

Kinetic mechanism and chemical oscillations in the branching chain decomposition of nitrogen trichloride

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On the basis of numerical simulation of the branching chain process of the decomposition of nitrogen trichloride it has been shown that suitable conditions for providing oscillating regimes are the following: (a) inclusion of adsorption–desorption of NCl_3 on the reactor walls; (b) inclusion of nonlinear chain branching and breaking reactions.

The occurrence of nonlinear homo- and heterogeneous reactions determines the behaviour of the great majority of branching chain processes (BCP) as nonlinear dynamical systems. It shows up in the rise of autowave regimes (e.g. nonthermal flame propagation¹) and structural organization as chemical oscillations in flow conditions and enclosed volumes. However, only the oscillations in liquid phase reactions in open systems have been adequately investigated.² The trends in the initiation and development of oscillations in an enclosed volume are not clearly understood. One of the causes considered is heat evolution,³ however, in BCP at low pressures energy is accumulated in the active intermediates, and in this case the warming-up is negligible.^{1,4} The chemical isothermic oscillations are generally caused either by autocatalysis with active intermediates^{2,5} or by a nonstationary surface state⁴ which is due to nonlinear heterogeneous reactions involving adsorbed intermediates. Oscillating regimes are inherent in gaseous BCP

$$\omega \equiv 5 \times 10^8, \chi \equiv 0.25, \xi \equiv 100, \alpha \equiv 0, t_0 = 0, t_1 = 70000, \beta \equiv 0.8 \times 10^4, \\ \gamma \equiv 2 \times 10^4, \psi \equiv 0.2, \eta \equiv 0, \mu \equiv 0, \delta \equiv 7 \times 10^4, \phi \equiv 0.35, \lambda \equiv 0.4, \\ N = 70000$$

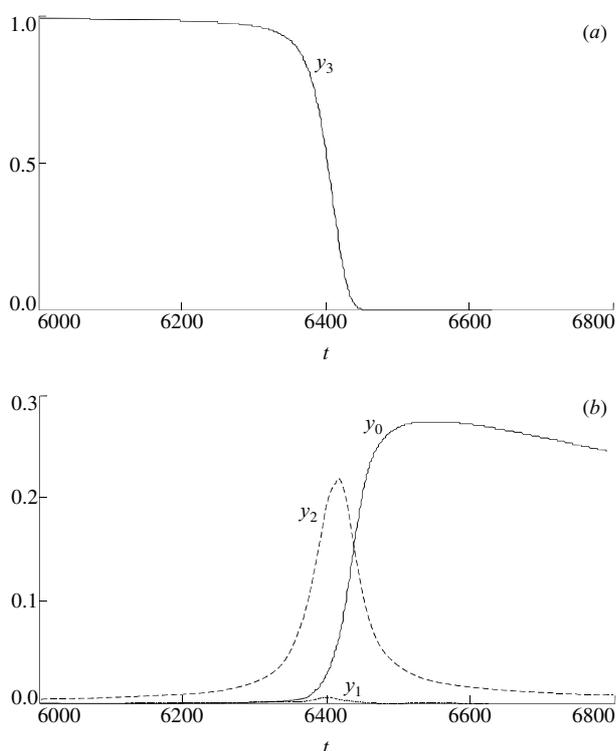


Figure 1 Numerical simulation of the self-ignition of NCl_3 : dimensionless coordinates t , time; y_0 , chlorine atoms; y_1 , $\text{Cl}_2^3 \text{ }_{\text{ou}}^+$; y_2 , NCl_2 ; y_3 , NCl_3 . (a) The dependence of y_3 on t ; (b) the dependence of y_0 , y_1 , y_2 on t . The dimensionless parameters $\omega = k_0/k_1(\text{NCl}_3)_0$; $\beta = k_2/k_1$; $\phi = k_3/k_1$; $\gamma = \gamma_0(1 - \mu t) = k_7/k_1(\text{NCl}_3)_0$; $\lambda = k_4/k_1(\text{NCl}_3)_0$; $\psi = k_5/k_1$; $\delta = k_8/k_1(\text{NCl}_3)_0$; $t = k_1(\text{NCl}_3)_0 \tau$; $\xi = k_6/k_1$; $\chi = k_0/k_1(\text{NCl}_3)_0$; $\alpha = \alpha_0(1 - \eta t)$ are also defined in equations (I) and (II). In subsequent Figures the definitions of the variables and parameters are the same. The calculated lower self-ignition limit occurs at $\gamma = 2.4 \times 10^{-3}$ under these conditions.

such as phosphorus, CO ,⁴ silane and dichlorosilane oxidation,^{6,7} and NCl_3 decomposition.^{8,9} The consideration of gaseous BCP allows the use of deterministic equations (ODE) without regard for fluctuations.²

It is known that the thermal decomposition of NCl_3 is an example of the branching chain low temperature decomposition of an individual substance in the gaseous phase, in which nonlinear chain branching plays an important role,^{10,11} leading in particular to nonthermal flame propagation^{11,12} and chemical oscillations.^{8,9} The number of elementary reactions in the kinetic mechanism is comparatively low, and the rate constants of most of them are known.⁹⁻¹⁵ It has also been shown that electronically excited $\text{Cl}_2^3 \text{ }_{\text{ou}}^+$ generated by this reaction takes part in chain branching, and in this case the fast quenching process $\text{Cl} + \text{Cl}_2^3 \text{ }_{\text{ou}}^+ \rightarrow \text{Cl} + \text{Cl}_2^1 \text{ }_{\text{g}}^-$ is of importance in chain breaking.^{11,16,17} This means that the decomposition of NCl_3 does not exhibit the peculiarities of linear BCP as, for instance, oxidation of H_2 .¹⁴ Therefore, the revealing of common trends in nonlinear gaseous BCP is of interest with respect to the theory of chemical transformation. The practical utility of this BCP lies in laserochemical applications¹⁸ and safety in explosions.¹⁹

Recently it has been shown^{8,9} that mixtures of 3–5% NCl_3 with He produce oscillatory self-ignitions in a closed vessel, if the surface is treated with NaCl. The warming-up does not exceed 5 °C, therefore the oscillations are chain in nature. The fact that NCl_3 appears in the enclosed volume after each individual oscillation is unambiguous evidence that the adsorption and desorption processes involving NCl_3 cause the oscillations. The chemical oscillations observed may be damped out, amplified or self-sustained with the position of the reaction mixture in the self-ignition area, and in this case the periods and amplitudes of oscillations strongly depend on the number of previous ignitions in the vessel.

This work is aimed at a numerical calculation of the observed regimes of chemical oscillations in enclosed vessels treated with NaCl at low pressures (< 10 Torr) and 293 K in NCl_3 decomposition (3–5 % NCl_3 in He).^{8,9} We tried to clarify whether the set of elementary steps known combined with an external

$$\omega \equiv 10^6, \chi \equiv 0.25, \xi \equiv 100, \alpha \equiv 3.5 \times 10^5, t_0 = 0, t_1 = 240000, \\ \beta \equiv 0.8 \times 10^4, \gamma \equiv 9 \times 10^4, \psi \equiv 0.2, \eta \equiv 0.5 \times 10^6, \mu \equiv 0.1 \times 10^6, \\ \delta \equiv 7 \times 10^4, \phi \equiv 0.35, \lambda \equiv 0.4, N = 240000$$

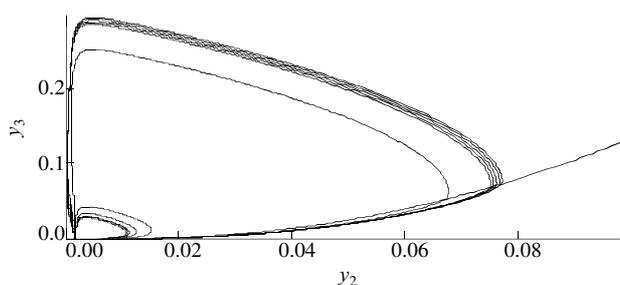


Figure 2 Calculated oscillatory regime with the depletion of surface and change in surface state through the desorption of NCl_3 taken into account: $\mu, \eta > 0$; the phase portrait includes an unstable focus inside stable limit cycle.

$$\begin{aligned} \omega &\equiv 10^{-6}, \chi \equiv 0.25, \xi \equiv 100, \alpha \equiv 3.5 \times 10^{-5}, t_0 = 0, t_1 = 240000, \\ \beta &\equiv 0.8 \times 10^{-4}, \gamma \equiv 8.8 \times 10^{-4}, \psi \equiv 0.2, \eta \equiv 0.5 \times 10^{-6}, \mu \equiv 0.1 \times 10^{-6}, \\ \delta &\equiv 7 \times 10^{-4}, \phi \equiv 0.35, \lambda \equiv 0.4, N = 240000 \end{aligned}$$

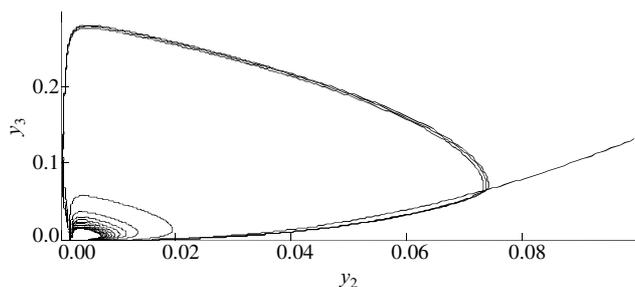
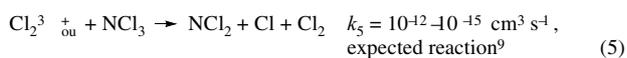
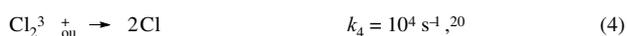
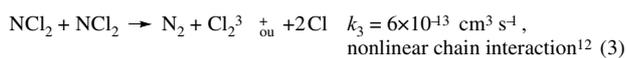
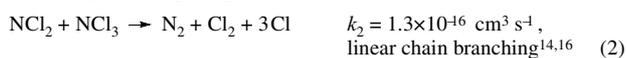


Figure 3 Calculated oscillatory regime under conditions similar to Figure 2, except $\gamma = 8.8 \times 10^{-4}$ (the surface state has changed in the previous self-ignition); the phase portrait includes an unstable focus inside a stable limit cycle.

source are sufficient for modelling the observed oscillation regimes, as well as whether the analysis of the one-dimensional system of ODE can give any new information about this process.

The kinetic mechanism of the thermal decomposition of NCl_3 at low pressures (the rates of termolecular chain break reactions are negligible) can be represented as follows:^{9,12,14–17,20}



The nonlinear chain branching process [steps (3)–(5)] is shown in accordance with refs. 4 and 9–12. These steps take into account either the high probability of the depletion of the upper vibronic levels Cl_2^3 ($\nu > 13$) in reaction (4), due to the ‘shallow depth’ of the potential-energy surface of this excited state ($\sim 7 \text{ kcal mol}^{-1}$), or the fact that the energy released in reaction (5) is enough for dissociation of the NCl_3 molecule.²⁰

We determined the dimensionless variables as $t = k_1(\text{NCl}_3)_0 \tau$ (τ/s); $Y_0 = (\text{Cl})/(\text{NCl}_3)_0$; $Y_1 = (\text{Cl}_2^3)/(\text{NCl}_3)_0$; $Y_2 = (\text{NCl}_2)/(\text{NCl}_3)_0$; $Y_3 = (\text{NCl}_3)/(\text{NCl}_3)_0$ and the dimensionless parameters as $\omega = k_0/k_1(\text{NCl}_3)_0$; $\beta = k_2/k_1$; $\phi = k_3/k_1$; $\gamma = k_7/k_1(\text{NCl}_3)_0$; $\lambda = k_4/k_1(\text{NCl}_3)_0$; $\psi = k_5/k_1$; $\delta = k_8/k_1(\text{NCl}_3)_0$; $\xi = k_6/k_1$; $\chi = k_9/k_1(\text{NCl}_3)_0$. The corresponding ODE for the kinetic mechanism above are:

$$\begin{aligned} dY_0/dt &= \omega Y_3 - Y_0 Y_3 + 3\beta Y_2 Y_3 + 2\phi Y_2^2 + \psi Y_1 Y_3 + \lambda Y_1 - \delta Y_0 - \xi Y_0 Y_1 \\ dY_1/dt &= \phi Y_2^2 - \lambda Y_1 - \psi Y_1 Y_3 - \xi Y_0 Y_1 - \chi Y_1 \\ dY_2/dt &= \omega Y_3 + Y_0 Y_3 - \beta Y_2 Y_3 - \psi Y_1 Y_3 - \gamma Y_2 \\ dY_3/dt &= -\omega Y_3 - Y_0 Y_2 - \beta Y_2 Y_3 - \psi Y_1 Y_3 \end{aligned} \quad (I)$$

Initial conditions were $Y_0 = Y_1 = Y_2 = 0, Y_3 = 1$.

It is evident that the inclusion of the reaction



gives another negative linear term in the second equation of system (I) of the εY_1 type. Therefore the step (10) is

$$\begin{aligned} \omega &\equiv 10^{-6}, \chi \equiv 0.25, \xi \equiv 100, \alpha \equiv 3.5 \times 10^{-5}, t_0 = 0, t_1 = 240000, \\ \beta &\equiv 0.8 \times 10^{-4}, \gamma \equiv 9.1 \times 10^{-4}, \psi \equiv 0.2, \eta \equiv 0.5 \times 10^{-6}, \mu \equiv 0.8 \times 10^{-6}, \\ \delta &\equiv 7 \times 10^{-4}, \phi \equiv 0.35, \lambda \equiv 0.4, N = 240000 \end{aligned}$$

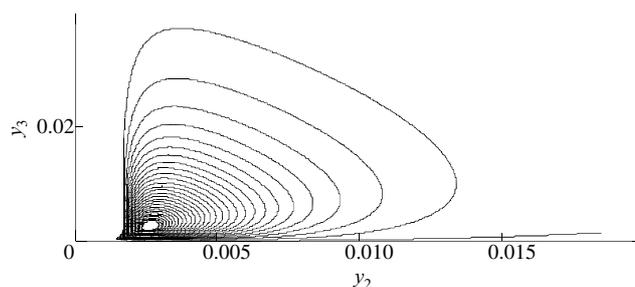


Figure 4 Calculated regime of damped oscillations; the phase portrait includes a stable focus.

incorporated implicitly by varying χ over a rather wide range, see step (9). In addition, the transition $3 \rightarrow 1$ is forbidden, *i.e.* the rate of step (10) is comparatively moderate. In fact, as shown in studies of Cl_2^3 generated by rf-discharge in Cl_2 -He (Ar, Cl_2) mixtures, reaction (6) is the predominant quenching process.²⁰

The real situation for numerical modelling matched the experimental conditions:^{8,9} 5 Torr, 3% NCl_3 at 293 K. It is easy to verify that 1 s corresponds to ~ 7000 time units along the ‘t’ axis. ‘1’ along the ‘Y’ axis corresponds to $\sim 4.5 \times 10^{15} \text{ cm}^{-3}$. t_0 and t_1 in Figures 1–4 c correspond to initial and final values of ‘t’ and N is a number of solution values on $[t_0, t_1]$.

System (I) was calculated by the fourth order Runge-Kutta method. Kinetic curves of the changes in concentrations of NCl_3 and other intermediates are shown in Figure 1. As seen from Figure 1, the calculated concentrations of NCl_3 and intermediates during the self-ignition and the lower self-ignition limit are in quantitative agreement with the experimental data, namely, the concentrations of NCl_2 and Cl_2^3 peak simultaneously,¹⁰ and the rate of decrease of NCl_3 at its maximum coincides with the maximum of Cl_2^3 ; in this case the maximum concentration of chlorine atoms is achieved later.²¹ The maximum NCl_2 concentration amounts to $\sim 10^{15} \text{ cm}^{-3}$ in accordance with ref. 10, and the concentration of chlorine atoms amounts to several tens of a percent of the initial NCl_3 concentration.²² The Cl_2^3 concentration is markedly low in comparison with that of other intermediates, which is in agreement with the low quantum yield of Cl_2^3 measured in ref. 23. It should be noted that the author of ref. 23 formed the conclusion that Cl_2^3 plays no marked role in NCl_3 decomposition only on the basis of the low quantum yield values observed. However, as seen from the calculations performed, the low quantum yield is either a result of the occurrence of the fast reaction (6), which causes the overall concentration of Cl_2^3 to decrease, or a consequence of the fact that the $3 \rightarrow 1$ transition is forbidden (see above).

The calculated value of the induction period ($\sim 1 \text{ s}$) is also in agreement with the experimentally observed value¹⁵ for the aforementioned conditions. From the above it might be assumed that the ODE (I) system based on the kinetic mechanism presented is entirely suitable for the fitting of experimental data.

Experimentally observed desorption of NCl_3 was simulated as follows. Into the fourth equation of system (I) for Y_3 an additional term was included to represent the rate of desorption of NCl_3 :²⁴

$$dY_3/dt = \alpha Y_3^{1/m}, \quad m = 2-6 \quad (II)$$

Evidently, for the adsorption rate of a substance A $w_{\text{ads}} = k_{\text{ads}} p_A (1 - q)$, where p_A is the partial pressure of A in the gas phase, and $(1 - q)$ is the proportion of free surface; for desorption $w_{\text{des}} = k_{\text{des}} q$. If adsorption processes are fast, an equilibrium takes place: $k_{\text{ads}} p_A (1 - q) = k_{\text{des}} q$, from which it follows that $q = b_A p_A / (1 + b_A p_A)$, $b_A = k_{\text{ads}} / k_{\text{des}}$, so $w_{\text{des}} = k_{\text{des}} b_A p_A / (1 + b_A p_A)$. The latter equation for $b_A p_A \sim 1$ might be approximated as $w_{\text{des}} = k p_A^{1/m}$, $m > 1$.

Note that the change in m from 3 to 6 causes a displacement of the area of the existence of oscillatory solutions to lesser α values, *i.e.* the increase in m requires choice of another (lesser) α value. In addition, the change in k_0 and k_9 on the above intervals has a comparatively slight effect only on the scale of the calculated curves.

It has been shown that in the absence of the desorption term the oscillatory solutions of (I) are missing, and in this case NCl_3 reacts completely during the first self-ignition. On the other hand, when the source of NCl_3 is included in (I), slowly damping oscillations arise at discrete values of α ; their period and intensity in 5–10 s become fixed. This is evidence for the existence of the stable limit cycle. It should be noted that the following conditions are necessary for the oscillatory solutions to exist: $k_4, k_6 > 0$ ($\lambda, \xi > 0$), $k_5 > 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ ($\psi > 0.03$), therefore the step (5) must be taken into account. These conditions are evident for experimentally investigated steps (4) and (6),²⁰ however, the calculations predict the existence of reaction (5). Outside the interval of α values corresponding to oscillatory solutions, a 'stationary combustion' takes place after the first self-ignition. During this process the concentrations y_i ($0 < i < 3$) are constant in time and do not exceed 4×10^{-3} on the scale of Figures 2–4.

Evidently, the amount of NCl_3 adsorbed on the reactor surface decreases in the course of the reaction and in doing so, the desorption rate of NCl_3 also decreases. Thus, α was represented as $\alpha = \alpha_0(1 - \eta t)$, where $\eta = (3-5) \times 10^{-7}$ and t is dimensionless time, *i.e.* essentially using the first term of the expansion in a series of some monotonic dependence that actually takes place. It has been shown that with this perturbation allowed for, two types of oscillations arise, depending on the k_7 (γ) value: amplified or damped oscillations with increasing or decreasing k_7 , respectively. Therefore, at $\eta > 0$ the above oscillatory solution falls into two types: the phase portrait of the first type includes an unstable focus located inside a stable limit cycle; and the phase portrait of the second type includes a stable focus. Notice that both regimes were experimentally observed.^{8,9}

However, in this case the amplification of an oscillation leads to the attainment of an initial concentration of NCl_3 ($y_3 = 1$), but this does not occur experimentally. In this connection the evident variation in the surface state was taken into account. In fact, in the course of desorption, molecules of NCl_3 leave the surface, and so if at the beginning of the oscillations the reactor surface was covered predominantly with NCl_3 , at the end of the oscillatory regime this surface would be chemically similar to NaCl . Therefore, the rate constants of the heterogeneous chain break of NCl_2 and Cl must change. It was found that in the solution of system (I) the regularities of self-ignition depend on k_7 more drastically than on k_6 (at $0.5 < k_6 < 3 \text{ s}^{-1}$), hence only the change in k_7 was considered.

This change was included much as it was performed above. γ was represented as $\gamma = \gamma_0(1 - \mu t)$, $\mu = (1-10) \times 10^{-7}$, t is dimensionless time. The calculated curves are shown in Figures 2–4. It is seen from Figures 2–4 that the inclusion of the change in surface state leads to a qualitative agreement between calculated and experimentally observed oscillatory regimes.^{8,9} It is also seen from Figures 2 and 3 that the nature of the amplification of the oscillations changes with a change in the rate 'constant' of the heterogeneous chain break k_7 in agreement with refs. 8 and 9. As this takes place, however, the change-over from damped to amplified oscillations is defined not only by η (η values are the same for Figures 2–4), but also by the value of μ (see Figures 2 and 4), so the phase portrait is fairly complicated.

Notice that the kinetic trends for the changes in concentrations of NCl_3 and intermediates for each specific oscillation, regardless of the character of the regime, are identical to those presented in Figure 1.

It is obvious that the negative sign of μ is prescribed arbitrarily because of a lack of experimental data on the recombination of atoms and radicals on surfaces covered with NCl_3 . This means that further numerical fitting would be worth

little, since various assumptions about either change in surface state or the real mechanism of NCl_3 desorption [instead of the rather simple model (II)] would be required. Strictly speaking, treatment of a two-dimensional problem would be more correct.

Therefore, it has been shown that the modelling of oscillatory regimes in NCl_3 decomposition requires not only an external source to exist, but also a consideration of nonlinear chain branching and breaking as well as a change in the state of the reactor surface.

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