Photo-initiation of chemical chain reactions in optically dense media

E. B. Gordon and Yu. L. Moskvin

Institute of Chemical Physics, USSR Academy of Sciences

(Submitted October 28, 1974)
Zh. Eksp. Teor. Fiz. **68**, 1252-1264 (April 1975)

The wave regimes of propagation of the initiating light is considered in media in which chemical chain reactions can occur. Dispersion relations are obtained for cases of direct and branched chains. It is shown that for branched chemical chain reactions the requirement of initial stability of the medium imposes stringent restrictions on the wave-regime rates that are attainable in principle. Propagation of photochemical-transformation waves in thermal self-acceleration of the chemical chain process is considered and the corresponding dispersion relation is derived. It is shown that in this case the transition from a "quasi-detonation" regime to a photochemical one has the properties of an extremal phenomenon.

PACS numbers: 82.50.—m

INTRODUCTION

The problem of rapid initiation of chemical processes in large volumes is quite pressing. The most universal method in this case is photochemical action on one of the reagents, which leads to the formation of chemically active particles (atoms, free radicals, excited molecules). Other methods of initiation either do not provide the necessary speed (for example, changes in reactor temperature), or are useable for relatively small volumes and pressures of a gaseous medium (electric discharge, microwave initiation).

In most interesting applications, the concentrations of the radiation-absorbing reagents are such that the dimensions of the medium can greatly exceed the characteristic length of the optical absorption, i.e., the case of the optically dense medium is realized, when the penetration of the initiating radiation into the interior of the substance can occur only as a result of its transparentization. Most frequently, chemical reactions are initiated by photodissociation of the component that absorbs the light.

Photodissociation in optically dense media (photodissociation (PD) waves) is the process investigated in greatest detail[1-3]. In the simplest case of a collimated monochromatic light beam, the fundamental equations take the form

$$\partial[N]/\partial t=-\sigma[N]I, \quad \partial I/\partial x=-\sigma[N]I, \tag{1}$$

where N is the photodissociating component, σ is its photodissociation cross section, and I is the intensity of the light. In an optically dense medium, the system of equations (1) leads to a wave whose propagation velocity V_{PD} can be obtained from the condition

$$V_{PD}[N]+I=\text{const},$$

from which follows the well known expression for the velocity of the photodissociation wave[1)]:

$$V_{PD}=I_0/[N]_0, \tag{2}$$

where I_0 is the intensity of the source and $[N]_0$ is the initial concentration of the dissociating component.

In the coordinate system connected to the wave front, the intensity of the light and the concentration of the photodissociating component vary with the distance z in accordance with the law (Fig. 1a)

$$j\equiv\frac{I}{I_0}=\frac{\exp(-z/z_\sigma)}{1+\exp(-z/z_\sigma)}, \quad n\equiv\frac{[N]}{[N]_0}=1-j, \tag{3}$$

where $z_\sigma = (\sigma[N]_0)^{-1}$ is the initial absorption length.

The solution (2)—(3) can be generalized to the important case of a moving light source (which is realized, for example, when light is used to initiate a shock wave propagating with velocity V_S through a medium [5]). In this case, if $V_S < V_{PD}$, we have as before the photodissociation wave described by Eqs. (2) and (3). If $V_S > V_{PD}$, photodissociation takes place only directly in front of the shock wave, and the concentration $[N]_S$ of the component N on the source surface, is in this case different from zero (there is no complete bleaching)

$$[N]_s/[N]_0=1-V_{PD}/V_s. \tag{4}$$

The light intensity and the concentration N are shown schematically in Fig. 1b as functions of the distance from the moving source. From (4) and Fig. 1b we see that the degree of dissociation of the medium ahead of the shock-wave front (i.e., of the photodissociation) decreases with increasing shock-wave velocity.

If chemical chain reactions in which a photodissociating component participates can take place in the medium, then the chemical depletion of the latter leads to an additional bleaching of the medium and, as a consequence, to an increase of the velocity of the photochemical transformation wave (these waves were called photochemical (PC) by Oraevskiĭ and Shcheglov, who were the first to investigate them [6]. The velocity V_{PC} of a photochemical wave is conveniently represented in the form

$$V_{PC}=V_{PD}\tilde{\nu}, \tag{5}$$

where $\tilde{\nu}$ is the effective length of the chain of the chemical conversion; in different cases, $\tilde{\nu}$ can be determined both by the singularities of the chemical kinetics (the kinetic chain length) and by the depletion of the initial components (when the kinetic chain length is large

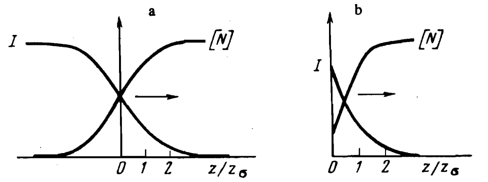

FIG. 1. Photodissociation wave. Dependences of the concentration [N] of the dissociating component and of the light intensity I on the relative coordinate z/z_σ in a coordinate system connected with the wave: a) immobile source, b) source moving with velocity $V_S > v_{PD}$.

enough). With increasing intensity of the light flux I_0 incident on the medium, the effective chain length $\tilde{\nu}$ decreases naturally, tending to unity, i.e., $V_{PD} \rightarrow V_{PD}$ ($I_0 \rightarrow \infty$). The usefulness of the representation (5) lies in the fact that the optical characteristics, such as the shape of the spectral emission lines of the source and the absorption lines of the medium, as well as the degree of collimation of the light beam, change in first-order approximation only the photodissociation-wave velocity, whereas the effective length of the chain is frequently determined exclusively by the chemical-kinetics characteristics of the medium.

We have investigated the influence of the kinetic singularities of chemical chain reactions on the character of photochemical-conversion waves. We consider two extreme cases, in which the kinetic length of the nonbranching chain has and does not have time to become established in the shock-wave front, and study the effect of acceleration of the chemical chain process resulting from the chemical branching and from the increase of the temperature of the medium.

1. NONBRANCHING CHEMICAL CHAIN REACTION

A chemical chain reaction can be schematically represented by the following aggregate of processes:

$N + \hbar\omega \rightarrow R$	photoinitiation (I)
$N + R \xrightarrow{k_2} N' + R$	continuation of chain (II)
$R + X \xrightarrow{k_{3a}} X'$	annihilation of active center by impurity (IIIa).
$R + N \xrightarrow{k_{3b}} N''$	annihilation by main component[2] (IIIb).

Here R is the chemically active center; X is the impurity; N′, X′, and N″ are optically transparent reaction products.

In the case of a sufficiently short chemical chain, the annihilation of the active particles (atoms and radicals) have time to be completed in the front of the chemical-conversion wave, i.e., the concentrations of these particles in the front are close to quasistationary, and the effective chain length $\tilde{\nu}$ is determined only by the chemical kinetics of the process. On the other hand, if the annihilation of the active centers does not have time to affect the time of the chemical conversion (the case of a long chain), then the effective chain length is determined only by depletion of the initial component.

The kinetic equations corresponding to processes (I)—(III) can be written in the form

$$\partial I/\partial x = -\sigma[N]I, \tag{6}$$

$$\partial[N]/\partial t = -\sigma[N]I - (k_2 + k_{3b})[N][R], \tag{7}$$

$$\partial[R]/\partial t = \sigma[N]I - (k_{3a}[X] + k_{3b}[N])[R]. \tag{8}$$

For the case of a short chain it is easy to obtain from (6)—(8) expressions for the velocity of the PC wave:

$$V_{PC} = V_{PD}\nu_a/\ln(1+\nu_a), \quad \nu_a = k_2[N]_0/k_{3a}[X]$$

(annihilation of active centers by impurity), and

$$V_{PC} = V_{PD}(1+\nu_b), \quad \nu_b = (k_2 + k_{3b})/k_{3b}$$

(annihilation of active centers by main component).

Here ν_a and ν_b are the kinetic lengths of the chains (on the initial section of the wave) for the corresponding models of active-center annihilation.

As expected, in the case of a short chain length we have $\tilde{\nu} \approx \nu_{a,b}$. The shape of the wave front for the model (b) is the same as in the case of a simple photodissociation wave, while for the model (a) it differs from it only insignificantly (Fig. 2).

The case of a long chain was considered in detail by Oraevskiĭ and Shcheglov[6]; for the velocity of the photochemical wave the authors obtained

$$V_{PC} = V_{PD}\{{}^1/_2 + ({}^1/_4 + k_2[N]_0/\sigma I_0)^{1/2}\}.$$

The profiles of the light intensity and of the concentration of the initial component are described by the same relations (3) as for the photodissociation wave.

The quantity $\kappa_2 \equiv k_2[N]_0/\sigma I_0$ that enters in the expression for V_{PC} is the quantum yield of the chemical conversion at the inflection point (z = 0, Fig. 1a). The effective length of the chain is much smaller than the quantum yield κ_2 ($\kappa_2 \gg 1$), this being connected with the burnout stage of the initial product, in which stage the quantum yield of the chemical conversion is close to unity. It follows therefore that for chemical systems in which the rate of conversion increases with completion of the reaction (for branching chain reactions and for reactions with thermal self-acceleration) one can expect noticeably higher velocities of the photochemical waves. These cases are considered in the following sections.

The formula for the velocity of a photochemical wave can easily be generalized (at $\kappa_2 \gg 1$) to the case of a nonmonochromatic source of initiating radiation

$$V_{PC}^2 = \frac{k_2}{[N]_0}\int \frac{I_0(\lambda)}{\sigma(\lambda)}d\lambda,$$

where the integration is carried out over the entire emission band.

The general wave solution of the system of kinetic equations (6)—(8) at $k_{3a}[X] = 0$ (the annihilation of the active centers is by the main component) can be represented in analytic form. In this case it follows from (6)—(8) that

$$\tilde{\nu}\,\partial n/\partial j = -1 - \varkappa r/j, \tag{9}$$

$$\tilde{\nu}\,\partial r/\partial j = 1 - \varkappa\nu_b^{-1}r/j, \tag{10}$$

where $n \equiv [N]/[N]_0$, $r \equiv [R]/[N]_0$, $j \equiv I/I_0$ are the reduced concentrations of the initial component, of the active centers, and of the intensity of the initiating light; $\tilde{\nu}$ is the effective length of the chemical-conversion chain in the PC wave; ν_b is the kinetic length of the chain; $\kappa \equiv (k_1 + k_{3b})[N]_0/\sigma I_0$ is the total quantum yield at the point of inflection of the wave profile[3].

From (10) we have

$$r = j\frac{\nu_b}{\varkappa + \nu_b\tilde{\nu}} + C_1 j^{-\mu} \tag{11}$$

and further from (9)

$$\tilde{\nu}n = C_2 - \left(1 + \frac{\varkappa\nu_b}{\varkappa + \nu_b\tilde{\nu}}\right)j + C_1\nu_b\tilde{\nu}j^{-\mu}, \tag{12}$$

C_1 and C_2 are the integration constants, and $\mu = \kappa/\nu_b\tilde{\nu}$. Using the boundary conditions

$$\begin{cases} n=1, \quad r=0 & j=0 \\ n=0 & j=1 \end{cases} \tag{13}$$

we obtain a dispersion relation for the effective chain length:

$$\tilde{\nu} = 1 + \varkappa\nu_b/(\varkappa + \nu_b\tilde{\nu}). \tag{14}$$

From (14), in particular, we get criteria for the already considered cases of short and long chains:

1) $\varkappa \gg 4\nu_b^2$, $\tilde{\nu} \approx 1+\nu_b$ —short chain,
2) $\varkappa \ll \nu_\sigma$, $\tilde{\nu} \approx 1/2+(1/4+\varkappa)^{1/2}$ —long chain.

Figure 3 shows plots of the effective chain length $\tilde{\nu}$ against κ (i.e., against I_0^{-1} at a fixed concentration of the initial component) for the values $\nu_b = \infty$, 4, and 1 (curves 3, 2, and 1, respectively).

2. BRANCHING CHEMICAL CHAIN REACTION

We introduce in addition to the photoionization process (I) and the chain continuation process (II) the chemical-branching process in the form[4)]

$$R+N \xrightarrow{k_4} 2R+N'''. \qquad \text{(IV)}$$

In this case we have for the wave regime a system of equations of the type (9) and (10), which differ only in that the chain length ν_b is replaced by $-\nu_{br}$, where ν_{br} is the length of the straight chain of the branching chemical reaction, equal to the number of acts of the chain between two branchings

$$\nu_{br} = (k_2+k_4)/k_4.$$

For the relative concentrations of the initial components and of the active centers we obtain expressions of the type (11) and (12) (with ν_b correspondingly replaced by $-\nu_{br}$). In this case, however, the boundary conditions (13) do not lead to an unambiguous dispersion relation for $\tilde{\nu}$, since the condition r = 0 is formally satisfied at j = 0 for arbitrary values of the integration constant C_1 in (11).

This result is the consequence of the poor physical formulation of the problem. Indeed, the stable existence of a reaction mixture capable of a branching chemical chain reaction can be attained only by inhibiting this reaction with impurities, walls, etc. In chemical language: under the initial conditions the mixture must be outside the ignition peninsula, and the transition of the reaction into the branching chain regime occurs only after the system is acted upon by a finite flux of initiating light quanta.

One can choose as the inhibiting process the annihilation of the active centers by a certain small impurity X (IIIa). For the system to be stable it is necessary, of course, to satisfy the condition

$$u \equiv k_{3a}[X]_0/k_4[N]_0 > 1,$$

where u is the stability factor[5)]. The transition of the reaction into a branching chain regime occurs at the instant when the concentration of the impurity decreases by a factor u as a result of burnout in process (IIIa).

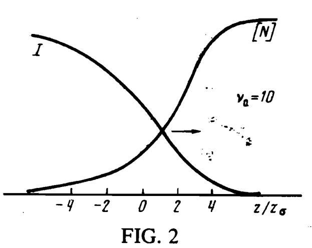

FIG. 2

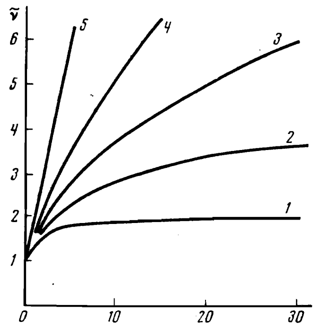

FIG. 3

FIG. 2. Plots of [N] and I in a photochemical wave against the relative coordinate z/z_σ for nonbranching chain reaction (annihilation of active centers by impurity).

FIG. 3. Dependence of the effective chain length $\tilde{\nu}$ on the quantum yield κ. Case of nonbranching chain reaction: 1—for $\nu_b = 1$, 2—for $\nu_b = 4$, 3—for $\nu_b = \infty$. Case of branching chain reaction: 4—for $\nu_{br} = 4$, 5—for $\nu_{br} = 1$.

With allowance for the reaction (IIIa), the system of equations for the photochemical wave can be written in the form

$$\tilde{\nu}\frac{\partial n}{\partial j} = -1-\varkappa\frac{r}{j}, \qquad (15)$$

$$\tilde{\nu}\frac{\partial r}{\partial j} = 1+\varkappa\nu_{br}^{-1}\left[1-u\frac{x}{n}\right]\frac{r}{j}, \qquad (16)$$

$$\tilde{\nu}\frac{\partial x}{\partial j} = -\Gamma\frac{x}{n}\varkappa\frac{r}{j}. \qquad (17)$$

Here x ≡ [X]/[X]$_0$ is the relative impurity concentration,

$$\varkappa \equiv \frac{(k_2+k_4)[N]_0}{\sigma I_0}, \quad \nu_{br} \equiv \frac{k_2+k_4}{k_4}, \quad \Gamma \equiv \frac{k_{3a}}{k_2+k_4} \gg 1,$$

and the remaining symbols are the same as in Eqs. (9) and (10).

If it is assumed that by the instant of burnout of the impurity X the concentration of the main component has changed little (n ≈ 1), then we get from (17)

$$x = \exp\left(-\int_0^j \frac{\varkappa\Gamma}{\tilde{\nu}}\frac{r(j')}{j'}dj'\right) \equiv e^{-s}.$$

For the function s we get from (16) the equation

$$j\frac{\partial s}{\partial j} = j\Gamma\frac{\varkappa}{\tilde{\nu}^2}+\frac{\varkappa}{\tilde{\nu}\nu_{br}}\Phi(s),$$
$$\Phi(s) \equiv s-u[1-e^{-s}]. \qquad (18)$$

Taking into account the trivial boundary condition s = 0 at j = 0 we get from (15), as a result of integration with respect to j in the interval (0, 1),

$$\tilde{\nu} = 1+\tilde{\nu}s(1)/\Gamma. \qquad (19)$$

The function Φ(s) is negative at small s, crosses the abscissa axis at a certain $s_0 < u$, and approaches the straight line s−u at large s.

For large values s ≫ 1 we obtain from (18) the asymptotic solution

$$s = s^* + j\Gamma\frac{\varkappa}{\tilde{\nu}^2}\frac{1-(j/j^*)^{\alpha-1}}{1-\alpha}$$

$$\alpha \equiv \frac{\varkappa}{\tilde{\nu}\nu_{br}} = \frac{k_4}{\sigma V_{PC}}, \qquad s^* \equiv s(j^*) \gg 1. \qquad (20)$$

To prevent self-ignition of the mixture during its preparation, it is mostly customary to work far enough from the chain self-ignition peninsula. In this case (for u ≳ 3) one can put with sufficient accuracy $s^* = s_0 \approx u$, and then j* has the meaning of the relative light flux at which the chemical reaction goes over into a branching chain regime. At this point, the degree of burnout of the main component, as follows from (15), is

$$\Delta n^* = \tilde{\nu}^{-1}j^* + \Gamma^{-1}s^*.$$

Thus, the criterion for the applicability of Eqs. (18) can be written in the form Γ ≫ u, or

$$\nu_{br}[X]_0/[N]_0 \ll 1.$$

Using (19), we can write down a dispersion equation for the effective chain length

$$\tilde{\nu} = 1+\frac{\varkappa}{\tilde{\nu}}\frac{1-(j^*)^{1-\alpha}}{1-\alpha}+\frac{s^*\tilde{\nu}}{\Gamma}. \qquad (21)$$

If we formally let the initial impurity concentration $[X]_0$ go to zero (corresponding to $\Gamma \to \infty$), then naturally $j^* \to 0$ and the dispersion relation (21) goes over into

$$\tilde{\nu}=1+\frac{\varkappa}{\tilde{\nu}(1-\alpha)}=1-\frac{\varkappa\nu_{br}}{\varkappa-\nu_{br}\tilde{\nu}}. \qquad (22)$$

The last expression differs from (14) only in that ν_b is replaced by $-\nu_{br}$, i.e., in the indicated limit, the integration constant C_1 in (11) vanishes, just as in the case of the nonbranching chain reaction.

It should be noted, however, that the concentration of the inhibiting impurity X can be decreased only for reactions with weakly pronounced branching with the mixture stability condition $u > 1$ satisfied, owing to the finite rate of the inhibition reaction (k_{3a} cannot exceed the rate constant of the gas-kinetic collisions). This means that the use of the dispersion relation (22) is possible when the branching effect introduces a small correction to the velocity of the photochemical conversion wave[6]. Indeed, even if $k_{3a} \approx 10^{-10}$ cm^3/molecule-sec and the relative impurity content is $[X]_0/[N]_0 = 10^{-2}$, satisfaction of the stability condition $u \gtrsim 3$ is possible for chain reactions with a branching rate constant $k_4 \lesssim 3 \times 10^{-13}$ cm^3/molecule-sec. Figure 3 shows plots of the effective length of the chemical-conversion chain in the PC wave, $\tilde{\nu}$, against κ for values $\nu_{br} = 1$ (complete branching reaction; curve 5) and $\nu_{br} = 4$ (curve 4). The case $\nu_{br} = \infty$ (nonbranching reaction) corresponds to curve 3 of this figure.

For large values of $\tilde{\nu}$ there follows from (22) the relation

$$\tilde{\nu}/\nu_{br}=\varkappa/2\nu_{br}^2+\left(\varkappa/\nu_{br}^2+\left(\frac{\varkappa}{2\nu_{br}^2}\right)^2\right)^{1/2}.$$

Figure 4 shows a plot of $\tilde{\nu}/\nu_{br}$ as a function of the parameter κ/ν_{br}^2 (curve 1). As follows from the foregoing, this curve corresponds to the limiting case $\Gamma \to \infty$.

It follows from (18) and (20) that at a finite value of the parameter Γ we have

$$j^*=\frac{\tilde{\nu}^2}{\Gamma\varkappa}i(s^*,\alpha),$$

where the function $i(s, \alpha)$ is obtained by numerically solving the differential equation

$$di/ds=i/[i+\alpha\Phi(s)]$$

with the boundary condition $i = 0$ at $s = 0$.

Using the dispersion relation (21), we obtain at $\tilde{\nu} \gg 1$

$$(\Gamma-s^*)i(s^*,\alpha)j^*=\frac{1-(j^*)^{1-\alpha}}{1-\alpha}.$$

From this we can calculate, at a fixed value of the parameter Γ, the dependence of j^* on α, which then, as the result of a simple procedure, is transformed into a parametric dependence of $\tilde{\nu}/\nu_{br}$ on κ/ν_{br}^2. Fig. 4 shows these dependences for the values $\Gamma = 10^4$ and 10^2 (curves 2 and 3 respectively); the stability factor is assumed to be $u = 3$. It follows from these curves that even at impurity concentrations $\approx 0.1\%$ ($\Gamma \approx 3 \times 10^3$) the effective length of the chain is much smaller than its limiting value.

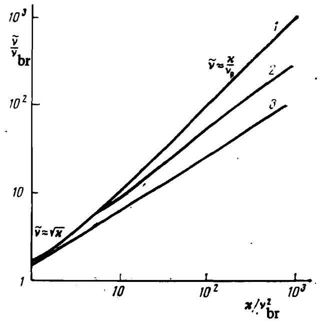

FIG. 4. Large values of the effective chain length ($\tilde{\nu} \gg 1$). Plot of $\tilde{\nu}/\nu_{br}$ against κ/ν_{br}^2 for the limiting case $\Gamma \to \infty$ (curve 1) and for the cases $\Gamma = 10^4$ (curve 2) and $\Gamma = 10^2$ (curve 3).

3. CHEMICAL CHAIN REACTION WITH THERMAL SELF-ACCELERATION

The results obtained in the preceding sections are essentially valid only for dilute systems (say with an inert gas), inasmuch as in their analysis no account is taken of the influence of the growth of the temperature during the course of the chemical reaction.

In this section we consider a case of practical interest, that of a nonbranching chain reaction in which the effective constant for the rate of continuation of the chain increases with temperature in accordance with the Arrhenius law

$$k_2=k_2^0\exp(-E_2/RT).$$

In addition to the photodissociation, account is taken also of the thermal dissociation of the main component (or else of molecular reactions that lead to the formation of active centers), which is essential during the concluding stage of the chemical conversion

$$N+M\xrightarrow{k_5}R, \qquad (V)$$

with

$$k_5=k_5^0\exp(-E_5/RT), \quad E_5\gg E_2.$$

In the considered system, as is well known, a wave combustion regime, namely detonation, can be realized even without photoinitiation. It is therefore natural to raise the question of the connection between the photoinitiated combustion regime and the pure detonation regime.

To answer this question it is necessary to take into account the compression of the medium (the degree of compression $\xi = [M]/[M]_0$) and the presence of a macroscopic velocity w due to the pressure gradient produced during the combustion. From the mass, momentum, and energy conservation laws there follow relations, well known from detonation theory[9], for the degree of compression ξ and for the temperature T as functions of the heat release q during the course of the reaction:

$$(\gamma+1)(1-\xi^{-1})=\left[1-\left(1-\frac{D^2}{V^2}\frac{q}{q_0}\right)^{1/2}\right]\left(1-\frac{V_{s0}^2}{V^2}\right),$$

$$\frac{R(T-T_0)}{\mu}=V^2(1-\xi^{-1})\left(\xi^{-1}-\frac{1}{\gamma}\frac{V_{s0}^2}{V^2}\right).$$

Here μ is the molecular weight and γ is the adiabatic constant, and are assumed independent of the degree of chemical conversion, while q_0 is the total energy released in the combustion of one gram of the initial mixture, V_{s0} is the speed of sound in the initial mixture, $D = (2(\gamma^2 - 1)q_0)^{1/2}$ is the velocity of the detonation wave (neglecting the initial pressure of the mixture), and V is the velocity of the wave.

In the coordinate system connected with the front of the chemical-conversion wave, the kinetic equations for the relative concentrations of the photodissociated component $n \equiv [N]/[N]_0\xi$ and of the active centers $r \equiv [R]/[N]_0\xi$ are written in the form

$$\tilde{\nu}\frac{\partial n}{\partial j}=-1-\varkappa(T)\frac{r}{j}-\frac{1}{j}\exp\left(\frac{E_5}{RT^*}\right)\left[\exp\left(-\frac{E_5}{RT}\right)-\exp\left(-\frac{E_5}{RT_0}\right)\right],$$

$$\tilde{\nu}\frac{\partial r}{\partial j}=1-\varkappa(T)\frac{r}{j}\nu_a^{-1}(T)+\frac{1}{j}\exp\left(\frac{E_5}{RT^*}\right)\left[\exp\left(-\frac{E_5}{RT}\right)-\exp\left(-\frac{E_5}{RT_0}\right)\right]; \tag{23}$$

$$\varkappa(T)\equiv\frac{k_2(T)[N]_0}{\sigma I_0}\xi,\quad \nu_a\equiv\frac{k_2(T)[N]_0}{k_{3a}(T)[X]_0},\quad \exp\left(\frac{E_5}{RT^*}\right)\equiv\frac{k_5{}^0[M]_0}{\sigma I_0}\xi. \tag{24}$$

In view of the very large activation energy of the thermal dissociation reaction (V), and consequently of the exceedingly strong dependence of its rate on the temperature, it becomes possible to break down the process of photochemical conversion into two temperature regions, $T < T^*$, when the thermal dissociation of the initial component can be neglected, and $T \gtrsim T^*$, when the thermal dissociation is decisive.

For $T < T^*$ we obtain from (24), assuming a weak dependence of the inhibition rate constant k_{3a} on the temperature:

$$\frac{j}{r}\approx\tilde{\nu}+\frac{\varkappa(T)}{\nu_a(T)}.$$

In this case it follows from (23) that

$$j=\tilde{\nu}\int_{T_0}^{T}\left[\frac{\tilde{\nu}}{\varkappa(T')}+\nu_a^{-1}(T')\right]\left|\frac{dn}{dT'}\right|dT'. \tag{25}$$

The derivative dn/dT is obtained under the assumption that

$$\frac{q}{q_0}=\frac{[N]_0-[N]}{[N]_0}=1-\frac{n}{\xi}.$$

We now show that the relative light flux j^* at the point of transition to the thermal-dissociation regime is close to unity. From (23) we have

$$\ln\frac{1}{j^*}<\tilde{\nu}\int_{T^*}^{T_\infty}\left|\frac{dn}{dT}\right|\left\{\varkappa(T^*)r^*\right.$$
$$\left.+\exp\left(\frac{E_5}{RT^*}\right)\left[\exp\left(-\frac{E_5}{RT}\right)-\exp\left(-\frac{E_5}{RT_0}\right)\right]\right\}dT, \tag{26}$$

where r^* is the relative concentration of the active centers at the transition point. In view of the strong dependence of the thermal-dissociation rate constant $k_5(T)$ on the temperature, the integral in (26) can be calculated asymptotically

$$\ln\frac{1}{j^*}<\tilde{\nu}\left|T\frac{dn}{dT}\right|_{T=T^*}\frac{RT^*}{E_5}\frac{\ln[\varkappa(T^*)r^*]}{\varkappa(T^*)r^*},$$

or, taking (25) into account,

$$\ln\frac{1}{j^*}<\frac{RT^*}{E_5}Z^{-1}\ln\left[Z\tilde{\nu}T^*\left|\frac{dn}{dT^*}\right|\right],$$

$$Z\equiv\int_{T_0}^{T^*}\frac{\Phi(T)}{\Phi(T^*)}\frac{dT}{T^*},\quad \Phi(T)\equiv\left[\frac{\tilde{\nu}}{\varkappa(T)}+\nu_a^{-1}(T)\right]T\left|\frac{dn}{dT}\right|\geqslant\Phi(T^*).$$

It follows therefore that at a sufficiently large value of E_5/RT^* we have indeed $j^* \approx 1$, i.e., the initiating light passes through the zone of thermal dissociation of the initial component without significant absorption, in view of the small thickness of this zone.

In this case the dispersion relation follows from (25) if we put $j = 1$ and assume $T = T^*$ as the upper limit of integration. If, in turn, the rate constant for the continuation of the chain also has an appreciable activation energy (such that $E_2/RT_0 \gg 1$), then the integral in (25) is calculated asymptotically in the vicinity of the point $T = T_0$ and the dispersion relation takes the form

$$\tilde{\nu}=\frac{\varkappa(T_0)A}{\tilde{\nu}+\varkappa(T_0)/\nu_a(T_0)},\quad A\equiv\frac{(\gamma-1)Q_0E_2}{(RT_0)^2}, \tag{27}$$

where Q is the thermal effect of the reaction per mole of the initial mixture.

From a comparison of the dispersion relations (14) and (27), we see that allowance for the influence of the self-heating on the rate of the PC wave reduces to replacement of the chain-continuation rate constant $k_2(T_0)$ by a much larger effective rate constant

$$k_2^{\text{eff}}=k_2(T_0)A=k_2(T_0)(\gamma-1)Q_0E_2/(RT_0)^2.$$

Thus, for example, if we assume $E_2 \approx 3$ kcal/mole and $E_5 \approx 30-40$ kcal/mole, then k_2^{eff} exceed $k_2(T_0)$ by two orders of magnitude.

In the preceding analysis we have implicitly assumed that a photoinitiated combustion regime sets in when the velocity of the chemical-transformation wave exceeds the velocity D of the detonation wave. With decreasing intensity of the initiating light flux I_0, the velocity of the chemical-transformation wave decreases and reaches the value D at a certain critical flux value I_0^{cr}, which is obtained from the dispersion relation by putting $V = D$. In particular, at an appreciable activation energy of the act of continuation of the chain ($E_2 \gg RT_0$), we get from (27)

$$\frac{I_0{}^{\text{cr}}}{[N]_0}=D\left[\frac{D\sigma}{k_2(T_0)}+\nu_a^{-1}(T_0)\right]A^{-1}. \tag{28}$$

Analysis shows that with further decrease of the light-source intensity ($I_0 < I_0^{\text{cr}}$), the wave velocity remains equal to the detonation-wave velocity, but at a certain degree of chemical conversion corresponding to the temperature T_S ($T_S < T^*$), a shock wave typical of the detonation sets in, and the following relation holds:

$$\frac{I_0}{I_0^{\text{cr}}}=\left[\int_{T_0}^{T}\left(\frac{D\sigma}{k_2}+\nu_a^{-1}\right)\left|\frac{dn}{dT}\right|dT\right]\left[\int_{T_0}^{T^*}\left(\frac{D\sigma}{k_2}+\nu_a^{-1}\right)\left|\frac{dn}{dT}\right|dT\right]^{-1}.$$

In the case $E_2 \gg RT_0$ it follows that

$$\frac{I_0}{I_0^{\text{cr}}}\approx\left[1-\exp\left(\frac{E_2}{RT_S}-\frac{E_2}{RT_0}\right)\right]\left[1-\exp\left(\frac{E_2}{RT^*}-\frac{E_2}{RT_0}\right)\right]^{-1},$$

or

$$\frac{T_S-T_0}{T_S}\approx\frac{RT_0}{E_2}\ln\left[1-\frac{I_0}{I_0^{\text{cr}}}+\exp\left(\frac{E_2}{RT^*}-\frac{E_2}{RT_0}\right)\right]. \tag{29}$$

The dependence of the temperature T_S at which the shock wave is produced on the ratio I_0/I_0^{cr} is shown in Fig. 5. As follows from (29) and from Fig. 5, the shock temperature T_S changes rapidly from the initial temperature T_0 to the temperature T^* near the critical light intensity I_0^{cr}. In other words, the transition from the pure detonation combustion regime (shock wave at $T_S = T_0$) to the photo-initiated regime takes place in a rather narrow zone $I_0/I_0^{\text{cr}} \approx 1$, i.e., we are dealing in essence with a limiting phenomenon.

The process of the transition from the detonation regime to the photo-initiated regime is shown schematically in Fig. 6.

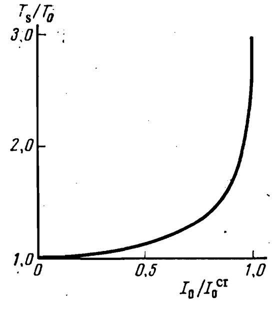

FIG. 5. Dependence of the temperature T_S of the gas mixture ahead of the shock wave on the relative light intensity. $E_2/RT_0 = 5$, $T^*/T_0 = 3$.

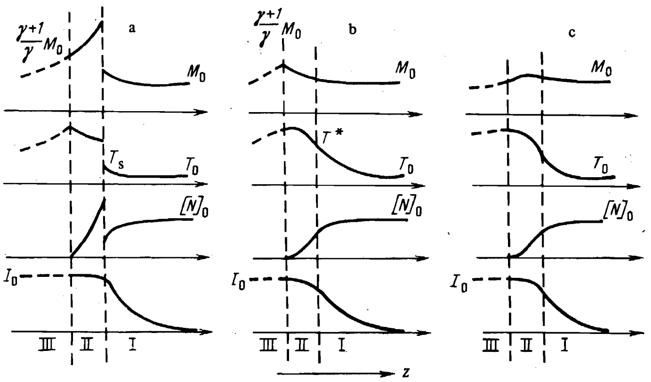

FIG. 6. Schematic profiles of the total density of the gas mixture, the temperature, the density of the dissociated component, and the intensity of light for different values of the source intensity: a) $I_0 < I_0^{cr}$, $V = D$; b) $I_0 = I_0^{cr}$, $V = D$; c) $I_0 > I_0^{cr}$, $V > D$. I) region of photochemical transformation, II) high-temperature zone of final combustion of the mixture, III) nonstationary rarefaction wave. For the sake of clarity, zone II is artificially broadened; actually, the dimension of this zone is smaller by several orders of magnitude than the region of the photochemical transformation. In the case $I_0 < I_0^{cr}$, a shock wave is produced on the boundary of regions I and II. The shock vanishes at $I_0 = I_0^{cr}$; with further increase of I_0, the maximum density of the gas mixture decreases, i.e., the case of an incompressible medium is realized at $V \gg D$.

CONCLUSION

What qualitative conclusions can be drawn on the basis of the foregoing analysis of a number of model problems?

The photodissociation wave makes it possible in principle to initiate chemical reactions in optically dense media with any specified velocity $V < c$. Since, however, the main loss to chemical transformation fall to the initiating light, the intensity of the initiating light in the cases of practical interest turns out to be quite high.

In the initiation of chain reactions, for a wide range of light-source intensities (where the dissociation rate is smaller than or comparable with the rate of the chain chemical process), it is possible to reach velocities greatly exceeding the velocity of the PD wave (i.e., the PC wave), because the quantum yield of the chemical conversion exceeds unity. Nonetheless, these velocities are much lower than the limiting value $V_{PD}\kappa_0$, where κ_0 is the average quantum yield. This is due to the presence of a final combustion stage, for which the quantum yield is close to unity and which therefore is due mainly to photodissociation.

Chemical reactions whose specific rate increases with the completeness of the conversion, namely, branching chain reactions and chain reactions with thermal self-acceleration, should lead in principle to larger velocities of the photochemical-conversion waves. In the former case, however, the increase in velocity turns out to be not very appreciable. The reason is the need for introducing an inhibitor of the branching-chain process in order to stabilize the initial mixture; in the cases of practical interest the inhibitor concentration amounts to either tenths of 1% or to several percent of the total mixture concentration. On the other hand, in the case of chain reactions with thermal self-acceleration, stability of the mixture is attained by the heat-transfer process (the dimension of the reactor is smaller than the characteristic dimension for thermal explosion, since the ratio of the heat-transfer time to the time of the chemical reaction amounts to several orders of magnitude, much higher values of the effective chain length $\tilde{\nu}$ can be reached.

For undiluted chemical systems, the photochemical-conversion wave propagates in the medium without shocks when $I_0 > I_0^{cr}$. At lower source intensities ($I_0 < I_0^{cr}$), a shock wave typical of a detonation wave is produced, and the wave velocity equals the detonation-wave regime to the photochemical-wave regime occurs in a narrow source-intensity interval. In other words, we are dealing with an extremal phenomenon, the experimental investigation of which would make it possible, in principle, to determine the generalized chemical characteristics of the gas mixtures.

The authors are grateful to V. L. Tal'roze for interest in the work and for useful discussions, and also to V. I. Matsaev for help with the mathematical calculations.

[1)] We confine ourselves to velocities much smaller than the light velocity c. When necessary, the finite value of c can be easily taken into account [1,4].

[2)] The annihilation reactions (IIIa) and (IIIb) can also be trimolecular (for example, $H + O_2 + M \rightarrow HO_2 + M$), in which case k_3 must be taken to mean the effective bimolecular rate constant, which depends on M.

[3)] The case of annihilation of active centers in their trimolecular reaction with impurity X, with participation of only the main component ($R + X + N \rightarrow X'' + N$, i.e., neglecting formally the stabilizing action of the reaction products even during the burnup stage), leads to a similar system of equations [7].

[4)] Allowance for the annihilation of the active centers (process IIIb) leads only to an effective decrease of the branching rate constant k_4.

[5)] The condition $u \leqslant 1$ defines the region of chain self-ignition.

[6)] The influence of branching (of the energetic type) on the character of the PC wave in mixtures that are stabilized by a small impurity was considered by Oraevskiĭ, Pimenov, and Shcheglov [8]. The dispersion equation obtained there, of the type (22), is the consequence of their assumption [8] that the initial section of the wave profile, in which complete burnout of the impurity takes place, is of the pure photolysis type. It is easy to show that for the model considered in the present paper this assumption is equivalent to the limiting case $\Gamma \rightarrow \infty$. Allowance for the finite value of Γ leads to a significant decrease of the PC-wave velocity.

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Translated by J. G. Adashko
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