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Kinetics and Mechanism of the Branched Chain Decomposition of Nitrogen Trichloride in the Gas Phase and Chemical Oscillations in This Process

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Abstract—Numerical simulations of the oscillating regimes of the nitrogen trichloride self-ignition in a closed volume are carried out using a one-dimensional system of ordinary differential equations (ODE). It is shown that the suggested mechanism agrees with the experimental data. To find a solution that allows oscillations, it is sufficient to take into account (a) NCl_3 adsorption and desorption on reactor walls, (b) nonlinear chain termination $Cl^{\cdot} + Cl_2\,{}^3\Pi_{ou}^+ \longrightarrow Cl^{\cdot} + Cl_2\,{}^1\Sigma_g^-$, and (c) energetic chain branching $Cl_2\,{}^3\Pi_{ou}^+ + NCl_3 - NCl_2 + Cl^{\cdot} + Cl_2\,{}^1\Sigma_g^-$. The assumption that NCl_3 desorption from the reactor surface takes place during oscillations and changes the properties of the reactor surface leads to oscillation regimes in simulation, which agrees qualitatively with the experiment.

Nonlinear homogeneous and heterogeneous reactions (that is, reactions characterized by a nonlinear dependence of the reaction rate on a concentration or other parameter, for example, temperature) determine the specific features of most gas-phase branched chain processes (BCP) as nonlinear dynamic systems. This is demonstrated by structural organization phenomena (nonthermal flame propagation [1]) and oscillation processes (chemical oscillations) in flow reactors and closed volumes. These regimes may result from nonlinear processes that provide a feedback in these chemical reactions. In the open systems, chemical oscillations in liquid-phase reactions are well studied [2]; however, in the closed systems, the problem of the generation and development of oscillations is not yet solved. Specifically, heat evolution is considered as a feedback factor [3]. However, in low-pressure BCP, energy is accumulated by active intermediate products, and the role of self-heating is insignificant [4]. Oscillations in chemical reactions under isothermal conditions are usually due to autocatalysis by intermediate products [2, 5] and, nonstationary state of the surface [4]. This nonstationary state of the surface is a result of nonlinear heterogeneous reactions with the participation of adsorbed intermediate species. Chemical oscillations are observed in gas-phase BCP, such as phosphorus, CO [4], monosilane [6], and dichlorosilane oxidation [7], and in the thermal decomposition of nitrogen trichloride [8, 9]. For the description of low-pressure gas-phase BCP, deterministic equations (sets of ordinary differential equations) can be applied without taking into account fluctuations [2].

Thermal decomposition of NCl_3 is known to be a branched chain process. In this process, nonlinear chain branching (so-called positive chain interaction, PCI [10, 11]) plays an important role. Not only autowave processes (that is, non-thermal flame propagation due to PCI [11, 12]), but also chemical oscillations [8, 9] are observed in NCl_3 decomposition. Nitrogen trichloride decomposition, which does not require an oxidant, includes few elementary steps. The rate constants for most of them are known [9, 10–15]. Energetic chains including nonlinear branching with the participation of electronically excited intermediate species and nonlinear chain termination play an important role in this process [11, 16, 17]. This means that BCP of NCl_3 decomposition does not have features that are assumed in model linear kinetic mechanisms, such as the mechanism for hydrogen combustion [1, 4]. Thus, it is of interest for the theory of chemical processes to reveal the general features of gas phase BCP, where homogeneous and heterogeneous nonlinear processes play an important role. Practical interest in NCl_3 decomposition is due to its promise as a reagent for chemical lasers [18] and in relation to explosion protection in electrolytic chlorine production [19], where NH_3 is produced as a by-product.

It was shown [8, 9] earlier that in a closed reactor over NaCl surface, the mixture of NCl_3 with He periodically ignites (Fig. 1). The appearance of NCl_3 in a closed volume after each self-ignition is evidence of its desorption from the reactor walls. It was found that, within the self-ignition range, both self-accelerating and damped oscillations can be generated. The period and the amplitude of these oscillations depend on the number (Fig. 1b) and conditions [9] of self-ignitions, which took place earlier in the reactor. Heating did not

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exceed 5°C that means that the oscillations had the chain nature rather than thermal.

The aims of this work were: (a) to describe experimental oscillatory regimes by a known set of elementary reactions, which was supplemented by a step that models the desorption process, and (b) to obtain information about the kinetics and mechanisms of the thermal decomposition of NCl_3 by analyzing a one-dimensional set of ODE.

When termolecular chain termination is neglected, the mechanism of the thermal decomposition of nitrogen trichloride at a low pressure can be described as follows [9, 12, 14–17, 20]:

$$NCl_3 \longrightarrow NCl_2^{\bullet} + Cl^{\bullet}, \quad k_0 = 10^{-4}\text{–}2\times10^{-5}\ s^{-1}\ [15]; \tag{0}$$

$$Cl^{\bullet} + NCl_3 \longrightarrow NCl_2^{\bullet} + Cl_2 \ \text{(chain propagation)}, \quad k_1 = (1.6\pm0.2)\times10^{-12}\ cm^3/s\ [15]; \tag{I}$$

$$NCl_2^{\bullet} + NCl_3 \longrightarrow N_2 + Cl_2 + 3Cl^{\bullet}$$
(linear branching),
$$k_2 = 1.3\times10^{-16}\ cm^3/s \tag{II}$$
(to within the accuracy of the diffusion coefficient of the $NCl_2^{\bullet}$ radical) [14, 16];

$$NCl_2^{\bullet} + NCl_2^{\bullet} \longrightarrow N_2 + Cl_2\,{}^3\Pi_{ou}^{+} + 2Cl^{\bullet}$$
(chain interaction), (III)
$$k_3 = (6.5\pm3.0)\times10^{-13}\ cm^3/s\ [12];$$

$$Cl_2\,{}^3\Pi_{ou}^{+} \longrightarrow 2Cl^{\bullet}, \quad k_4 = 10^4\ s^{-1}\ [20]; \tag{IV}$$

$$Cl_2\,{}^3\Pi_{ou}^{+} + NCl_3 \longrightarrow NCl_2^{\bullet} + Cl^{\bullet} + Cl_2$$
(probable process), (V)
$$k_5 = 10^{-12}\text{–}10^{-15}\ cm^3/s\ [9];$$

$$Cl_2\,{}^3\Pi_{ou}^{+} + Cl^{\bullet} \longrightarrow Cl_2\,{}^1\Sigma_g^{-} + Cl^{\bullet}$$
(nonlinear chain termination), (VI)
$$k_6 = (2.5\pm1.5)\times10^{-10}\ cm^3/s\ [20];$$

NCl_2 radical decay on the wall,
$$k_7 = 2\text{–}16\ s^{-1}\ [16, 17]; \tag{VII}$$

$Cl^{\bullet}$ radical decay on the wall,
$$k_8 = 1\ s^{-1}\ [12, 16]; \tag{VIII}$$

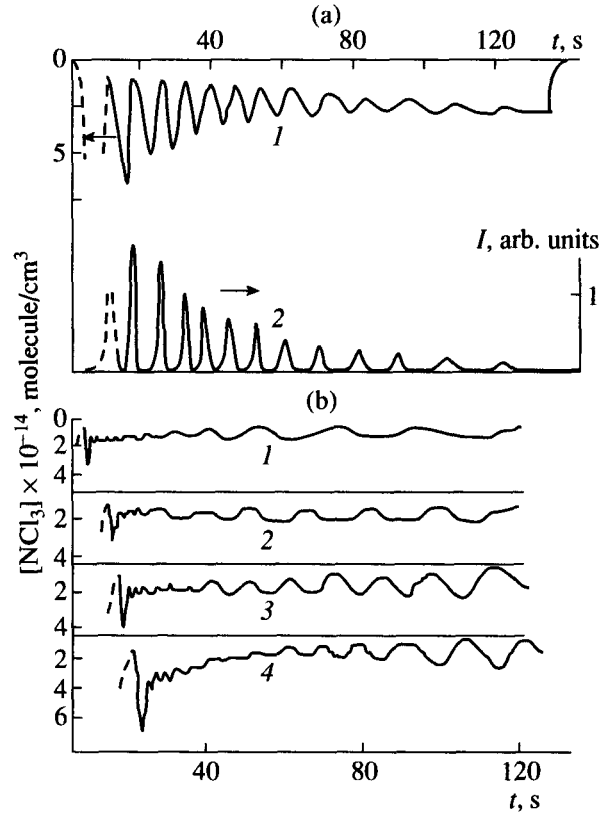

Fig. 1. Chemical oscillations in NCl_3 decomposition over the NaCl surface [9]: (a) (*1*) a change in the NCl_3 concentration and (*2*) in the integral intensity of chemiluminescence (3% of NCl_3 in He, 5 torr, 293 K, cylindrical reactor 4 cm in diameter); (b) a change in the NCl_3 concentration in a spherical reactor (10 cm in diameter, 3% NCl_3, 7 torr, and 293 K) after (*1*) 1, (*2*) 5, (*3*) 11, and (*4*) 20 preliminary ignitions.

deactivation $Cl_2\,{}^3\Pi_{ou}^{+} + M$,
$$k_9 = 8\times10^{-13}\text{–}10^{-13}\ cm^3/s\ [20]. \tag{IX}$$

In the calculation, the value of the rate constant of chain propagation was assumed equal to $k_1 = 1.6\times10^{-12}$ cm^3/s, the rate constant of chain interaction was $k_3 = 6\times10^{-13}$ cm^3/s, the rate constant of nonlinear termination was $k_6 = 1.6\times10^{-10}$ cm^3/s.

The process of energetic branching (reactions (III)–(V)) was presented in the scheme according to the data of [4, 9–12]; that is, we took into account that (i) the probability of the depletion of high vibrational states of $Cl_2\,{}^3\Pi$ ($v > 13$) in reaction (IV) is high because the potential well of the excited state is not deep (~7 kcal), and (ii) energy released in reaction (V) is sufficient for the dissociation of the NCl_3 molecule [20].

Let us introduce dimensionless coordinates $\tau = k_1[NCl_3]_0 t$, $Y_0 = [Cl]/[NCl_3]_0$, $Y_1 = [Cl_2\,{}^3\Pi]/[NCl_3]_0$, $Y_2 = [NCl_2]/[NCl_3]_0$, $Y_3 = [NCl_3]/[NCl_3]_0$, and dimensionless parameters $\omega = k_0/k_1[NCl_3]_0$; $\beta = k_2/k_1$; $\phi = k_3/k_1$; $\gamma = k_7/k_1[NCl_3]_0$; $\lambda = k_4/k_1[NCl_3]_0$; $\psi = k_5/k_1$; $\delta =$

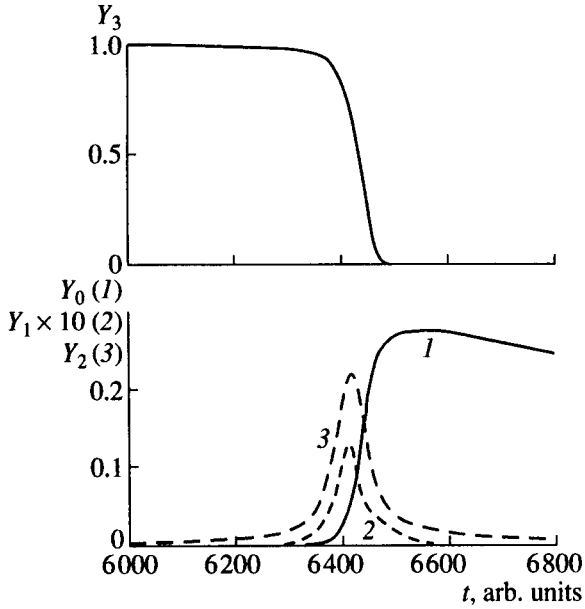

Fig. 2. Numerical calculation of the self-ignition of NCl_3. ($\omega = 5 \times 10^{-8}$, $\chi = 0.25$, $\xi = 100$, $\alpha = 0$, $t_0 = 0$, $t_1 = 70000$, $\beta = 0.8 \times 10^{-4}$, $\gamma = 2 \times 10^{-5}$, $\psi = 0.2$, $\eta = 0$, $\mu = 0$, $\delta = 7 \times 10^{-4}$, $\phi = 0.35$, $\lambda = 0.4$, $N = 70000$). Calculated lower limit of self-ignition is reached at $\gamma = 2.4 \times 10^{-3}$.

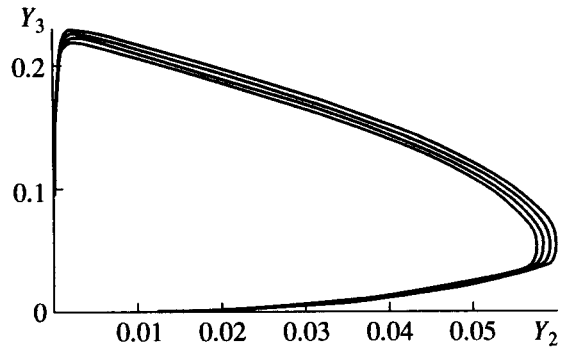

Fig. 3. Numerical calculation of the oscillations without taking into account the surface depletion and changes in its state due to the desorption of NCl_3 ($\omega = 10^{-6}$, $\chi = 0.25$, $\xi = 100$, $\alpha = 0.000013$, $t_0 = 0$, $t_1 = 240000$, $\beta = 0.8 \times 10^{-4}$, $\gamma = 9.1 \times 10^{-4}$, $\psi = 0.2$, $\eta = 0.0000005$, $\mu = 0.0000001$, $\delta = 7 \times 10^{-4}$, $\phi = 0.35$, $\lambda = 0.4$, $N = 240000$). The phase portrait illustrates the presence of a stable limit cycle.

$k_8/k_1[NCl_3]_0$; $\xi = k_8/k_1$; $\chi = k_9/k_1[NCl_3]_0$. The system of kinetic equations takes the following form:

$$dY_0/d\tau = \omega Y_3 - Y_0 Y_3 + 3\beta Y_2 Y_3 + 2\phi Y_2^2 + \psi Y_1 Y_3 + \lambda Y_1 - \delta Y_0 - \xi Y_0 Y_1,$$

$$dY_1/dt = \phi Y_2^2 - \lambda Y_1 - \psi Y_1 Y_3 - \xi Y_0 Y_1 - \chi Y_1, \quad (1)$$

$$dY_2/d\tau = \omega Y_3 + Y_0 Y_3 - \beta Y_2 Y_3 + \psi Y_1 Y_3 - \gamma Y_2 \phi Y_2^2,$$

$$dY_3/d\tau = -\omega Y_3 - Y_0 Y_2 - \beta Y_2 Y_3 - \psi Y_1 Y_3.$$

System (1) was solved with the initial conditions $Y_0 = Y_1 = Y_2 = 0$, and $Y_3 = 1$. The real situation, which was simulated, corresponds to the conditions mentioned in the caption to Fig. 1a; that is, the pressure is 5 torr, the NCl_3 concentration is 3%, and the temperature is 293 K. It is easily seen that 1 s in Figs. 2–6 corresponds to ~7000 arbitrary units (t-axis); the concentration unit in the ordinate axis corresponds to 4.5×10^{15} cm^{-3}. The parameters t_0 and t_1 correspond to the beginning and end of the integration time interval, respectively, N is the number of integration steps.

System (1) was integrated numerically using the forth-order Runge–Kutta method. Figure 2 shows the concentration profile for the initial reactants and intermediate products in simulated self-ignition. The results agree with the experimental data. Indeed, the maxima for NCl_2^* and $Cl_2(^3\Pi)$ are attained simultaneously (see Fig. 1 in paper [10]), the maximum rate of NCl_3 consumption coincides with the $[Cl_2(^3\Pi)]$ maximum and the maximum for the chlorine atom concentration is achieved later (see Figs. 2 and 3 in paper [21]). In addition, the concentration of NCl_2^* reaches a value of $\sim 10^{15}$ cm^{-3} during self-ignition, which agrees with [10] (see Fig. 1 in paper [10]). The concentration of chlorine atoms is equal to tens of percents of the initial NCl_3 concentration [22], and the concentration of $Cl_2(^3\Pi)$ is low in comparison to the concentrations of other intermediate products. This fact agrees with a low quantum yield of $Cl_2(^3\Pi)$ measured in [23]. The value of the induction period (~1 s) also compares well to the experimental values [15]. This means that the system of ODE based on the above mechanism is applicable to the description of experimental data.

Specifics of a function describing desorption is that, after each self-ignition (which probably takes place at the equilibrium concentration of desorbing substance in the volume, at least at the end of the oscillation regime), the initial reactant rapidly burns out as a result of self-ignition. Then, desorption has a rate corresponding to a lower surface coverage and a lower concentration of initial reactant in the volume. The absence of detailed information on the mechanism of NCl_3 adsorption and desorption prevented us from constructing a function for the complete description of this process. NCl_3 desorption was simulated by using an additional term to the forth equation of system (1). This term describes the rate of NCl_3 desorption:

$$dY_3/d\tau = \alpha Y_3^{1/m}, \text{ where } m = 2, \ldots, 6. \quad (2)$$

The choice of an equation to describe the supply of the initial reactant into the volume is, in fact, arbitrary because of the lack of experimental data. Therefore, the results presented below are only qualitative. Expression (2) was chosen on the basis of the rate law of des-

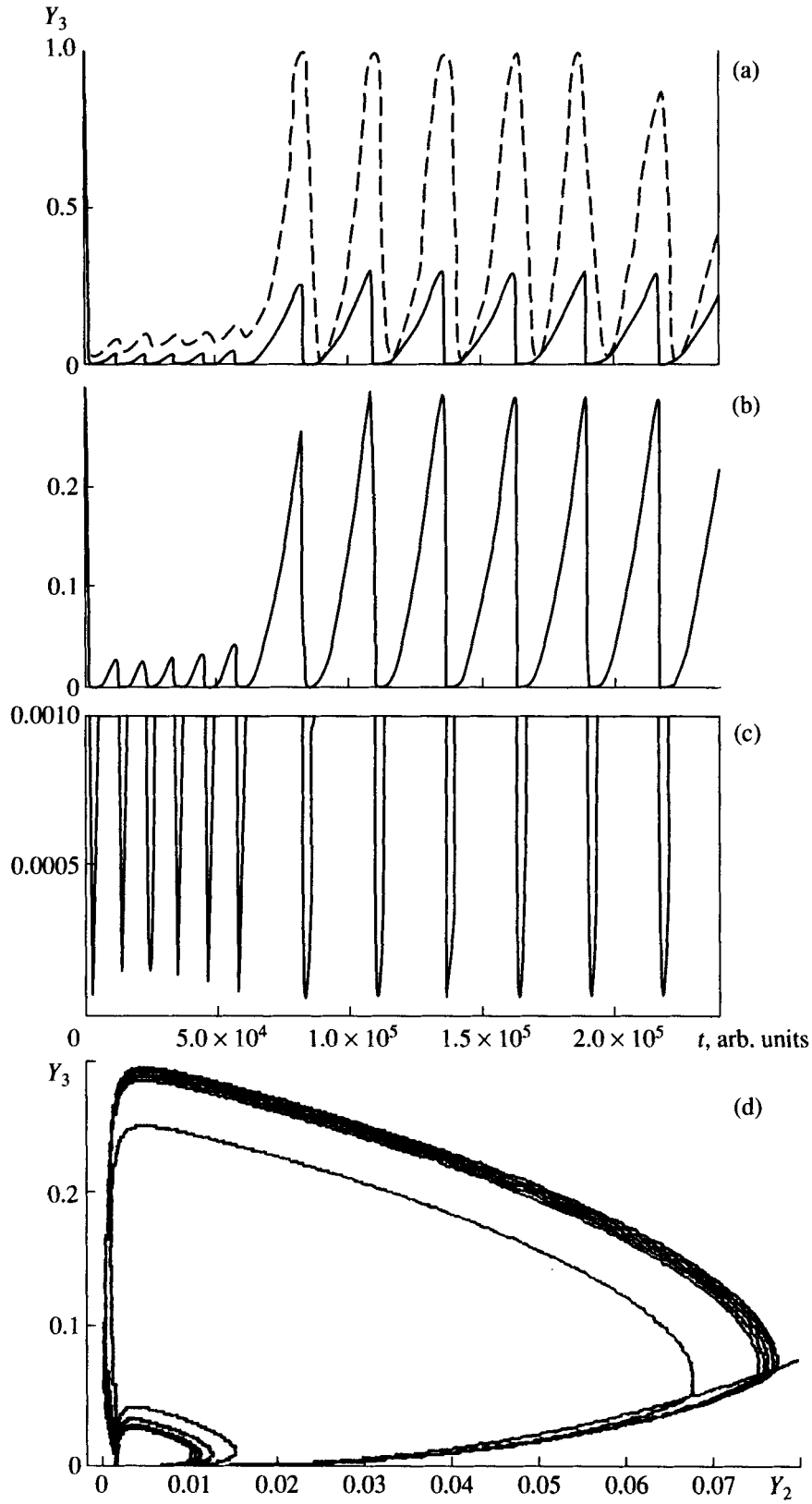

Fig. 4. Oscillation regime calculated taking into account the depletion of the surface and a change in its state as a result of NCl_3 desorption ($\alpha = 0.000035$, other parameters have the same values as in Fig. 3). (a, b, and c) differ only in the scale of the ordinate axis (to demonstrate the qualitative agreement with Fig. 1b). A dashed line corresponds to the case of $\mu = 0$; (d) is the phase portrait including an unstable focus in a stable limit cycle.

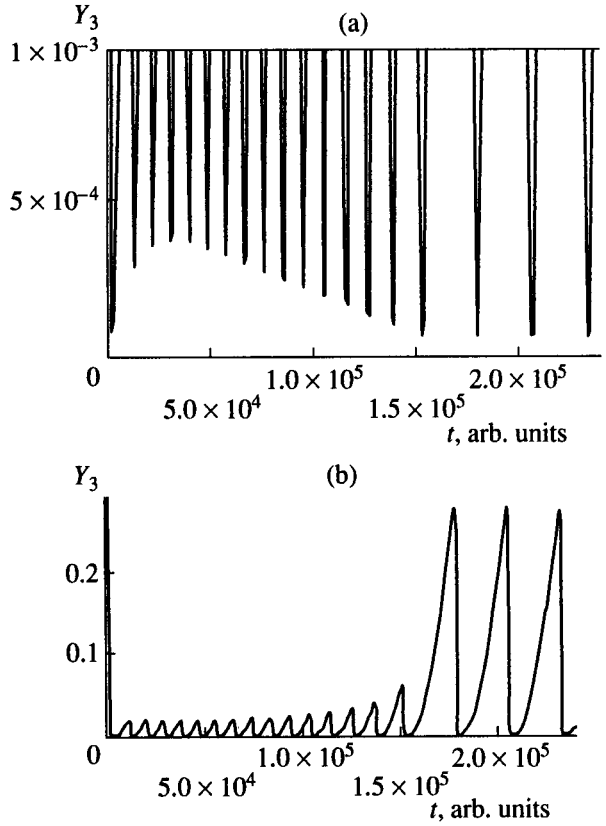

Fig. 5. Oscillation regime calculated for the same conditions as Fig. 4, except for the parameter $\gamma = 8.8 \times 10^{-4}$ (compare with Fig. 1b). (a and b) differ in the scale of the ordinate axis.

orption within the model of the exponentially nonuniform surface

$$w_d = k_d p_A^{b+1/n},$$

where w_d is the rate of desorption, k_d is the rate constant of desorption, $b < 1$ is a fraction of the difference in the activation energy for desorption in the heat of adsorption when passing from one site of nonuniform surface to another, p_A is the partial pressure of the adsorbate, and n is the exponent in the equation of isotherm presented by a power function $\theta = C p_A^{1/n}$ (C is a coefficient and θ is surface coverage) [24].

Note, that a change in the value of m from 3 to 6 in equation (2) leads to a shift of the region of oscillating regimes, similar to the regimes presented in Fig. 3, to lower values of α. This means that an increase in m requires a choice of another (lower) value of α. Thus, the region of oscillations in limited in the α–m coordinates.

Note also that a change in the values of k_1 and k_9 within limits mentioned above affects only the scale of calculated curves. Moreover, this effect is relatively small.

The solution to system (1) shows that, without an additional desorption term, the oscillatory regimes are impossible at the values of parameters used in our calculations because NCl_3 is completely consumed during the first ignition. If desorption is taken into account, slowly damping oscillations are generated in a certain range of α values. Then these oscillations transform into the oscillations a constant period and intensity. This is indicative of a stable limit cycle with phase trajectories coiled round (Fig. 3). It is necessary to note that the conditions $k_4, k_6 > 0$ ($\lambda, \xi > 0$) and $k_5 > 10^{-13}$ cm^3/s ($\psi > 0.03$) should be met for the existence of periodic solutions within the range of parameters under consideration. This means that we should take into account reactions (IV)–(VI). Reactions (IV) and (VI) were experimentally studied in [20], and they in fact take place. The calculation also predicts that reaction (V) takes place. Outside the range of α values corresponding to periodic solutions, stationary combustion begins after the first ignition. The stationary concentrations of the initial reactant and intermediate products characterize this regime. The concentrations of intermediate products are lower than 4×10^{-3} in the units used in Figs. 2–6.

Obviously, the quantities of NCl_3 adsorbed on the reactor walls decreases during desorption. Therefore, the rate of NCl_3 desorption also decreases. We took this fact into account in our calculations by using the formula $\alpha = \alpha_0(1 - \eta\tau)$, where $\eta = (3–5) \times 10^{-7}$. That is, in fact we used the first term from expanding some real monotonic function into a series. Taking into account this small perturbation, we obtain two types of oscillations: accelerating and damped (compare, for example, Figs. 4 and 6) in the range of α where oscillations can exist. The type of oscillations depends on the value of the rate constant of heterogeneous termination k_7 (γ). Thus, at $\eta \neq 0$, the solution presented in Fig. 3 divides into two. The phase portrait of the first solution includes an unstable focus located inside the stable limit cycle (Fig. 4d). The phase portrait of the second solution is a stable focus (Fig. 6c). Figure 4a (dashed line) presents the calculated regime of accelerating oscillations. Thus, the numerical experiment shows that the account of the surface depletion leads to two possible types of system behavior. The phase trajectories for these two types of behavior correspond to the stable limit cycle (including an unstable focus) or to the stable focus, depending on the value of k_7. Both these oscillation regimes are experimentally observed (Fig. 1).

The qualitative difference between the calculated (a dashed line in Fig. 4a) and experimental (Fig. 1b) accelerated oscillatory regimes is that the calculation suggests that the initial NCl_3 concentration ($Y_3 = 1$) is reached, whereas the experiment suggests that it is not. Therefore, it is necessary to take into account the obvious fact that the surface changes during oscillations. Indeed, the NCl_3 molecules leave the surface because of desorption. Therefore, in the beginning of the oscillatory regime, the surface is covered by a layer or several layers of NCl_3, whereas at the end of the oscillations, its properties are close to the properties of NaCl. Therefore, the coefficients of the heterogeneous decay of $NCl_2^{\cdot}$ and $Cl^{\cdot}$ radicals should change. It was shown

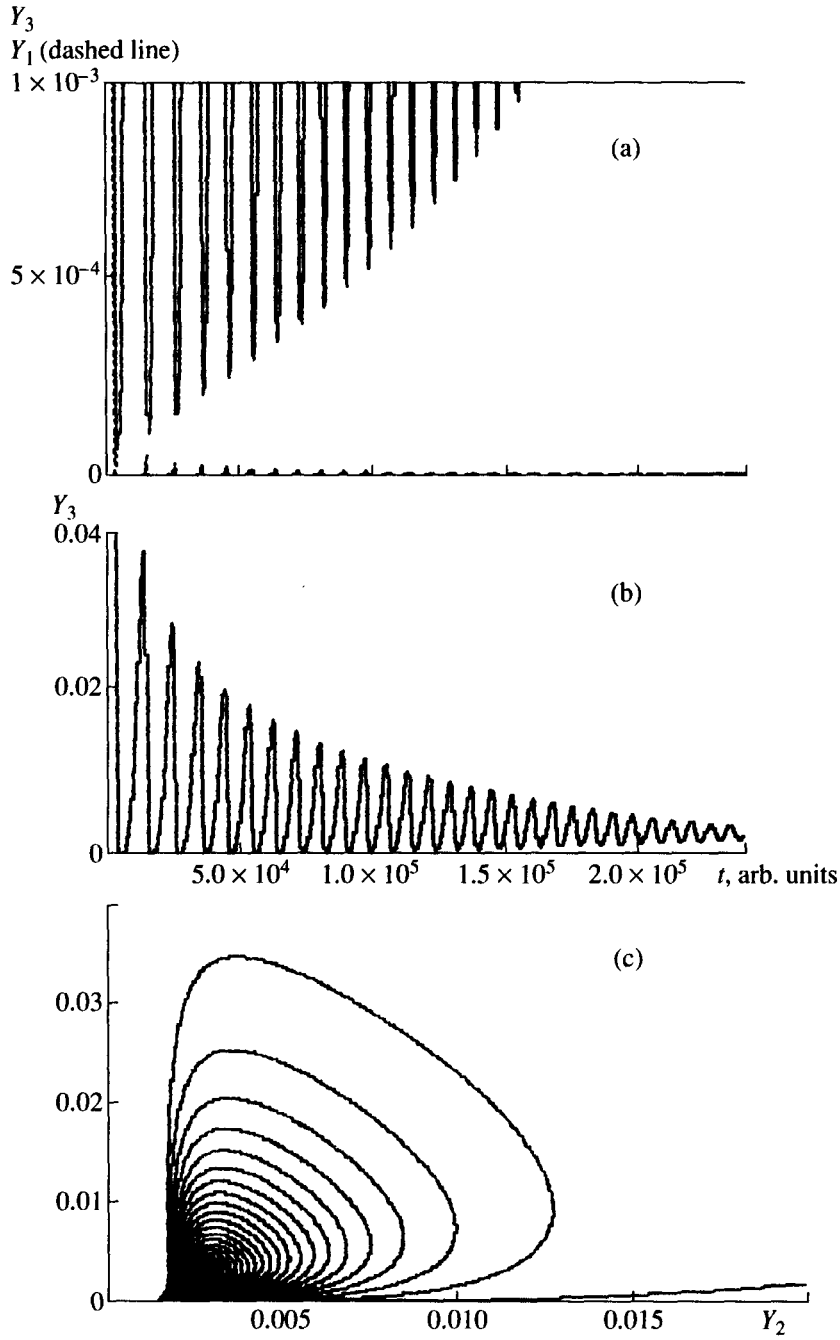

Fig. 6. (a, b) Calculated regime of damped oscillations ($\mu = 0.0000008$, other parameters are the same as in Fig. 4); (a and b) differ in the scale of the ordinate axis (to demonstrate the agreement with Fig. 1a); (c) the phase portrait including a stable focus.

that, according to the conditions of the numerical experiment, the regularities of self-ignition (for example, the induction period) are more sensitive to the value of k_7 stronger than to k_8 (at $0.5 < k_8 < 3\ s^{-1}$). Therefore, we considered only a change in k_7 with time. This change was taken into account by analogy with the consumption of NCl_3, assuming that $\gamma = \gamma_0(1 - \mu\tau)$, where $\mu = (1\text{–}10) \times 10^{-7}$. The results of the numerical experiment are presented in Figs. 4–6. The consideration of a change in the state of the surface leads to quantitative agreement between the calculated and experimental oscillation regimes. It is also seen that, if the rate constant of heterogeneous termination k_7 changes from one experiment to another, then the character of the acceleration of oscillations also changes. This is evidence for the qualitative agreement between the experiment (Fig. 1b) and calculation (Figs. 4, 5). However, not only the value of η but also the value of μ determines the transition from damped to accelerating oscillations because the values of η in Figs. 4–6 are equal. This is illustrated by the comparison of Figs. 4 and 6,

showing that the phase portrait becomes much more complex. Note that, in each separate oscillation, the rate laws of a change in the concentrations of the initial reactant and intermediate products are the same as in Fig. 2 independently of the nature of an oscillatory regime.

The choice of the negative value of μ is arbitrary because the experimental data on the coefficient of heterogeneous recombination of atoms on a surface covered by NCl_3 layer are not available in the literature. Moreover, our calculation shows that, for positive μ, both accelerated and damped regimes of oscillations are observed. This means that the value of further fitting of the experimental data does not make much sense because too many parameters are involved. In addition, some additional assumptions are needed on a change in the properties of the surface during the oscillations and on the mechanism of NCl_3 desorption from the reactor surface, described by simple expression (2). Moreover, the strict solution to the problem requires the consideration in two dimensions.

One of the main results of this work is the confirmation of the agreement of the mechanism of radical chain decomposition of NCl_3 suggested in [8–17] with experimental data. In addition, the numerical calculation based on this mechanism and taking into account the experimentally proven desorption of NCl_3 from the reactor walls allows the qualitative description of experimentally observed regimes of chemical oscillations in a closed volume in the branched chain decomposition of NCl_3 over the surface of NaCl.

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