), which moreover must exhibit low chemical activity. However, in view of the preceding, the values obtained for k_9 can be considered only as the upper limits of this rate constant for various diluents. Therefore, the solution of the inverse kinetic problem on the isothermal flame propagation in dilute mixtures of nitrogen trichloride with consideration for the experimental data on the upper limit of self-ignition calls for further investigation.

We are grateful to Corresponding member of the RAS V. V. Azatyan (Institute for Structural Macrokinetics and Materials Science RAS) for many useful discussions.

This work was supported by the Russian Foundation for Basic Research (grant no. 00-03-32979a).

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Received: 9th December 2000; Com. 00/1736