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CRITICAL PHENOMENA IN THERMAL IGNITION WITH INVERTED EXCITATION OF THE PRODUCTS

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The possibility of combining vibrational chemical excitation with thermal explosion as a method of achieving an inverted medium is analyzed. The relaxation of laser levels imposes a limit on the velocity of elementary acts and leads to the appearance of critical conditions in the explosive process including the formation of population inversion in the explosion products. Examples of reactions of halogens with hydrogen are considered from this point of view. It is shown that the action of monochromatic radiation of suitable frequency on the reacting mixture decelerates the reaction in the presence of inverted excitation of the product energy levels in an elementary chemical act. In particular the diversion of energy to radiation amplification shifts the threshold of spontaneous thermal ignition. The critical conditions of radiation-induced quenching of the reaction are discussed.

1. INTRODUCTION

THE developing interaction between chemistry and quantum electronics is due to the opportunity to use coherent radiation in selective control of chemical processes on the one hand, and to the application of chemical activation processes accompanied by the formation of inverted states as energy sources for chemical lasers on the other[1]. Furthermore the availability of chemical lasers provides a new viewpoint in the investigation of fundamental characteristics of the elementary chemical act.

Concerning the techniques of producing population inversion based on chemical pumping we note a considerable interest in branched chain reactions[2-5]. However examples of such systems that would be promising for chemical laser technology are far from numerous. The thermal explosion is a much more widespread mechanism of spontaneous ignition. As we show in this work, under certain conditions thermal acceleration of reaction favors the progressive increase of inversion in the explosion products. Such a combination of chemical pumping with spontaneous thermal ignition can significantly broaden the class of reactions serving as the working systems in chemical lasers.

It is generally considered that radiation acting on a reacting mixture can only accelerate the speed of chemical reaction. It is further assumed that the result of such action can be either the heating of the reacting mixture by radiation absorption or the generation of chemical active centers due to molecular dissociation. A different situation results from the presence of inverted excitation of reaction products. The radiation acting on a system with inverted population of energy levels tends to equalize the populations by means of stimulated transitions. A portion of energy liberated in the course of the reaction can be removed from the system through amplification of the radiation acting on the reacting mixture. This means that the effect of radiation can suppress the development of reaction. Reaction suppression can be either purely thermal or due to variations of the kinetic process stemming from different reactive capacity of the excited and unexcited reaction products. In particular this can strongly affect the energy branching of the reaction[2].

2. PRODUCTION OF POPULATION INVERSION IN SPONTANEOUS THERMAL IGNITION

We consider that in an elementary act leading to the emission of energy a portion of the energy is emitted in the form of rotational and translational components, causing a rapid increase of temperature of the reacting mixture, and another portion is distributed among the vibrational degrees of freedom. The distribution has an inverted population in relation to some pairs of vibrational-rotational transitions. For the sake of simplicity we consider a two-level system of excitation. The rate of population of the upper level depends on temperature according to Arrhenius' law: $\ln \omega_1 \sim -\epsilon/RT$, where ϵ is the activation energy. The thermal dependence of the relaxation rate under adiabatic collision conditions is described by the Landau-Teller formula[6]: $\ln \omega_2 \sim -\frac{3}{2}(\epsilon'/kT)^{1/3}$. The origin and physical interpretation of the quantity ϵ' are obtained from the vibrational relaxation theory[6]. In the case of resonance collisions the thermal dependence of ω_2 is generally less pronounced: $\omega_2 \sim T$[6].

As we see from the above expressions the functional dependence of ω_1 and ω_2 on temperature is significantly different and there is always a temperature region with an upper limit, for which

$$\frac{1}{w_2}\frac{dw_2}{dT} \ll \frac{1}{w_1}\frac{dw_1}{dT},$$

i.e., the temperature dependence of the chemical reaction rate ω_1 for $T \ll T^*$ is much more pronounced than the temperature dependence of the relaxation rate ω_2. In a number of practically important cases the limiting temperature T^* can be fairly high. Thus if $\omega_2(T)$ is described by the Landau-Teller formula, the maximum of the ratio ω_1/ω_2 is reached for $T^* = (\epsilon'/k)^{-1/2}(2\epsilon/R)^{3/2}$. In particular for the vibrational-vibrational energy transfer of hydrogen halides $\epsilon'/k \sim 10^4$ (theoretical computation). Setting $\epsilon = 2 - 5$ kcal/mol as an approximate value, we obtain $T^* = (1 - 3) \times 10^{3}$°K. Increasing activation energy shifts T^* towards the region of still higher temperatures.

Thus if the activation energies are not too small (we note that it is this condition that makes thermal explosion possible) the rise in the mixture temperature in the range of practical interest (room temperature and above) creates more favorable conditions for the formation of inversion. This is also confirmed by a number of experiments with chemical lasers[7]. The preparation of a mixture of initial reagents at $\sim T^*$ is not practically feasible and thus the problem can be solved with the aid of a pulse gas heating by spontaneous thermal ignition. The following significantly different reaction regimes are possible in principle: (a) an increase of inversion that always occurs at the initial reaction stage is quickly replaced by a drop at low burnout rates to that the process continues inversion; (b) only an inversion increase occurs in the development of explosion. Mathematical analysis should provide an answer to the problem, what values of the system parameters determine the transition from one regime to the other. In analyzing this problem we henceforth consider the dependence $\omega_2(T)$ as weak in comparison with the Arrhenius dependence; this is valid if the initial temperature $T_0 \ll T^*$. Furthermore we expand the Arrhenius function as is customary in the theory of thermal explosion[8]: $e^{-\epsilon/RT} = e^{-\epsilon/RT_0}e^{\vartheta}$, where $\vartheta = \epsilon(T - T_0)/RT_0^2$. In this approximation the system of rate equations for the populations of working levels and the thermal balance equation is written in the following form:

$$\frac{dx^*}{dt} = \sigma_1 e^{\vartheta} - \sigma_{21}x^*, \tag{1}$$

$$\frac{dx}{dt} = \sigma_{21}x^*, \tag{2}$$

$$\frac{d\vartheta}{dt} = \sigma_3 e^{\vartheta} - \sigma_4\vartheta + \sigma_5 x^*, \tag{3}$$

where x^* and x are the populations of the upper and lower levels respectively, $\sigma_1 = ke^{-\epsilon/RT_0}\rho^n$ is the chemical pumping rate for the initial temperature ($w_1 = \sigma_1 e^{\vartheta}$), $ke^{-\epsilon/RT_0}$ is the reaction rate constant, ρ is the mixture concentration, n is the kinetic order of the reaction, $\sigma_{21} = k_R\rho$ is the relaxation rate constant ($w_2 = \sigma_{21}x^*$),

$$\sigma_3 = (1-\eta)\frac{Q}{c}\frac{\varepsilon}{RT_0^2}\frac{1}{\rho}\sigma$$

is the initial rate of heat emission, $(1 - \eta)$ is the portion of energy distributed among the rotational-translational degrees of freedom of reaction products, c is specific heat capacity, $\sigma_4 = hS/\rho cV$ is a quantity characterizing heat emission, V is the volume, S is the surface area, h is heat emission coefficient, and

$$\sigma_5 = \eta\frac{Q}{c}\frac{\varepsilon}{RT_0^2}\frac{1}{\rho}\sigma_{21}$$

is the heat emission rate constant in the relaxation process.

Equating the right-hand sides of (1) and (3) to zero we obtain equations for the stationary concentration $\overline{x}^*$ of excited molecules and the stationary heating $\overline{\vartheta}$:

$$\bar{x}^* = \sigma_4(\sigma_5 + \sigma_{21}\sigma_3/\sigma_1)^{-1}\overline{\vartheta}, \tag{4}$$

$$\overline{\vartheta}e^{-\overline{\vartheta}} = \sigma_4^{-1}(\sigma_3 + \sigma_1\sigma_5/\sigma_{21}) = \mu. \tag{5}$$

Substituting the variables $\xi = x^* - \overline{x}^*$, $\eta = \vartheta - \overline{\vartheta}$ and linearizing equations in the neighborhood of the equilibrium point we reduce (1) and (3) to

$$d\xi/dt = -\sigma_{21}\xi + \sigma_1 e^{\overline{\vartheta}}\eta, \tag{6}$$

$$d\eta/dt = \sigma_5\xi + (\sigma_{21}e^{\overline{\vartheta}} - \sigma_4)\eta. \tag{7}$$

The rest point $\xi = 0$, $\eta = 0$ is a saddle for $\overline{\vartheta} > 1$ and a stable node for $\overline{\vartheta} < 1$. The function $\overline{\vartheta}e^{-\overline{\vartheta}}$ has a single maximum for $\vartheta = 1$ whence it follows that for $\mu < e^{-1}$ (5) has two solutions, $\overline{\vartheta}_1$ and $\overline{\vartheta}_2$, where $\overline{\vartheta}_1 < 1$, $\overline{\vartheta}_2 > 1$. Consequently for $\mu < e^{-1}$ there are two stationary temperature regimes, one of which is stable ($\overline{\vartheta}_1$) and the other unstable ($\overline{\vartheta}_2$), analogously to the case of absent vibrational chemical excitation of the resulting fragments. For $\mu > e^{-1}$ stationary solution is not possible. Thus the critical condition of the explosion is expressed by

$$\sigma_3 + \frac{\sigma_1\sigma_5}{\sigma_{21}} - \frac{\sigma_4}{e} = 0. \tag{8}$$

We can show that (8) is identical with Semenov's equation of the thermal explosion limit[9]. This result is quite understandable since we assumed that σ_5 is proportional to σ_{21}, i.e., the relaxation of the upper level is accompanied by thermalization of the excitation energy. In this case the mixture heating is in the last analysis determined by a complete heat emission from an elementary chemical act and the critical explosion condition remains in force. The spontaneous ignition limit is shifted in the presence of nonthermal scattering mechanism of the excited-state energy (stimulated emission) or when the relaxation process weakly affects gas heating (vibrational-vibrational energy transfer). In particular assuming $\sigma_5 = 0$ we obtain the explosion condition in the form

$$\sigma_3 > \sigma_4/e. \tag{9}$$

Since beyond the limit (9) a thermal explosion can proceed without loss of the energy stored in the vibrational pool during the reaction (almost without loss near the limit), given a rapid reaction rate the energy of vibrational degrees of freedom of the excited products can be utilized for the generation of coherent emission. Nevertheless, generally speaking the shift of limit (9) does not guarantee a progressive increase of inversion upon thermal ignition. The possibility of affecting the time variation of inversion by the thermal acceleration of the reaction is limited by the ratio of heating rate to relaxation rate of the laser transition.

In analyzing this problem we consider thermal explosion beyond limit (9) as adiabatic ($\sigma_4 = 0$). Integrating (1), (2), and (3) we find

$$\vartheta(t) = -\ln(1 - \sigma_3 t), \tag{10}$$

$$x^*(t) = \sigma_1 e^{-\sigma_{21}t}\int_0^t \frac{e^{\sigma_{21}\tau}}{1 - \sigma_3\tau}d\tau, \tag{11}$$

$$x(t) = \sigma_{21}\int_0^t x^*(\tau)\,d\tau. \tag{12}$$

Thermal explosion is characterized by an induction period when the temperature varies weakly up to the time of pre-explosion heating, $\vartheta = 1$. It follows from (1) that the adiabatic period of induction is

$$t_i = \frac{e-1}{e}\frac{1}{\sigma_3}. \tag{13}$$

The extremal value of population inversion $x^* - x$ is reached at time t_m determined from

$$\frac{e^{\sigma_{21}t_m}}{1-\sigma_3 t_m} = 2\sigma_{21}\int\limits_0^{t_m}\frac{e^{\sigma_{21}\tau}}{1-\sigma_3\tau}d\tau. \tag{14}$$

We consider two limiting cases: $\sigma_{21} \gg \sigma_3$ and $\sigma_{21} \ll \sigma_3$. In the first case the solution of (14) is

$$t_m = \ln 2/\sigma_{21}. \tag{15}$$

Then

$$(x^* - x)_m = \frac{\sigma_1}{\sigma_{21}}(2 - \ln 2). \tag{16}$$

Thus with a strong relaxation $t_m \ll t_i$ and the maximum value of inversion is determined by the ratio of reaction to relaxation rates at the initial mixture temperature. In the second case (14) has no solutions. This means that when $\sigma_3 \gg \sigma_{21}$ we have an unstable state where a rise in inversion is limited only by the consumption of reagents and gas heating up to temperatures no longer capable of justifying the approximations made in the analysis. It is clear that the kinetic inversion curve changes form for $\sigma_3 \sim \sigma_{21}$.

We analyze (14) in the general case. We introduce the dimensionless parameter $\nu = \sigma_3/\sigma_{21}$ and dimensionless time $u = \sigma_3 t$. Then (14) is reduced to

$$\Phi(u_m, \nu) \equiv \frac{2}{\nu}(1-u_m)e^{(1-u_m)/\nu}\cdot\left[\mathrm{Ei}\left(-\frac{1}{\nu}\right) - \mathrm{Ei}\left(\frac{u_m-1}{\nu}\right)\right] = 1, \tag{17}$$

$$\mathrm{Ei}(z) = \int\limits_{-\infty}^{z}\frac{e^t}{t}dt,$$

Ei(z) is an integral exponential function. The uniform convergence of $\Phi(u, \nu)$ to zero within the interval $0 < u < 1$ as $\nu \to \infty$ shows directly that (17) has no solutions if ν is large enough. Figure 1 shows a family of curves $\Phi(u, \nu)$ within the interval $0 < u < 1$ with ν as a parameter. For $\nu < \nu_{cr}$ $\Phi(\mu, \nu) = 1$ has two solutions, $u_m^{(1)}$ and $u_m^{(2)}$. These two solutions existing for $\nu < \nu_{cr}$ correspond to the maximum and minimum of the inversion curve $x \quad - x$. The presence of a minimum for any small value of ν is the result of the approximations and has no physical meaning when ν is small enough since the necessary heating cannot be reached due to spent reagents and changes in the temperature dependence of the rate constants. However when $\nu \lesssim \nu_{cr}$ such a time variation of the inversion is quite real: the inversion drop is replaced by vigorous rise caused by pulse heating of gas. When $\nu > \nu_{cr}$ the extremes are not possible. In this case only an increase of inversion occurs and is limited by the supply of reagents. According to Fig. 1 $\nu_{cr} \sim 0.45$. Thus the inequality

$$\sigma_3/\sigma_{21} > \nu_{cr} \tag{18}$$

together with the spontaneous thermal ignition criterion (9) qualitatively determine the "inversion region" of the explosion process. These conditions guarantee an exponential increase of population inversion at least in the initial stage of reaction. The controlling role of relaxation in determining the course of the reaction is thus again manifested, just as in the case of chain ignition[4]. In deriving criterion (18) we neglected the lower level population in the elementary reaction act for the sake of simplicity. It is easy to take it now into account, and inequality (18) assumes the form

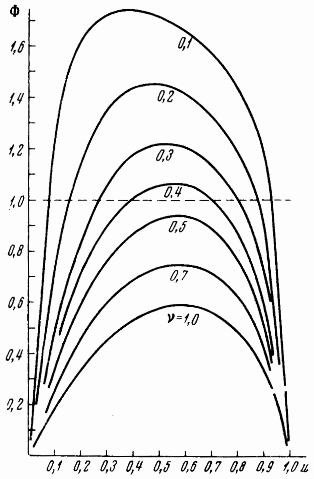

FIG. 1. Graphical solution of (17)

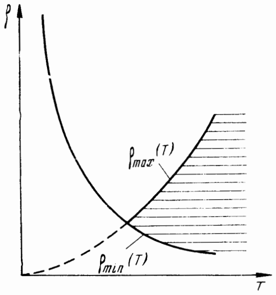

FIG. 2. "Inversion region" for n < 2 (shaded).

$$(\alpha^* - \alpha)\frac{\sigma_3}{\sigma_{21}} > \nu_{cr}, \tag{18a}$$

where α^* and α are the probabilities of formation of a molecule at the upper and lower working levels respectively.

Conditions (9) and (18) can be transformed into a form that explicitly includes pressure, temperature, kinetic constants, and the thermal effect of the reaction. Criterion (9) is thus brought to a standard form:

$$(1-\eta)Qke^{-\varepsilon/RT_0}\rho^n\frac{\varepsilon}{RT_0^2}\frac{r^2}{\lambda} > \delta_{cr}, \tag{19}$$

where λ is the heat conductivity of the medium, r is the radius of the cell, and $\delta_{cr} = 2$ for a cylindrical cell. We made use of the fact that for the conductive form of heat transfer[8] $hS/eV = \lambda/\delta_{cr}r^2$.

Expanding σ_3 and σ_{21} in (18) we obtain

$$(1-\eta)\frac{Q}{c}\frac{\varepsilon}{RT_0^2}\frac{ke^{-\varepsilon/RT_0}}{k_R}\rho^{n-2} > \nu_{cr}. \tag{20}$$

We note that the mathematical relation between pressure and temperature of the initial reagents in the limit (20) does not contain parameters characterizing the geometry of the experiment and is merely determined by the kinetics of the processes.

Another conclusion derived from the formulated conditions concerns the shape of the "inversion region" in the pressure-temperature coordinates. When the

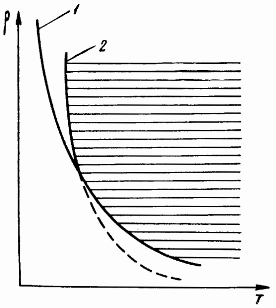

FIG. 3. "Inversion region" for $n < 2$ (shaded). Curve 1 is determined by condition (19), curve 2 by condition (20).

kinetic reaction order $n < 2$, conditions (19) and (20) can be met simultaneously within a pressure interval $\rho_{\min} < \rho < \rho_{\max}$ if the initial temperature T_0 is above a certain minimum value. Its upper limit is determined by inequality (20) and increases with temperature. The position of the lower limit is determined by the condition of thermal instability (19) and depends on the diameter of the reaction cell, decreasing with rising T. Thus the "inversion region" has the shape of a "peninsula" for $n < 2$ (Fig. 2). When $n \geq 2$ the inversion region is limited only from below, $\rho > \rho_{\min}(T)$ and $\rho_{\min}(T)$ is determined for a given T by the stronger of the two inequalities (19) and (20) (Fig. 3).

The physical cause of these phenomena is the fact that as the reaction rate increases in proportion to the factor ρ^n so the heat capacity of the initial mixture increases in proportion to pressure; this leads to a drop in the heating rate and in addition the relaxation rate increases linearly with pressure. It is the competition among all these factors that accounts for the presence of the "inversion region" in the pressure-temperature coordinates.

As an example of a merely illustrative nature we consider the chain reaction of hydrogen with chlorine assuming a purely thermal initiation. The rate of formation of active molecules is expressed by a well-known relation

$$w_1 = k_1 K^{1/2} [\mathrm{Cl}_2]^{1/2} [\mathrm{H}_2] = k_1 K^{1/2} \xi^{1/2} (1 - \xi) \rho^{3/2}, \qquad (21)$$

where $k_1 = 2 \times 10^{-10} e^{-4300/RT}\ \mathrm{cm^3/sec}$ is the reaction rate constant for $\mathrm{Cl + H_2}$[10], $K = 10^{24} e^{-58000/RT}$ is the reaction equilibrium constant for $\mathrm{Cl_2 + M = 2Cl + M}$, and ξ is the proportion of $\mathrm{Cl_2}$ in the initial mixture.

Using this kinetic law and drawing on the known experimental data on vibrational relaxation of HCl we can evaluate the upper limit of the "inversion peninsula" for a given temperature. According to[11] the relaxation time of HCl* is $\rho\tau = 1\ \mu$sec-atm ($T = 1000$°K), whence $k_R(T = 1000°\mathrm{K}) = 0.2 \times 10^{-12}$ $\mathrm{cm^3/sec}$. Assuming in (20) the following values of parameters: $Q = 45$ kcal/mol, $\eta = 0.5$, $\epsilon = 33{,}300$ cal/mol, $\xi = 0.5$, and $T_0 = 1000$°K, we find $\rho_{\max}(1000°\mathrm{K}) = 10^{15}\ \mathrm{cm^{-3}}$. While it is possible to achieve ignition at such low pressures by, say, increasing the diameter of the reaction cell, the limiting pressures are hardly adequate to secure a sufficiently high emission power density.

In the case of photolysis or electric discharge initiation the expression for the reaction rate does not contain slow thermal decay of molecules:

$$w_1 = k_1 [\mathrm{X}][\mathrm{H_2}] = k_2 [\mathrm{H}][\mathrm{X_2}], \qquad (22)$$

where [X] is the concentration of halogen atoms created by the initiation pulse, and k_1 and k_2 are the reaction rate constants for the development of chains $\mathrm{X + H_2}$ and $\mathrm{H + X_2}$ respectively.

Criterion (18) permits us to evaluate the quantity [X] necessary to push the reaction into the "inversion region" for a given reagent pressure. On the other hand if concentration of active centers is the given quantity, our evaluation determines the pressure at the upper limit of the "inversion peninsula." Considering that at room temperature the vibrational-vibrational energy exchange is the dominant relaxation process, we write for the relaxation rate:

$$w_2 = k_{v-v} [\mathrm{HX}][\mathrm{HX}^*], \qquad (23)$$

where k_{V-V} is the constant of the vibrational quantum exchange rate.

To evaluate the quenching rate we assume that [HX] is determined by isothermal burnout of material during the adiabatic induction period:

$$[\mathrm{HX}] = w_1 \sigma_3^{-1} = \frac{\rho}{B}, \qquad B = (1 - \eta) \frac{Q}{c} \frac{\varepsilon}{R T_0^2}.$$

In reality relaxation is significantly nonlinear so that our evaluation yields the lower limit of the necessary degree of initiation. For a stoichiometric mixture of $\mathrm{H_2 + X_2}$ we can readily find

$$\frac{\sigma_3}{\sigma_{21}} = \frac{1}{4} \frac{k_1}{k_{v-v}} \left[(1 - \eta) \frac{Q}{c} \frac{\varepsilon}{R T_0^2} \right]^2 \frac{[\mathrm{X}]}{[\mathrm{X_2}]}. \qquad (24)$$

For the reaction of $\mathrm{H_2 + Cl_2}$ the ratio (24) yields $\sigma_3/\sigma_{21} = 14.7\,[\mathrm{Cl}]/[\mathrm{Cl_e}]$, assuming that $k_{V-V}(T = 300°\mathrm{K}) = 1.8 \times 10^{12}\ \mathrm{cm^3/mol \cdot sec}$ (computed from formulas in[6]). In the case of the $\mathrm{H_2 + F_2}$ reaction the parameter values are as follows: $k_1 = 1.2 \times 10^{14} \exp(-1000/RT)$ $\mathrm{cm^3/mol \cdot sec}$[12], $k_{V-V} = 5.34 \times 10^{11}\ \mathrm{cm^3/mol \cdot sec}$ (computed from formulas in[6]), $T_0 = 300$°K, $Q = 130\ \mathrm{kcal\text{-}mol^{-1}}$, $\eta = 0.5$, and $c = 5$ kcal/mol. Then $\sigma_3/\sigma_{21} = 5.5 \times 10^4\,[\mathrm{F}]/[\mathrm{F_2}]$.

It follows from these calculations that limit (18) can be shifted in the reaction $\mathrm{H_2 + Cl_2}$ only with a high concentration of chlorine atoms due to the initiation pulse, i.e., $\sim 10^{-1}$ of the reagent concentration. In the case of the reaction $\mathrm{H_2 + F_2}$ the necessary concentration of atomic fluorine is three orders lower. With less intense initiation inversion decay occurs already in the initial isothermal stage of the reaction.

The specific feature of the above example is the low activation energy of the total process. In this connection we note an important consideration regarding the above approach. The most significant factor in the attempt to obtain population inversion in vibrational levels from thermal explosion is the sharp exponential acceleration of the chemical reaction accompanied by increased temperature. We know from combustion theory[8] that the following conditions must be satisfied for this purpose:

$$\frac{\varepsilon}{R T_0} \gg 1; \qquad \frac{\varepsilon}{R T_0^2} \frac{Q}{c} \gg 1.$$

The first of these conditions calls for activation energies that are not too small at room and higher temperatures. For the reaction of halogens with hydrogen initiated by a discharge or by photochemical means, $\epsilon/RT_0 \gtrsim 1$. Therefore we can expect that spontaneous heating of the mixture will enhance the energy yield of generation by virtue of the optimal temperatures reached; however there is no sharp change in the kinetic inversion curve even if criterion (18) is satisfied.

Moderate activation energies are typical of reactions involving free atoms and radicals. The formation of these reactive fragments as a rule calls for considerable energy expenditures. Consequently the total process has a moderate activation energy only when the system includes an external initiation source. However if the generation of active centers is accomplished by chemical interactions of valence-saturated molecules the activation energy is usually high enough. On the other hand criterion (20) limits the maximum values of the activation energy. In the case of very large ϵ (20) cannot be satisfied within a sufficiently broad and useful interval of pressures at moderate temperatures of the initial mixture. The compromise that is thus sought does not in principle appear unfeasible. Since the "inversion region" can be directly adjacent to the region of slow stationary process we can prepare the initial reagent mixture so as to have it fall near the lower limit of the "inversion peninsula" and thus reduce to a minimum energy expended on initiation. This consideration renders the use of thermal explosion an attractive method of achieving chemical laser action.

3. IGNITION LIMITS IN THE PRESENCE OF RADIATION

In this section we use the rate equations to analyze the effect of resonance emission on the limit of thermal explosion. Such an approach enables us to write the equation for the thermal explosion limit in the presence of radiation; the equation includes relaxation rate constants for the excited quantum states. In particular this equation predicts the possibility of quenching the reaction by resonance emission given a specific ratio between the relaxation rates of the vibrational levels.

The kinetics of this system in the presence of radiation includes the following physical processes: excitation of working levels by the reaction, their relaxation, and stimulated optical transitions. The rate equations describing these processes are analogous to (1)–(3). The right-hand sides of (1) and (2) should be supplemented by the term $\sigma_2(x^* - x)$ where $\sigma_2 = BI$ is the rate constant of radiative transitions that is proportional to the irradiation intensity I, and B is the Einstein coefficient. It is significant that equations that take the resonance field effect into account allow for a stationary solution only in the presence of relaxation from the lower level. In order to take this process into account it is necessary to introduce the term $-\sigma_{10}x$ into (10) where σ_{10} is the relaxation rate constant for the lower level and the term $\sigma_6 x$ into the temperature equation (3) (since relaxation is accompanied by heat emission) where σ_6 is determined analogously to σ_5.

The stationary state of such a system can be easily analyzed. Elementary analysis shows that the equation of the thermal explosion limit taking the resonance field effect into account is analogous to Semenov's equation (8), except that in this case the right-hand side depends on the irradiation intensity according to

$$G = \sigma_3 + \frac{\sigma_1\sigma_5}{\sigma_{21}}\varkappa(\sigma_2) + \frac{\sigma_1\sigma_6}{\sigma_{10}} - \frac{\sigma_4}{e} = 0, \tag{25}$$

where

$$\varkappa(\sigma_2) = \frac{\sigma_{21}}{\sigma_{10}}\frac{\sigma_2 + \sigma_{10}}{\sigma_2 + \sigma_{21}}. \tag{26}$$

We denote the explosion limit excess coefficient in the absence of radiation by

$$g = \sigma_3 + \frac{\sigma_1\sigma_5}{\sigma_{21}} + \frac{\sigma_1\sigma_6}{\sigma_{10}} - \frac{\sigma_4}{e} \tag{27}$$

It follows from (25) that radiation shifts the thermal explosion limit. The effect can be either positive or negative depending on the ratio between the kinetic relaxation constants. A significant feature of the effect is the presence of an irradiation intensity threshold. If

$$\sigma_{10} > \sigma_{21} \tag{28}$$

and

$$\sigma_2 > \left[\frac{\sigma_{10}}{\sigma_{21}}\left(1 - \frac{\sigma_{21}}{\sigma_1\sigma_5}g\right) - 1\right]^{-1}\frac{\sigma_{10}\sigma_{21}}{\sigma_1\sigma_5}g, \tag{29}$$

then $G < 0$ and the explosive reaction does not occur even if in the absence of radiation the explosion condition ($g > 0$) is satisfied. In this case radiation quenches the reaction. However reaction quenching is possible only if

$$g < \frac{\sigma_1\sigma_5}{\sigma_{21}}(1 - \varkappa(\infty)), \tag{30}$$

where $\kappa(\infty) = \sigma_{21}/\sigma_{10}$.

In case when

$$\sigma_{21} > \sigma_{10}, \tag{31}$$

radiation tends to accelerate reaction. In particular if $G > 0$ the stationary thermal regime is no longer possible even if $g < 0$ in the absence of radiation. This happens when the condition

$$g > -\frac{\sigma_1\sigma_5}{\sigma_{21}}[\varkappa(\infty) - 1] \tag{32}$$

has been met and the irradiation intensity is over the threshold (29).

All the above relations have a clear physical meaning. If (28) is satisfied, the incident light flux is amplified; a portion of the energy is removed from the reaction region by stimulated emission. The existence of a lower limit of light intensity capable of suppressing the reaction (29) is due to the fact that the process of removal of energy from the reacting system by stimulated transitions is in competition with the relaxation process tending to thermalize this energy. Since the probability of stimulated transitions is low when the intensity of incident radiation is too low, practically the entire energy emitted in the reaction is expended on heating the system. The physical meaning of condition (30) is clear enough. If $g > (1 - \kappa(\infty))\sigma_1\sigma_5/\sigma_{21}$, the system generates so much heat that explosion occurs even when the light flux is infinitely strong and stimulated emission diverts the maximum possible energy.

Finally if $\sigma_{21} > \sigma_{10}$ only the absorption of incident emission is possible in the stationary state. If light intensity is above threshold (29) in some pre-explosion region of g values (32), the radiation initiates thermal ignition. If

$$g < -(\varkappa(\infty) - 1)\sigma_1\sigma_5/\sigma_{21}, \tag{32}$$

the heating of the mixture due to emission absorption is insufficient to develop the explosion process even with infinitely strong light flux, and a stationary reaction is observed.

As we know the probability of vibrational-to-translational energy conversion increases with increasing vibrational quantum number. In our system this means that $\sigma_{21} > \sigma_{10}$ if the relaxation of excited levels is directly due to the scattering of vibrational energy to translational degrees of freedom. In such systems radiation can only initiate thermal explosion. The satisfaction of the condition $\sigma_{10} > \sigma_{21}$ involves the search for impurities capable of effectively quenching the lower working level. This capability can be based, in particular, on the resonance of vibrational frequencies of colliding molecules. For example in the reacting mixture of hydrogen and fluorine the $v = 1$ level of the HF molecule can be effectively depopulated due to the quasi-resonance of the vibrational transition frequencies $v = 1 \rightarrow v = 0$ of the H_2 ($\nu_{10} = 4161\ \text{cm}^{-1}$) and HF ($\nu_{10} = 3962\ \text{cm}^{-1}$) molecules. In some cases an effective vibrational deactivation is observed in the absence of resonance and is due to the formation of complexes. A strong effect on the relaxation of HF and DF of such additives as HCl, DCl, and CO_2 excited in the process of chemical reactions was reported in[13].

We note that the above system is not general. A modification of the system is possible that includes the transfer of energy from "hot" molecules excited by the reaction to "cold" molecules of the inert diluent. Such a situation occurs in the explosion of HN_3 in CO_2[14,15] where energy is transferred from N_2 to CO_2. Generation in CO_2 (10.6 μ) upon the addition of CO_2 to the reacting mixture of $F_2O - D_2$ was reported in[16]. If the energy transfer in such systems is effective enough and if the condition $\sigma_{10} > \sigma_{21}$ can be satisfied for diluent molecules capable of accepting vibrational energy (the relaxation of CO_2 is a typical example), then radiation acting on diluent molecules is capable of suppressing the reaction.

Reaction suppression can occur in the mode of coherent emission generation when the reactor is placed in an optical resonator, i.e., in the absence of an external source of resonance radiation. This effect is apparently more pronounced in the chain mechanism of spontaneous ignition with energy branching of chains as noted already in[17]. The reactions $H_2 + F_2$ and $D_2 + F_2$ may serve as potentially possible examples. Reaction suppression in these mixtures is possible because of depopulation in the generation process of upper vibrational states of HF* and DF* responsible for the branching. This effect was recently discussed in[18] in relation to the $H_2 + F_2$ system.

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