Transition from isothermal to chain-thermal flame-propagation regimes in the branching-chain decomposition of nitrogen trichloride

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The title transition has been detected in a mixture of nitrogen trichloride (4%) with helium. The occurrence of a non-linear branching step in the branched-chain reaction shortens the time interval of the development of a chain-thermal flame.

Two general types of the propagation of subsonic flames are known in the theory of combustion: an isothermal regime and a thermal[1] (or, more precisely, chain-thermal) regime. The velocity of isothermal flames is determined by the diffusion of the active centres (atoms and radicals) of a branched-chain reaction (BCR) into an unreacted mixture.[1] The BCR mechanism must include non-linear chain branching (in this reaction, an increase in the number of free valences is due to the interaction of active centres).[2,3] The area of isothermal flame propagation (IFP) (I in Figure 1) is broader than self-igniton area II. The structure of the ignition area in BCR (a pressure–temperature plot) is shown in Figure 1. Chain-thermal flame propagation (CTFP), as distinct from IFP, is due to heat evolution in the front of a developing BCR. The non-Arrhenius dependence[5] of the branching on temperature is the positive feedback, which provides the occurrence of the stationary front of combustion. Chain-thermal flames have been widely investigated in BCR, including only linear branching.[4,6,7] The self-ignition area of these linear BCR II includes isothermal area IIa and chain-thermal explosion area IIb, which corresponds both to developing chain avalanche and accelerating heat accumulation.[4] The stationary flame propagation in linear BCR in the vicinity of the lower self-ignition limit (IIa) is ruled out because the warming-up is missing. At pressures close to the lower boundary of IIa, the warming-up is reasonably large to warm the nearest layers of an unreacted gas up to the self-ignition temperature (arrows 1 in Figure 1; in this case, the stationary combustion wave, namely CTFP, occurs). Therefore, in order that a stationary flame may develop, linear BCR must be initially in self-ignition area, or the initiating impulse (*e.g.*, a spark) must provide the warming-up that is sufficient to transfer the BCR to the area close to IIb (arrow 0 in Figure 1). However this limitation does not take place for non-linear BCR, in which

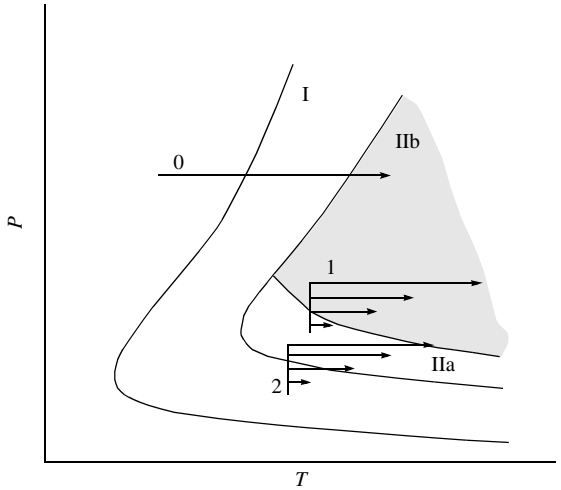

Figure 1 The ignition areas in BCR. (I) IFP area; (IIa) isothermal self-ignition area and (IIb) chain-thermal explosion area. Arrows: (0) initiated ignition in linear BCR; (1) transition of a chain self-ignition to a chain-thermal one (or to CTFP); (2) transition of an isothermal flame propagation to a chain-thermal one. The lengths of the arrows correspond to the warming-up.

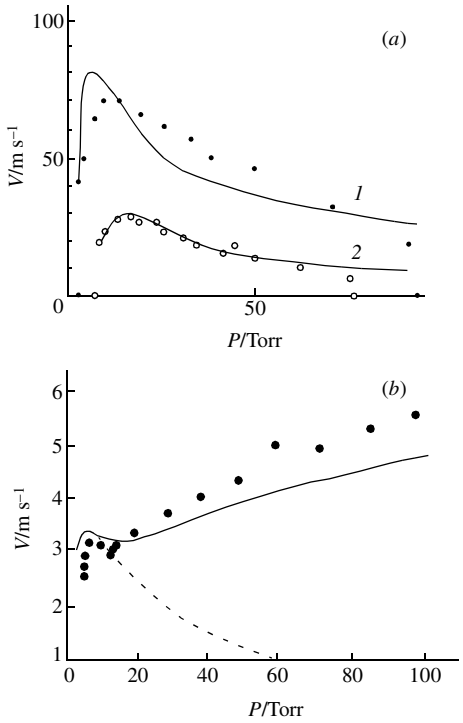

Figure 2 Dependence of the flame propagation velocity on total pressure in the mixtures of NCl_3 with He. (*a*) Isothermal flame,[9] (1) points (experiment); NCl_3, 0.38%; curve indicates numerical simulation for 0.38% NCl_3 in He; (2) circles (experiment); NCl_3, 0.11%, curve indicates numerical simulation for 0.11% NCl_3 in He; (*b*) chain-thermal flame, points (experiment), 4% NCl_3 in He; curves indicate numerical simulation, solid line: $Q_1 = 17$ kcal mol^{-1}, $Q_2 = 34$ kcal mol^{-1}, dotted line: $Q_1 = 0$, $Q_2 = 34$ kcal mol^{-1}.

the stationary flame propagation may occur in both areas I and II. In this work, the transition of the flame propagation regime from area I to II (arrows 2 in Figure 2), which is possible only in non-linear BCR, is studied.

IFP can be observed in dilute mixtures of CS_2 with O_2,[2,3] thermal decomposition of NCl_3,[8] fluorination of difluoromethane,[9] and oxidation of silane and dichlorosilane.[10,11] Since IFP occurs at very low fuel contents (> 0.03%[2,3]), the interest in IFP is connected directly with explosion safety problems: NCl_3 is formed in the commercial production of Cl_2,[12] and silanes are widely used in microelectronics.[13] Therefore, a topical problem is to study flame propagation in non-linear BCR, namely the transition from IFP to CTFP. Thermal decomposition of gaseous nitrogen trichloride (NCl_3) is an example of low temperature BCR. The BCR is convenient for attacking the problem because both linear and non-linear chain branching play an important role in this BCR. The kinetics and mechanism of the BCR were considered previously.[8,14–17]

The aim of this work was to detect and study the transition from IFP to CTFP by the example of the decomposition of nitrogen trichloride in a gaseous phase. The regularities obtained

were applied to develop a one-dimensional model of flame propagation.

The experiments were carried out under static conditions at 293 K, total pressures of 2–100 Torr and $[NCl_3]$ = 1–4%. A cylindrical quartz reactor (80 cm in length and 6 cm in diameter) had inlets for gas evacuation and optical windows. A rapidly heated small furnace placed on the butt end of the reactor provided ignition. After the ignition, a flame propagated into the cool part of the reactor (at 293 K). The velocity of flame travelling was recorded by three photomultiplier tubes equipped with light guides placed 20 cm apart using an oscilloscope. The inner surface of the reactor was covered with magnesium oxide, which provides the diffusive area of chain termination.[8,14] The total pressure was measured with a sensitive pressure gauge (10^{-3} Torr). The concentration of NCl_3 in helium was determined from a change in the total pressure after ignition by the stoichiometry of the reaction $2NCl_3 \rightarrow N_2 + 3Cl_2$.[17] Liquid NCl_3 was obtained and gaseous mixtures were prepared by the published procedures.[14] The reactor was evacuated to 4×10^{-4} Torr before each experiment.

It was found[8] that a pressure range in which an isothermal flame propagation occurs [Figure 2(*a*)] expands with an increase in the NCl_3 concentration. As this takes place, the flame propagation area expands in such a way that the upper limit of the flame propagation no longer exists over a certain concentration of NCl_3 in He [Figure 2(*b*), points]. This means that the role of warming-up markedly increases over certain ranges of total pressures and concentrations of NCl_3. Let us consider this phenomenon. The kinetic mechanism of the chemical decomposition of NCl_3 can be represented as follows:[8,14–17]

$NCl_3 \longrightarrow NCl_2 + Cl$, $k_0 = 10^{-3}$–10^{-5} s^{-1},[18] chain origination;

$Cl + NCl_3 \longrightarrow NCl_2 + Cl_2 + Q_1$, $k_1 = 1.6\times10^{-12}$ cm^3 s^{-1},[18] chain propagation;

$NCl_2 + NCl_3 \longrightarrow N_2 + Cl_2 + 3Cl + Q_2$,
$k_2 = 3.4\times10^{-11} \exp(-\varepsilon_1/T)$ cm^3 s^{-1}, $\varepsilon_1 = 3050/R$ [K],[19,20] linear chain branching, specific heat Q_1 was varied in a range of 0–17 kcal mol^{-1} in order to reveal the contribution of step 1 to heat evolution. The range of Q_2 (20–34 kcal mol^{-1}) is determined by the accuracy of the N–Cl bond energies in the molecule of NCl_3;[21]

$NCl_2 + NCl_2 \longrightarrow N_2 + Cl_2\ ^3\Pi_{ou}^+ + 2Cl$, $k_3 = 6.0\times10^{-13}$ cm^3 s^{-1},[22,23] non-linear branching;

$Cl_2\ ^3\Pi_{ou}^+ \longrightarrow 2Cl$, $k_4 = 4.8\times10^2$ s^{-1};[24]

$Cl_2\ ^3\Pi_{ou}^+ + NCl_3 \longrightarrow NCl_2 + Cl_2 + 2Cl$, $k_5 = 1.6\times10^{-12}$ cm^3 s^{-1};[15,16]

$Cl_2\ ^3\Pi_{ou}^+ + Cl \longrightarrow Cl_2\ ^1\Sigma_g^- + Cl$, $k_6 = 1.6\times10^{-10}$ cm^3 s^{-1},[25,26] non-linear chain termination;

$NCl_2 \longrightarrow$ reactor wall, k_7, chain termination in a diffusive area;

$Cl \longrightarrow$ reactor wall, k_8, chain termination in a diffusive area (see below);

$Cl_2\ ^3\Pi_{ou}^+ + M \longrightarrow Cl_2\ ^1\Sigma_g^- + M$, $k_9 = 8\times10^{-13}$–10^{-13} cm^3 s^{-1},[25] deactivation.

It should be noted that the set of reactions (1)–(9) is identical to that considered previously.[15,16] The results[16] of numerical calculations of IFP in dilute mixtures of NCl_3 with He, CO_2 and Cl_2 based on reactions (1)–(9) are in good agreement with experimental data. The reaction of termolecular chain termination is unclear.[18] However, step (9) can explain the occurrence of the upper limit of IFP.[16] Thus, the value of k_9 can be considered only as its upper limit, *i.e.*, both deactivation and termolecular termination are approximated by properly choosing k_9. As is known, the stationary propagation of a reaction wave must be considered with no regard for a chain origination reaction.[27] The one-dimensional problem was examined. We determine the dimensionless variables and parameters similarly to ref. 16: $\tau = k_1[NCl_3]_0 t$, $Y_0 = [Cl]/[NCl_3]_0$, $Y_1 = [Cl_2\ ^3\Pi_{ou}^+]/[NCl_3]_0$, $Y_2 = [NCl_2]/[NCl_3]_0$, $Y_3 = [NCl_3]/[NCl_3]_0$ $\beta = k_2/k_1$, $\phi = k_3/k_1$, $\gamma = k_8/(k_1[NCl_3]_0)$, $\lambda = k_4/(k_1[NCl_3]_0)$, $\psi = k_5/k_1$, $\rho = k_7/(k_1[NCl_3]_0)$, $\mu = k_6/k_1$, $\chi = k_9/(k_1[NCl_3]_0)$; t is time (s), the total pressure (Torr) is designated as P, *i.e.*, $[NCl_3]_0 = sP$, where s is the mole fraction of NCl_3 in the initial mixture. The dimensionless velocity and coordinate of a propagating flame were defined in terms of the diffusivity of NCl_3 (D_3): $\varpi = U/(D_3k_1[NCl_3]_0)^{1/2}$, $\xi = x/(D_3/k_1[NCl_3]_0)^{1/2}$, where U and x are the corresponding dimensional values. The dimensionless diffusivities (D_i/D_3, i = 0–4) δ_0, δ_1, δ_2 in helium correspond to chlorine atoms, $Cl_2\ ^3\Pi_{ou}^+$, NCl_2 radicals, respectively. The system of non-linear second-order differential equations for the above kinetic mechanism is the following:

$$dY_0/d\tau = \delta_0 d^2Y_0/d\xi^2 + 2\phi(Y_2)^2 + \psi Y_1Y_3 + 3Y_2Y_3\beta\exp(-3050/T) + 2\lambda Y_1 - Y_0Y_3 - \gamma Y_0$$
$$dY_1/d\tau = \delta_1 d^2Y_1/d\xi^2 + 2\phi(Y_2)^2 - \psi Y_1Y_3 - \lambda Y_1 - \chi PY_2$$
$$dY_2/d\tau = \delta_2 d^2Y_2/d\xi^2 - 2\phi(Y_2)_2 + \psi Y_1Y_3 - \rho Y_2 - Y_2Y_3\beta\exp(-3050/T) \quad \text{(I)}$$
$$dY_3/d\tau = d^2Y_3/d\xi^2 - \psi Y_1Y_3 - Y_0Y_3 - Y_2Y_3\beta\exp(-3050/T)$$
$$dT/d\tau = \delta_4 d^2T/d\xi^2 + s\beta[k_2Y_2Y_3\exp(-3050/T)Q_1 + Y_0Y_3Q_2]/(c_p\rho) - \alpha L(T - 298)/(c_p\rho)$$

As heat evolution takes place in the chain unit, the last equation corresponds to a heat balance, where Q_1 and Q_2 are the specific heats, c_p is the heat capacity at a constant pressure (1.25 cal g^{-1} K^{-1} for He[19]), α is the temperature conductivity, L is the surface-to-volume ratio (cm^{-1}), T is the temperature (K), $\alpha = L\delta\lambda e/r^2$,[1] where r is the reactor radius (cm), e = 2.718..., δ is a critical parameter (2.0),[1] the thermal conductivity $\lambda = D_{(He–He)} \approx D_{(He–He)}$ in dilute mixtures,[28] $\delta_4 = D_{(He–He)}/(D_3c_p\rho)$, ρ is the density of helium (g cm^{-3}).[28]

The set of equations (I) was solved numerically as described previously.[16] As the heterogeneous chain termination was considered to occur in a diffusive area,[8] the rate constants k_7 and k_8 were calculated by the equation $k = 23.2D_i/(d^2P)$,[3] where $d = 2r$. The values of D_i in He (cm^2 s^{-1}, 293 K, 760 Torr) were taken from refs. 23 and 28.

Cl	NCl_2	$Cl_2\ ^3\Pi_{ou}^+$	NCl_3	He
0.73	0.44	0.55	0.41	1.62

The results of the numerical calculation of the evolution of system (I) at $[NCl_3]$ = 4% are shown in Figures 3(*a*) and 3(*b*) for total pressures of 5 and 35 Torr. As can be seen, the stationary velocities of flame propagation correspond to different BCR regimes: at a pressure of 5 Torr, the calculated warming-up is small (~10° in agreement with experimental data[14]) and the maximum $[Cl_2\ ^3\Pi_{ou}^+]/[NCl_3]$ ratio is as high as 0.07. It is evident that this regime of the flame propagation is practically isothermal. At a pressure of 35 Torr, the calculated value of maximum warming-up is about 200°; in this case, $[Cl_2\ ^3\Pi_{ou}^+]/[NCl_3] << 0.07$. The latter regime is already chain-thermal. Therefore, system (I) at $[NCl_3]$ = 4% admits at least two auto-wave solutions, which describe the stationary front of a propagating flame: one of them corresponds to CTFP, and the other corresponds to IFP. It was shown[29] that the dependence of the integral chemiluminescence intensity of $Cl_2\ ^3\Pi_{ou}^+$ on total pressure increases from 0.1 to 2 Torr (at $[NCl_3]$ = 15%) and then sharply decreases with a further increase in pressure. This fact is consistent with the calculations performed [*cf.* $Cl_2\ ^3\Pi_{ou}^+$ concentrations in Figures 3(*a*) and 3(*b*)] and is evidently due to the transition from the isothermal to the chain-thermal regime of flame propagation.

The upper limit of flame propagation at 4% NCl_3 is missing in experiments, as well as in calculations. It is easy to verify that two auto-wave regimes corresponding to chain-thermal and isothermal flame propagations hold for different concentrations of NCl_3 at similar pressures [*cf.* Figures 2(*a*) and 2(*b*) at total pressures > 35 Torr]. Actually, at $[NCl_3]$ = 0.4%, a chain-thermal regime of flame propagation is missing at the studied pressures in both experiments and calculations. It means that the transition to a chain-thermal regime is determined by both the initial pressure and the initial concentration of NCl_3 in the mixture. The transition shows a critical character in total pressure, as is seen in Figure 2(*b*). IFP occurs at low pressures; an increase in the pressure causes the transition to CTFP in the pressure range (about 20 Torr) where calculated isothermal and chain-thermal solutions become separated. Note that the inclusion of heat evolution in only the linear chain branching reaction [step (2), Q_2 = 34 kcal mol^{-1} (ref. 21)] does not cause the transition to a chain-thermal flame at pressures up to 100 Torr (Figure 2, dotted line). Therefore, the heat evolution in step (1) was also taken into account. The dependence of the calculated wave solution on the total pressure is shown in Figure 2(*b*) (solid line). However, a

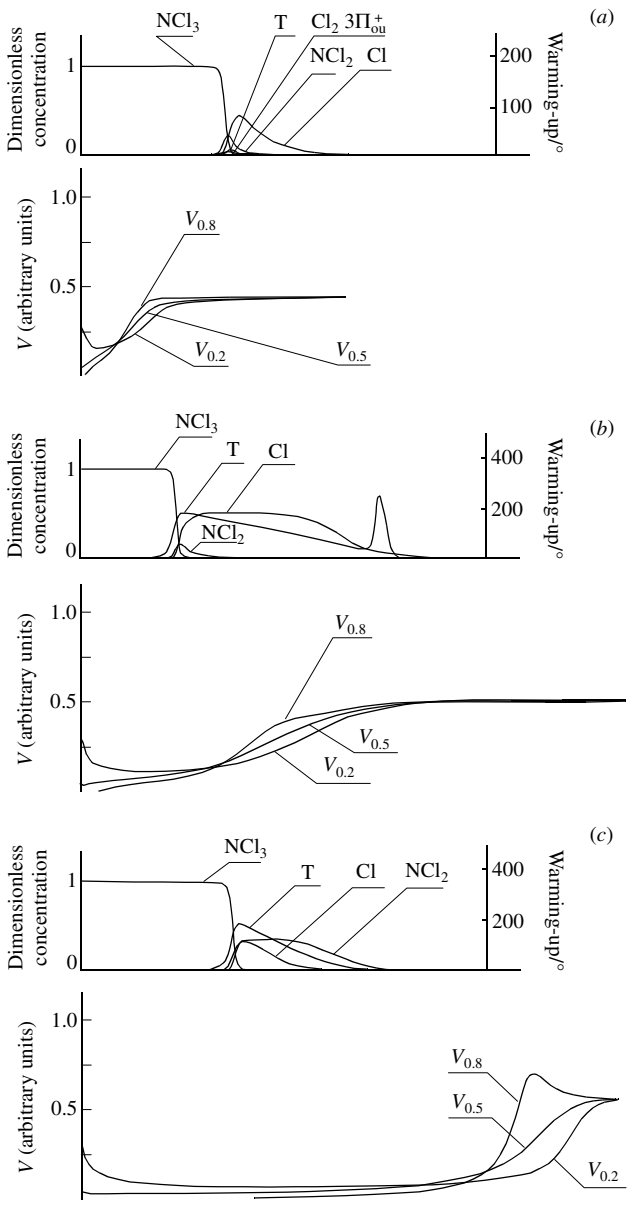

Figure 3 Evolution of system (I) upon calculation, 4% NCl_3 in He, initial temperature of 300 K, Q_1 = 17 kcal mol^{-1}, Q_2 = 34 kcal mol^{-1}. (*a*) P = 5 Torr; (*b*) P = 35 Torr; (*c*) P = 35 Torr, k_3 is assumed to be zero.

wide range of parameters dealing with heat evolution (Q_1, Q_2, α, ε_1) is responsible for only qualitative agreement between calculated and experimental data because the accuracy of these parameters is inadequate. Moreover, the above one-dimensional problem does not allow us to investigate the occurrence of spatial regimes inherent in BCR as non-linear dynamic systems.[30]

Numerical calculations allowed us to establish whether the occurrence of non-linear branching in the mechanism of BCR has an effect on the transition to a chain-thermal regime of flame propagation. For this purpose, in solving system (I) under conditions of Figure 3(*b*), the value of k_3 was taken equal to zero, *i.e.*, non-linear chain branching was eliminated from system (I). The results are shown in Figure 3(*c*). It can be seen that the transition to an auto-wave chain-thermal regime occurs within a larger time interval than that in Figure 3(*a*). Thus the occurrence of non-linear branching enhances the inflammability of BCR. As would be expected, an auto-wave regime is missing under conditions of Figure 3(*a*) (at 5 Torr): neither IFR ($k_3 = 0$) nor CTFP (low warming-up) can occur. The numerical calculations can also illustrate the fact that the rate of the linear branching influences the kinetics of BCR to a greater extent than the specific heat of this reaction. Actually, the occurrence of CTFP, with k_3 taken 10 times lower and with Q_2 taken 10 times higher than in previous calculations [in this case, the fifth equation of system (I), which describes heat evaluation, remains unchanged] is realized in the time interval that is four times larger than that presented in Figure 3(*c*).

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