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Nitrogen Trichloride Decomposition in the Presence of Molecular Hydrogen: I. Promotion of Nitrogen Trichloride Decomposition by Molecular Hydrogen Additives Near the Lower Self-Ignition Limit

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Abstract—The promotion of the branched-chain decomposition of nitrogen trichloride by molecular hydrogen additives at room temperature and 20 torr manifests itself in a decrease in the induction period and the acceleration of reactant consumption with an increase in the hydrogen concentration in the $NCl_3 + H_2 + He$ mixtures. The emission spectrum of the $H_2 + NCl_3$ flame contains the intense bands of $NCl^{\bullet\bullet}$ ($b^1\Sigma^+ – X^3\Sigma^-$, $v = 1 – 0$, $v = 0 – 1$, and $v = 0 – 0$, where v is the vibrational quantum number) and the bands of a hydrogen-free compound. The latter bands can be assigned to electronically excited $NCl_2^\bullet$ radicals formed in the $H + NCl_3$ reaction. The calculations restrict the number of elementary reactions favoring promotion. The promotion effect in the system studied should be due to the side reaction of linear branching. The occurrence of the $H + NCl_3$ reaction via two pathways ($NHCl^\bullet + 2Cl$ and $NCl_2^\bullet + HCl$) ensures the qualitative agreement between the experimental data and calculation.

INTRODUCTION

The promotion of gas-phase chain reactions is important for the development of methods of combustion intensification. However, this phenomenon has been described for few systems. The oxidation of CO in the presence of hydrogen-containing compounds was studied in detail in [1]. The promotion by these compounds is due to the involvement of the main elementary reactions of H_2 combustion into the mechanism of the above process. In contrast to the ignition of rather hydrogen-rich $H_2 + O_2$ mixtures involving only branched chains, the chains of this reaction are less branched. Taking this into account, promotion is perfectly interpreted based on the linear kinetic scheme of H_2 combustion. Earlier [2], we studied the promotion of the gas-phase process involving nonlinear branching reactions for hydrogen oxidation in the presence of SiH_4 and CS_2 additives. Promotion was related to an increase in the contribution of nonlinear branching $H + HO_2^\bullet \longrightarrow 2OH^\bullet$ resulting in the formation of the active $OH^\bullet$ radical instead of the inert $HO_2^\bullet$ radical; that is, the phenomenon is also interpreted on the basis of the mechanism of hydrogen combustion.

The thermal decomposition of NCl_3 is a branched-chain process involving nonlinear chain branching [3–5] and resulting in nonthermal flame propagation and chemical oscillations [6]. The $Cl_2(^3\Pi^+_{ou})$ molecules formed in the reaction of the $NCl_2^\bullet$ radicals with each other participate in chain branching (energetic branching). The rapid reaction of quadratic chain termination $Cl + Cl_2(^3\Pi^+_{ou}) \longrightarrow Cl + Cl_2(^3\Sigma^-_g)$ plays an important role in this branched-chain process. The calculations performed in [5, 7] allowed the interpretation of the main kinetic regularities of NCl_3 decomposition, including nonthermal flame propagation [4], as well as the kinetics and chemical oscillations [6] on the basis of the nonlinear reactions of chain branching and termination. The introduction of hydrogen atoms into the reaction with NCl_3 favors the formation of the $NCl^{\bullet\bullet}$ radicals (including the electronically excited ones) via the reactions [8]

$$H + NCl_3 \longrightarrow NCl_2^\bullet + HCl$$

and

$$H + NCl_2^\bullet \longrightarrow NCl^{\bullet\bullet} + HCl.$$

Taking into account the process energetics and the liberation of ~78 kcal/mol in the former reaction, it can occur via some other pathways, for example,

$$H + NCl_3 \longrightarrow NCl^{\bullet\bullet} + Cl + HCl + 46\ \text{kcal/mol} \quad \text{(I)}$$

or

$$H + NCl_3 \longrightarrow NHCl^\bullet + Cl_2 + 74\ \text{kcal/mol [10].} \quad \text{(II)}$$

The hydrogen atoms may be generated by the reaction $Cl + H_2 \longrightarrow H + HCl$ in the course of the NCl_3 + H_2 process. Taking into account that Cl_2 is the product of NCl_3 decomposition, this reaction in the presence of H_2 involves two chain processes: branched-chain NCl_3 decomposition and the H_2 + Cl_2 reaction. In this case, it is *a priori* unclear whether or not these chain processes will accelerate each other, that is, whether or not the mutual promotion will take place.

The investigation of the reaction between NCl_3 and H_2 is also important for practice, namely, for the preparation of optically active media [8, 11] and for the explosion safety in the chlorine industry [12, 13].

The aim of this work was to study the regularities of the promotion of the branched-chain decomposition of NCl_3 by H_2 additives and to interpret them using computer simulation.

EXPERIMENTAL

Experiments were performed in static and jet parts of a vacuum setup described in [14, 15]. The reaction under static conditions was conducted in a spherical vessel (diameter, 10 cm) equipped with optical windows, including two antipodal ones. The emission of a probing source or the reaction chemiluminescence was focused at an inlet slit of an OSA-500 optic spectrum analyzer (200–800 nm; resolution, 0.144 nm) or a DMR-4 monochromator. In the second case, the emission was registered with a photomultiplier tube, the signal from which was transmitted to an S8-2 electron-beam memory oscilloscope. The emission in the UV region was induced with a DVS-25 mercury–helium lamp, and its intensity was measured with an FEU-39 photomultiplier (sensitivity, 200–600 nm). The emission in the visible region was registered with an FEU-62 photomultiplier (sensitivity, 500–1200 nm), the signal from which was also transmitted to an S8-2 oscilloscope through a light guide. The reaction under jet conditions was conducted in a cylindrical quartz reactor (length, 0.5 m; diameter, 0.9 cm), whose surface was treated with hydrofluoric acid or potassium tetraborate to retard the heterogeneous recombination of hydrogen [16] and chlorine [17] atoms. The reactor was equipped with a discharger (13.6 MHz) to produce chlorine and hydrogen atoms and with inlets located under the discharge zone to supply the reactants in the molecular form to the reaction zone. The reactor was placed into the resonator of an EPR-20 IKhF spectrophotometer. The self-ignition limit was determined with an experimental error of ±2% by averaging two pressures, at which the mixture does (the higher value) and does not self-ignite (the lower value). In a different experimental series, NCl_3 was liberated into He (reagent grade) or the He (reagent grade) + H_2 (reagent grade) (D_2 (reagent grade)) mixture. The NCl_3 concentration was varied from 3 to 25 vol % at 0.5–20 torr and 293–400 K. The procedures of NCl_3 synthesis and the preparation of its mixture with gases were described in [18]. The absorption of emission from NCl_3 was registered at a wavelength of 220 nm (an extinction coefficient of 1760 l mol^{-1} cm^{-1} [19]). The method allowed the determination of the NCl_3 concentration above 10^{13} cm^{-3}.

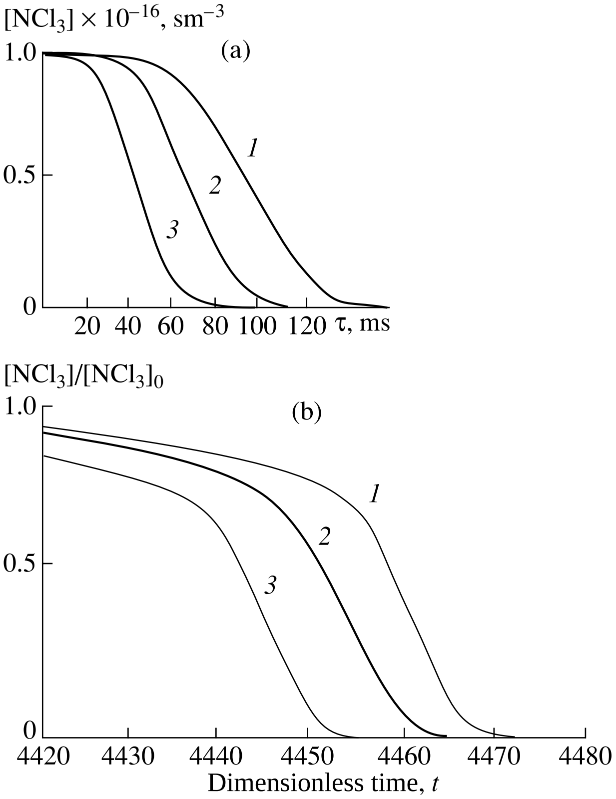

Fig. 1. Time variations in the NCl_3 concentration on its self-ignition (*1*) without additives and in the mixtures with H_2 at the concentration of the latter with respect to $[NCl_3]_0$ (*2*) 5 and (*3*) 10 vol %, $[NCl_3]_0$ = 25%, and P = 1.5 torr. (a) Experimental curves and (b) calculation results.

RESULTS AND DISCUSSION

In the first series of experiments, we studied the effect of H_2 additives (at concentrations higher than that of the initial NCl_3 by more than 5%) on NCl_3 decomposition at pressures that were nearly three times higher than the lower self-ignition limit. The reaction rate was registered as a function of the duration of UV-light absorption by the NCl_3 molecules at a wavelength of 220 nm (Fig. 1a). Even 5% H_2 additive causes both a decrease in the induction period and the acceleration of NCl_3 decomposition under the conditions of developed ignition. This suggests that the addition of molecular hydrogen promotes NCl_3 decomposition. Figure 2 presents the emission spectra of the NCl_3 flame in He with the H_2 additives. Along with the emission bands of Cl_2^* ($^3\Pi^+_{ou}$ – $^1\Sigma^-_g$) [9], the spectrum contains the $NCl^{\bullet\bullet}$

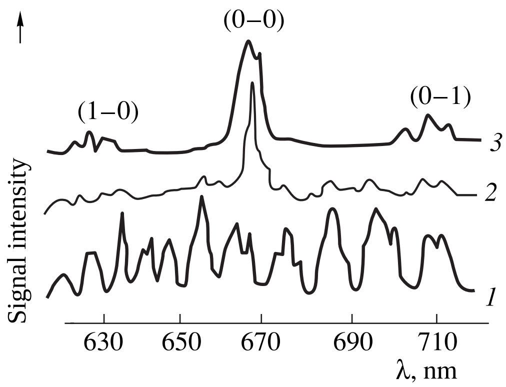

Fig. 2. Stationary flame spectra: (*1*) 20% NCl_3 in He, $P = 2.0$ torr; (*2*) 20% NCl_3 in He (1.5 torr) + H_2 (0.5 torr); and (*3*) 20% NCl_3 in He (1.0 torr) + H_2 (1.0 torr).

lines [8] ($b^1\Sigma^+ - X^3\Sigma^-$ and $v = 1-0, 0-0$, and $0-1$ transitions, where v is the vibrational quantum number) with an intensity that markedly increases with an increase in the H_2 concentration in the mixture. Note that the $NCl^{\bullet\bullet}$ lines ($b^1\Sigma$, $a^1\Delta$) were observed in the reaction of hydrogen atoms with NCl_3 [8].

To elucidate the effect of minor H_2 additives on the lower self-ignition limit of NCl_3 (P_1), the P_1 value was determined at a certain NCl_3 concentration. Then, a small part of NCl_3 was replaced by He (with the overall pressure remaining unchanged) so that the mixture was beyond the self-ignition region (Fig. 3a, curve *2*). Curve *1* in Fig. 3a describes the integral chemiluminescence intensity during NCl_3 decomposition at the same pressure, which is slightly higher than the P_1 value. In the next run (Fig. 3a, curve *3*), the He additive was replaced by an identical H_2 additive. The addition of H_2 in a concentration of 40% of that of NCl_3 causes a decrease in the P_1 value because NCl_3 decomposition in the presence of H_2 occurs more intensively, resulting in the promotion of the process. The H_2 additives in 20% concentrations with respect to initial NCl_3 cause a decrease in the P_1 value. Therefore, the reactions involving H_2 and resulting in promotion strongly affect NCl_3 decomposition at $P \gg P_1$. However, the influence of the H_2 additives on this process is less pronounced near the P_1 limit.

For the NCl_3 + He + H_2 mixture, the flame emission is observed at 380–390 nm and its intensity passes through a maximum as the H_2 concentration increases (Fig. 4). We failed to assign this emission to any compound based on the available data. To elucidate whether or not the emitting compound contained hydrogen atoms, we replaced molecular hydrogen with deuterium. In this case, the emission bands did not shift. Therefore, the emitting intermediate lacks hydrogen atoms (accurate to the resolution of the OSA-500 spectrum analyzer). This emission may be attributed to the electronically excited NCl_2^* radicals generated in the virtually thermally neutral reaction $H + NCl_3 \longrightarrow NCl_2^* + HCl$.

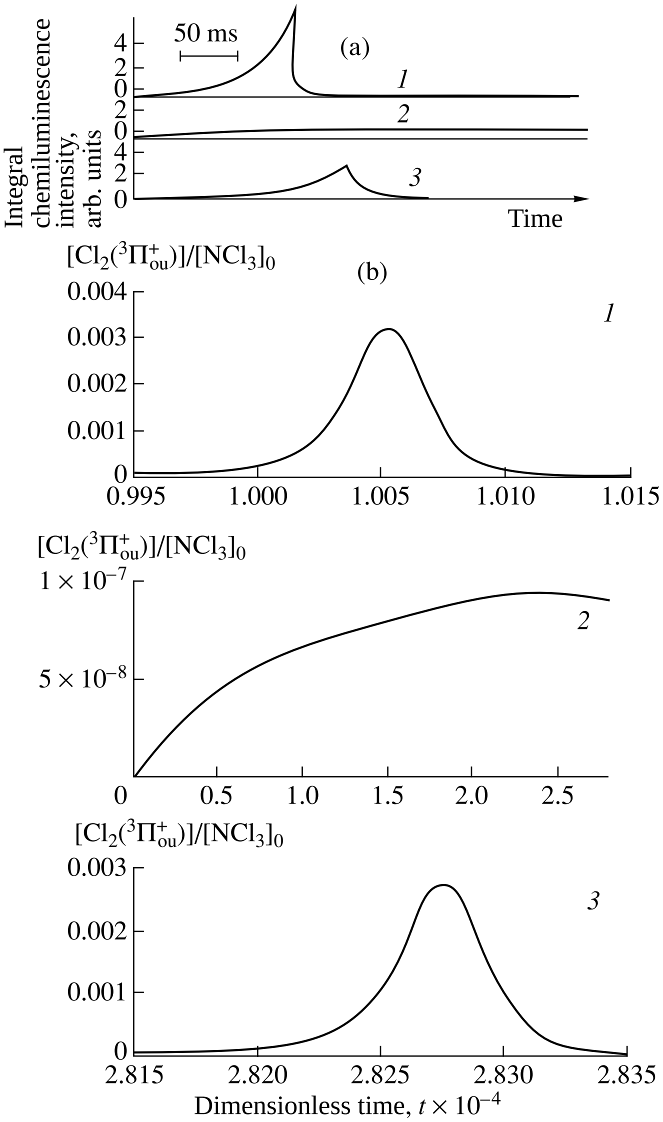

Fig. 3. Integral chemiluminescence intensity during NCl_3 decomposition: (*1*) NCl_3 + He (1.47 torr); (*2*) NCl_3 + He (1.35 torr) + He (0.12 torr); (*3*) NCl_3 + He (1.35 torr) + H_2 (0.12 torr). $[NCl_3]_0 = 5.6\%$. (a) Experimental oscillograms and (b) calculated kinetic curves.

Within several minutes after the ignition of the NCl_3 c H_2 mixture, the inner reactor surface is coated with a white crystalline substance which is readily soluble in water and sublimated on heating. From its aqueous solution, a white curdled sediment of AgCl precipitates upon the addition of silver nitrate. This indicates that NH_4Cl is formed as a final product on the walls of the reaction vessel. Therefore, the reaction between NCl_3

and H_2 results in the formation of N–H bonds. Compounds with these bonds may be generated via the abstraction of the chlorine atoms from the nitrogen atoms

$$H + NCl_2^{\cdot} \longrightarrow NCl^{\cdot\cdot} + NCl,$$

$$H + NCl^{\cdot\cdot} \longrightarrow N + HCl$$

or recombination

$$N + H + M \longrightarrow NH^{\cdot\cdot} + M,$$

where M is the third body; etc.

A similar situation is observed in the reaction of hydrogen atoms with $NFCl_2$ [20]. In this case, nitrogen atoms are formed in the following reaction series

$$NF^{\cdot\cdot}(a^1\Delta) + H \longrightarrow HF + N(^2D)$$

with spin conservation,

$$N(^2D) + NF^{\cdot\cdot} \longrightarrow N_2(B) + F;$$

$$N_2(B^3\Pi_g) \longrightarrow N_2(A^3\Sigma_u^+) + h\nu.$$

However, in contrast to the results of Exton *et al.* [20], the $N_2(B^3\Pi_g) \longrightarrow N_2(A^3\Sigma_u^+)$ transition (560–660 nm) is observed in the emission spectrum neither in the H + NCl_3 system [8] nor under our experimental conditions. Indeed, the reaction of the hydrogen atoms with $NF^{\cdot\cdot}(a^1\Delta)$ is more exothermic than that with $NCl^{\cdot\cdot}(a^1\Delta)$ by ~30 kcal/mol and its rate constant is 2.5×10^{-13} cm^3/s. Therefore, the H + $NCl^{\cdot\cdot}(a^1\Delta)$ reaction should still be slower. This suggests that N–H bond formation in the fluorine-free system is due to some other process. Let us consider the above exothermic reaction (II) as such a process. Note that the energy evolved in this reaction is sufficient for the chlorine molecule to dissociate into two chlorine atoms if this energy is appropriately distributed over the degrees of freedom in the transition state.

In NCl_3 and H_2 mixtures (1 : 1 + 50% He) under jet conditions at 2–10 torr, a stationary flame arises that consists of the dark red and blue luminescence zones along the steam. The second zone disappears when H_2 is replaced by He. Heating, measured with a thermocouple (d = 30 μm) placed in the flame zone, is less than 100°C. We failed to register any atoms or radicals using the ESR method under these conditions at a magnetic field intensity up to 8000 Oe. However, Azatyan *et al.* [14] registered the chlorine atoms (sensitivity, $\sim 10^{12}$ cm^{-3}) when H_2 is replaced by He in the NCl_3 + He flame. The ESR spectrum of the chlorine atoms disappeared upon the addition of molecular hydrogen or hydrogen atoms (the pressure in a stream changed within 10%). On the contrary, the ESR spectrum of hydrogen atoms was not observed upon the addition of NCl_3 to the hydrogen atom flow (sensitivity, $\geq 10^{13}$ cm^{-3}).

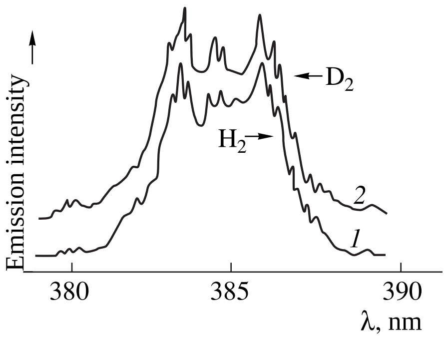

Fig. 4. Emission spectrum assigned to the $NCl_2^{\cdot}$ radicals during the ignition of the NCl_3 + He mixture with (*1*) hydrogen and (*2*) deuterium additives $[H_2] = [D_2] \sim 15\%$, $[NCl_3]_0 \sim 20\%$, and P = 4.0 torr.

Taking this into account, we can estimate the lower limit of the rate constant for the H + NCl_3 overall reaction. For typical experimental conditions ($[NCl_3]$ = 10%, $[H_2] \sim [H] \sim 1\%$, P = 1 torr; flow rate, 5 m/s; reaction zone length, 2 cm), the estimate shows that the rate constant for the overall reaction is 1.5×10^{-13} cm^3/s. We note the specific feature of the phenomenon observed comprising a decrease rather than an increase in the chain carrier concentrations under promotion conditions.

Using the available rate constants for most elementary reactions of the branched-chain decomposition of NCl_3 and $H_2 + Cl_2$ in calculations, one can easily eliminate those elementary reactions that certainly do not cause promotion and, thus, determine which processes are responsible for the observed phenomenon. The kinetic mechanism of NCl_3 decomposition in the presence of H_2 at low pressures (ignoring the reactions of termolecular chain termination) may be represented as follows:

(0) $NCl_3 \longrightarrow NCl_2^{\cdot} + Cl, \quad k_0 = 10^{-5}\ s^{-1}$ [15];

(1) $$Cl + NCl_3 \longrightarrow NCl_2^{\cdot} + Cl_2,$$
$$k_1 = 1.6 \times 10^{-12}\ cm^3/s \ \ [15];$$

(1) $$NCl_2^{\cdot} + NCl_3 \longrightarrow N_2 + Cl_2 + 3Cl,$$
$$k_2 = 3.4 \times 10^{-11} e^{-3250/T}\ cm^3/s$$

[21, 22] (3250 = E (cal/mol) /R(1.98 cal mol^{-1} $°C^{-1}$). E is the activation energy, R is the gas constant, and T is the temperature.

The rate constants for chain termination consistent with the data of [14, 19, 23] were chosen so that the calculated P_1 values in hydrogen-free mixtures coincide with their experimental values [7].

(2) $$NCl_2^{\bullet} + NCl_2^{\bullet} \longrightarrow N_2 + Cl_2(^3\Pi^+_{ou}) + 2Cl,$$
$$k_3 = 6 \times 10^{-13}\ \text{cm}^3/\text{s} \quad [5];$$

(3) $$Cl_2(^3\Pi^+_{ou}) \longrightarrow 2Cl, \quad k_4 = 10^4\ \text{s}^{-1}\ [23];$$

(4) $$Cl_2(^3\Pi^+_{ou}) + NCl_3 \longrightarrow NCl_2^{\bullet} + Cl + Cl_2,$$
$$k_5 = 3 \times 10^{-13}\ \text{cm}^3/\text{s}\ [5];$$

(5) $$Cl_2(^3\Pi^+_{ou}) + Cl \longrightarrow Cl_2(^1\Sigma^-_g) + Cl,$$
$$k_6 = 1.6 \times 10^{-10}\ \text{cm}^3/\text{s}\ [21];$$

(6) $$NCl_2^{\bullet} \xrightarrow{\text{wall}} \text{termination}, \quad k_7 = 10\ \text{s}^{-1}\ [19, 23];$$

(7) $$Cl \xrightarrow{\text{wall}} \text{termination}, \quad k_8 = 1\ \text{s}^{-1}\ [14].$$

Note that reactions (0)–(9) and their rate constants are identical to those used in the calculations of [7].

(8) $$Cl_2(^3\Pi^+_{ou}) + M \longrightarrow Cl_2(^1\Sigma^-_g) + M,$$
$$k_9 = 10^{-13}\text{–}10^{-10}\ \text{cm}^3/\text{s} \quad [5, 17];$$

(9) $$Cl + NCl_2^{\bullet} \longrightarrow NCl^{\bullet\bullet} + Cl_2,$$
$$k_{10} = 0.67 \times 10^{-11} e^{-1900/T}\ [23];$$

(10) $$H + Cl_2 \longrightarrow Cl + HCl,$$
$$k_{11} = 0.92 \times 10^{-10} e^{-717/T}\ \text{cm}^3/\text{s}\ [24];$$

(11') $$H + Cl_2(^3\Pi^+_{ou}) \longrightarrow Cl + HCl,$$
$$k_{11'} = k_{11};$$

(11) $$Cl + H_2 \longrightarrow H + HCl,$$
$$k_{12} = 0.4 \times 10^{-11} e^{(-1088/T)}\ \text{cm}^3/\text{s}\ [25].$$

Note that the consideration of the reaction reversible to reaction (12) does not virtually influence the calculation results.

(12) $$H + NCl_3 \longrightarrow NCl_2^{\bullet} + HCl,$$
$$k_{13} = 4 \times 10^{-12}\ \text{cm}^3/\text{s}\ [8];$$

(13) $$H + NCl_2^{\bullet} \longrightarrow NCl^{\bullet\bullet} + HCl,$$
$$k_{14} = 10^{-10}\ \text{cm}^3/\text{s}\ [8].$$

Note that the k_{13} value obtained in [8] agrees with the above estimate ($\geq 1.5 \times 10^{-13}$ cm^3/s). When simulating the kinetics of $NCl^{\bullet\bullet}$ chemiluminescence ($b^1\Sigma^+$) formed in reaction (14), we took into account the lifetime of these excited radicals, the reciprocal of which is 1580 s^{-1} [8].

We assumed that heat is mainly released in reaction (11) because NCl_3 decomposition at low pressures is virtually isothermic: the energy is consumed for the formation of atoms, radicals, and excited species [3, 14]. The heat balance equation is [26]

$$dT/dt = Qw(T)/(C_p\rho) - \alpha L(T - 298)/(C_p\rho), \quad (1)$$

where Q is the heat effect of reaction (11) equal to ~55 kcal/mol [24], C_p is the heat capacity of the mixture (0.05 cal g^{-1} °C^{-1}) for He [27], α is the heat transfer coefficient, L is the surface/volume ratio (cm^{-1}), ρ is the gas density, and $w(T)$ is the reaction rate. In the calculation scheme, T is expressed in °C. The α value was estimated by the following equation [26]:

$$\alpha = L\delta\Lambda e/r^2,$$

where r is the reactor radius (cm); e is the base of natural logarithms; δ is the critical parameter (3.32); Λ is the coefficient of the mixture thermal conductivity, which we assumed in calculations to be equal to that of He [27].

The dimensionless time t was determined as $t = k[NCl_3]_0\,\tau$ (where τ is time, s), and the dimensionless concentrations were calculated as $Y_i = A_i/[NCl_3]_0$ (where A_i are the current component concentrations). We obtained the following kinetic equations:

$$dY_i/dt = -\sum_{i,j} k_j Y_i Y_j + \sum_{i,\, l \neq i} k_l Y_l Y_j - \sum_i k_i Y_i + \sum_j k_j Y_j. \quad (2)$$

The initial conditions were $Y_i = 0$, the dimensionless concentrations of NCl_3 and hydrogen were $Y_1 = 1$ and $Y_6 = 0.1$–1.0, respectively; and the initial temperature was 298 K. The system of Eqs. (1) and (2) was integrated using the fourth-order Runge–Kutta method.

As follows from the calculations, the consideration of reactions (0)–(14) fails to explain the increase in the rate of NCl_3 consumption, the decrease in the induction period, both of which were observed experimentally (Fig. 1a), and even a decrease in the lower self-ignition limit P_1 (Fig. 2a) in the presence of H_2 additives. This suggests that the reactions of quadratic chain termination (reactions (6) and (9) in our case) do not change the P_1 value.

As noted above,

(14) $$H + NCl_3 \xrightarrow{k_{15}} NCl^{\bullet\bullet} + Cl + HCl + 46\ \text{kcal/mol}\ [9]$$

is a branching reaction. However, the consideration of this reaction at $k_{15} = k_{13}$ does not cause promotion without any additional assumptions on the reactions of the resulting $NCl^{\bullet\bullet}$ radicals, which are hypothetical because of the lack of literature data. For example, branching may be ensured by involving the exothermic reaction

$$\text{(15)}\qquad \mathrm{NCl^{\bullet\bullet} + NCl_3} \xrightarrow{k_{16}} \mathrm{N_2Cl_2 + 2Cl} + \sim 110\ \mathrm{kcal/mol}.$$

into the scheme. Indeed, the introduction of this reaction results in promotion at $k_{16}/k_1 > 10$. In agreement with the available experimental data [7, 15, 22], its role should be insignificant because of slow step (10) during NCl_3 decomposition in He in the absence of H_2 at 298 K.

However, there is one more reaction of additional linear branching (which is obviously a necessary condition for experimentally observed promotion) that does not require any assumptions on the $NCl^{\bullet\bullet}$ reactions. This is the exothermic process

$$\text{(16)}\qquad \mathrm{H + NCl_3} \xrightarrow{k_{17}} \mathrm{NHCl^{\bullet} + 2Cl} + 17\ \mathrm{kcal/mol},\quad k_{17} = k_{13}. \qquad \text{(III)}$$

The coincidence of the rate constants is assumed in calculations. Note that the occurrence of steps (13) and (14) was explained in [8] by the existence of a maximum on the experimental curve describing time variations in the $NCl^{\bullet\bullet}$ concentration ($b^1\Sigma^+$) and the linear dependence of the $NCl^{\bullet\bullet}$ signal on the initial NCl_3 concentration, as follows from the consideration of the kinetics of consecutive reactions (13) and (14). By solving the set of Eqs. (1)–(2) with due regard to steps (0)–(15) and (17) under conditions of [8] ([H] ~ 10^{13} $cm^{-3} \gg [NCl_3]_0$), we obtained the time dependence of the $NCl^{\bullet\bullet}$ concentration with characteristic times of a decrease and an increase close to the experimental ones shown in Fig. 3 of [8] and the linear dependence of the $NCl^{\bullet\bullet}$ concentration on the initial NCl_3 concentration. This verifies the agreement between the calculation results and the experimental data of [8]. Figure 1b presents the calculated kinetic curves for the reaction between NCl_3 and H_2 under the same conditions as the experimental data given in Fig. 1a. As can be seen, the 5% H_2 additive (Fig. 1b, curve *2*) favors promotion in agreement with the experiment. However, the calculated decrease in the induction period in the presence of 5% H_2 compared to that observed during NCl_3 decomposition in pure He is ~5 ms, which is less than the experimental one, as can be seen from Fig. 1b (curves *1* and *2*) when passing to the dimensional time. The calculated heating (~60 °C) (see Fig. 5a) is close to the experimental one (100 °C). Moreover, Fig. 5b is consistent with the presence of two luminescence zones in the flame caused by $Cl_2(^3\Pi^+_{ou})$ and $NCl(^1\Sigma^+)$ emissions. Note that, if all the energy of the H + NCl_3 reaction is evolved as heat, the calculated heating would be higher than 1000°C, which contradicts the experimental results. Figure 5b also shows that the chlorine atom concentration (which is ~30% of the initial NCl_3 in the absence of H_2 [7, 14]) decreases with an increase in the H_2 concentration, and the hydrogen atom concentration is low compared to those of other intermediates. These calculation results agree with the fact that hydrogen and chlorine atoms were not registered in the $H_2 + NCl_3$ flame (at the reactant ratio 1 : 1 + 50% He) under jet conditions. Nevertheless, a nearly threefold decrease in the chlorine atom concentration in the presence of H_2 is not strong enough to prevent the ESR registration of chlorine atoms (see above). Therefore, only the qualitative agreement between the experimental results and the calculation data were obtained.

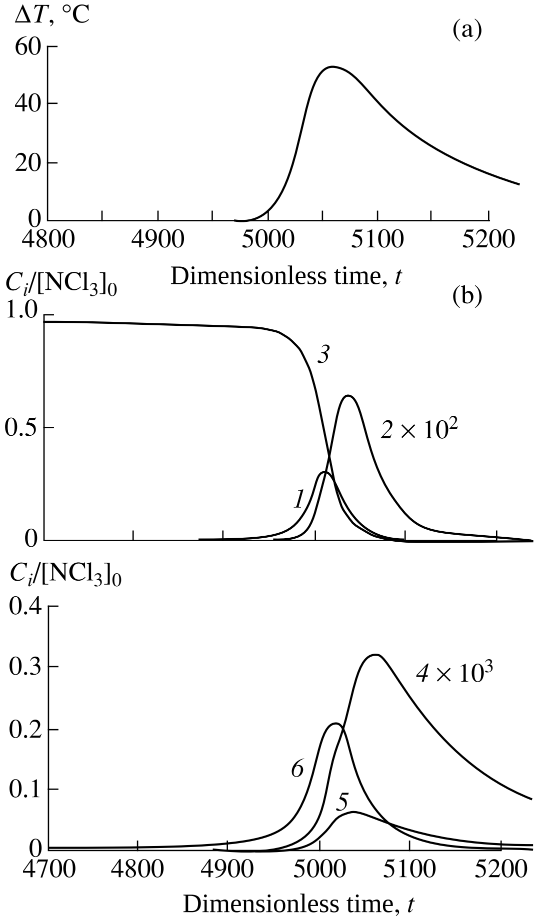

Fig. 5. Calculated kinetic curves of (a) self-heating and (b) relative concentrations of (*1*) $Cl_2{}^3\Pi^+_{ou}$, (*2*) $NCl^1\Sigma^+$, (*3*) NCl_3, (*4*) H atoms, (*5*) Cl atoms, and (*6*) $NCl_2^{\bullet}$ radicals. The calculation conditions: 25% of NCl_3 in He, 25% H_2, and P = 1.5 torr.

Figure 3b presents the calculation results for the kinetics of the $H_2 + NCl_3$ reaction under the conditions corresponding to Fig. 3a. Comparison of these figures suggests that the calculation gives a perfect qualitative description of the promotion of NCl_3 decomposition by molecular hydrogen near P_1.

Note that the product of the H + NCl_3 reaction (the $NCl_2^{\bullet}$ radical) should be in an electronically excited state (because of the significant exothermicity of this reaction (~78 kcal/mol, see above), thus ensuring the emitting transition of NCl_2^* to the ground state. As noted above, a band system is observed in the emission spectrum of the H_2 + NCl_3 reaction at 381–387 nm (Fig. 4) that was not assigned to any species and that does not shift on replacing molecular hydrogen with deuterium. This indicates that the emitting intermediate lacks the hydrogen atoms and that the assignment of the spectrum to the NCl_2^* species is correct.

CONCLUSION

The promotion of the branched-chain decomposition of NCl_3 by molecular hydrogen is observed both near the lower self-ignition limit P_1 and in developed ignition under non-steady-state conditions, which manifests itself in a decrease in the induction periods and the acceleration of NCl_3 decomposition with an increase in the H_2 concentration. The emission spectrum of this reaction contains the bands of electronically excited NCl* radicals ($b^1\Sigma^+ - X^3\Sigma^-$) along with the $Cl_2(^3\Pi^+_{ou})$ bands. The occurrence of exothermic reactions (II) and (III) results in promotion. On the other hand, promotion cannot be explained exclusively by the change in the rates of quadratic reactions.

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