PHYSICAL CHEMISTRY

L. A. LOVACHEV

1958

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

L. A. LOVACHEV

ON THE ROLE OF CHAIN BRANCHING AND TERMINATION IN CHAIN-THERMAL FLAME PROPAGATION

(Presented by Academician V. N. Kondrat' ev, 7 VII 1958)

The chain mechanism of the decomposition reaction of A, including two active centers that react successively with A and restore one another, is represented in the form of a simplified scheme with an active center of one kind, P (^{1}):

$$\begin{aligned}
&A \rightarrow 2P \quad \text{(initiation)}, \& Q_R = h_R R(T');\\
&P + A \rightarrow 2C + P \quad \text{(propagation)}, \& Q_n = hFn = hK(T')\, n_A n;\\
&P \rightarrow 3P \quad \text{(branching)}, \& Q_V n = h_V V n = h_V K_V(T')\, n_A n;\\
&(P \rightarrow \text{linear termination})\\
&P + P \rightarrow A \quad \text{(termination)}, \& Q_W n^2 = h_W W(T')\, n^2.
\end{aligned}$$

On the right are written the expressions for the rates of heat release. Here h_i is the heat effect; K_i is the reaction-rate constant; W is the rate constant of quadratic chain termination; n_A is the dimensionless weight concentration of A; n is the dimensionless weight concentration of P. The rate of linear branching or chain destruction may be written as $K_V n_A n = iKn_A n$, whence $i = V/F = K_V/K$, where i is the chain-branching coefficient (linear chain termination corresponds to $i < 0$).

For $\lambda = c\rho D_A$, for the stationary propagation of a laminar one-dimensional flame, we obtain the system of equations

$$\lambda p p' - Bcp + Q_\Sigma n + Q_W(n^2 - n_t^2) - Q_R = 0, \tag{1}$$

$$Dp^2 n'' - p(B - Dp')n' + R + Vn - W(n^2 - n_t^2) = 0, \tag{2}$$

where $B = u\rho$; $D = \rho D_P$; $Q_\Sigma = Q + Q_V$; $T' = T + T'_0$; $D_0 = D_m q$; $D_P \sim (T')^a$;

$q = \dfrac{\mu_0}{\mu_m}\left(\dfrac{T'_0}{T'_m}\right)^{a-1}$; $p = \dfrac{dT}{dx}$; $p' = \dfrac{dp}{dT}$; $n' = \dfrac{dn}{dT}$; $n'' = \dfrac{d^2n}{dT^2}$; x is the coordinate; u is

the flow velocity; ρ is the density; T' is the temperature (°K); D_A is the diffusion coefficient of A; D_P is the diffusion coefficient of P; λ is the thermal conductivity of the mixture; c is the heat capacity; n_t is the current equilibrium concentration of P.

Quantities in the initial state ($T' = T_0'$) will be denoted by the subscript zero, in the final state ($T' = T_r'$) by the subscript r, and in the state corresponding to the maximum value of the temperature gradient $p = p_m$ ($T' = T_m'$) by the subscript m. The limiting values of the reaction-rate functions are equal to zero, and the boundary conditions for (1) and (2) coincide with those adopted in (1).

The concentration n_m at $T = T_m$ will be written (1) in the following form:

$$n_m = t + \left[R_{pm} + V_m n_m - W_m n_m^2 - Blp_m\right] N, \tag{3}$$

where

$$l = \frac{n_r - n_0}{T_r}; \quad t = n_0 + lT_m; \quad r = T_m(T_r - T_m); \quad R_p = R + Wn_t^2; \quad N =$$

$$= \frac{r}{2D_m p_m^2}; \quad T_m = 0.5T_r.$$

Determining n_m from (3) and substituting into (1) for $p = p_m$ and $\dot{p}_m = 0$, we obtain, for $B = \eta p_*^{(1)}$, where $\eta = 4L_0/\chi T_m'$ and $\chi = cD_0/\lambda_0$:

$$p_*^6 \eta A_1 - p_*^4(\eta^2 A_2 + \eta A_3 + A_5) - p_*^2(\eta A_4 - A_6 - \eta A_7 + A_8) + A_9 = 0, \tag{4}$$

where

$$A_1 = 4cL^2 mf; \quad A_2 = (c + lhw)^2 gr^2; \quad A_3 = 2D_{mr}(c + 2cV_{mf} - lhw - 2tlQ_{wm}f - 2ctfW_m);$$
$$A_4 = r^2(lQ_{\Sigma m} - cV_m + lV_{mhw} - cV_m^2 f); \quad A_5 = 4D_m^2(t^2 lQ_{wm} + lhw - fQ_{pm});$$
$$A_6 = 2D_{mtr}(Q_{\Sigma m} + V_{mhw}); \quad A_7 = 2r^2(lfQ_{wm}R_{pm} + cfW_m R_{pm} - cgQ_{pm} - lfW_m Q_{pm});$$
$$A_8 = 2D_{mr}(Q_{pm} + 2tR_{pm}Q_{wm}f - 2tfW_m Q_{pm} + 2fV_m Q_{pm} + hwR_{pm});$$
$$A_9 = r^2(Q_{\Sigma m}R_{pm} + V_m Q_{pm} + V_m hwR_{pm} + fV_m^2 Q_{pm} + 2fW_m R_{pm} Q_{pm}$$
$$- fQ_{wm}R_{pm}^2 - gQ_{pm}^2); \quad Q_{pm} = Q_{Rm} + Q_{wm}n_t^2; \quad f = hw/Q_{\Sigma m} \text{ and } g = W_m/Q_{\Sigma m}.$$

Determining p_* from (4), we find the flame-propagation velocity

$$u_0 = \frac{B}{\rho_0} = \frac{1}{\rho_0}\eta p_*. \tag{5}$$

If, as before (1), the magnitude of the initiation rate R is neglected, i.e., if one sets $A_7 = A_8 = A_9 = 0$ (it is also assumed that $W_m n_t^2 = 0$), then from (4) we obtain, for determining p_*,

$$p_*^4 \eta A_1 - p_*^2(\eta^2 A_2 + \eta A_3 + A_5) - (\eta A_4 - A_6) = 0, \tag{6}$$

whence

$$p_*^2 = \frac{(\eta^2 A_2 + \eta A_3 + A_5) - \left[(\eta^2 A_2 + \eta A_3 + A_5)^2 + 4\eta A_1(\eta A_4 - A_6)\right]^{1/2}}{2\eta A_1}. \tag{7}$$

Expanding the radical in (7) into a series and assuming that $A_4 \simeq A'_4 = r^2(lQ_{\Sigma m} - cV_m)$, $A_3 \simeq A'_3 = 2D_{mr}(c + 2cV_{mf})$, $A_5 \simeq A'_5 = 0$, we obtain from (5)

$$u_0 = \varphi\psi \frac{1}{\rho_0} \left(\frac{n_\Gamma Q_{\Sigma m} D_m}{2cT_\Gamma} \right)^{1/2} = \varphi\psi \frac{1}{2\rho_0} \left[n_\Gamma \left(K + \frac{h\nu}{h} K_V \right)_m (\rho D_P)_m \right]^{1/2}, \tag{8}$$

where

$$\varphi = 2\left[\frac{2q}{\chi} \left(1 - \frac{2q}{\chi} \right) \right]^{1/2}, \tag{9}$$

$$\psi = \left(\frac{1 + \dfrac{K_{Vm}}{K_m} \left[\dfrac{h\nu}{h} + \dfrac{\chi}{(\chi - 2q)} \dfrac{h_W}{h} + \dfrac{2qnA_m}{t(\chi - 2q)} \right]}{1 + \dfrac{K_{Vm}}{K_m} \left[\dfrac{h\nu}{h} + 2\dfrac{h_W}{h} \right] + \dfrac{2q}{\chi} \dfrac{W_m}{K_m}} \right)^{1/2} \tag{10}$$

or

$$\psi \simeq \left(\frac{1 + \dfrac{2qnA_m}{t(\chi - 2q)}}{1 + \dfrac{2q}{\chi} \dfrac{W_m}{K_m}} \right)^{1/2}. \tag{11}$$

The coefficient φ expresses the dependence of u_0 on the ratio of the diffusion coefficient P, multiplied by the heat capacity and density, to the thermal conductivity (the quantity χ). However, χ also enters into the relation for ψ (10). The influence of the rate of quadratic chain termination depends on the ratio of the constant W_m to the constant K_m. Therefore it is evident that the influence of quadratic chain termination will be the stronger, other conditions being equal, the lower the ignition temperature T'_Γ, since with a decrease in T'_Γ, K_m decreases and W_m increases. A decrease in χ will increase the degree of influence of W

on u_0. In the presence of linear chain branching, the influence of W will appear the less, the greater the branching-rate constant will be.

K_{Vm}. The influence of linear chain branching on u_0 will be the more significant, the smaller $t = n_r/2$ is (as n_r decreases, the role of the rate of initiation and branching of chains relatively increases, since the diffusion flux of active centers decreases), and the smaller x is (since in this case the number of active centers delivered into the reaction zone by diffusion relatively decreases).

The influence of linear chain termination ($K_V < 0$ or $i < 0$) is the more significant, the smaller n_r is under otherwise similar conditions (as n_r decreases, the role of branching and termination of chains relatively increases, since the diffusion flux decreases). This influence is manifested mainly as a result of a change in the second term in the numerator of (10) or (11). For the same reason, a decrease in x increases the degree of influence of linear chain termination on u_0. The constant K_{Vm} also enters relation (8) and lowers u_0, if $h_V \neq 0$.

To illustrate the foregoing, numerical calculations were carried out for the example of a hydrazine decomposition flame, which had already been investigated in ([1]). All initial data were taken without change from ([1,2]). The additional initial data adopted in the present calculations are: $h_V = 0$; $Q_V = 0$; $Q_\Sigma = Q$; $h_W = 3 \cdot 10^3$ cal/g; $h_R = 2 \cdot 10^3$ cal/g. The coefficients of equation (4) were calculated, and it was established that p_*, calculated from (4), practically does not differ from p_* calculated from (6). This proves the validity of the assumption made earlier ([1]) and used in obtaining equation (6), namely that the rate of initiation of active centers may be neglected, since their delivery by diffusion is much greater.

From a comparison of the data for $i = 0,\ W = 0$ with the data for $i = 0,\ W \neq 0$, it follows that the rate of quadratic chain termination has a very small influence on u_0 at high T_r' and a more considerable influence at low T_r'. Calculation by the most approximate relations (8) and (9) using (10) or (11) gives results close to those obtained from relations (5) and (6). In ([1]), an estimate was made of the value $i > 0$ necessary to compensate for the influence of the rate of quadratic chain termination. The data of Table 1 confirm the correctness of this estimate.

Table 1

Influence of branching and termination of chains on the flame propagation velocity u_0 (cm/sec), for the example of a hydrazine decomposition flame

	Linear branching i	Linear branching i											
	0	0	$5 \cdot 10^{-3}$	10^{-2}	$5 \cdot 10^{-2}$	10^{-1}	0	0	$5 \cdot 10^{-5}$	10^{-4}	$5 \cdot 10^{-4}$	10^{-3}	$5 \cdot 10^{-2}$

	Linear branching i	Linear branching i											
	$W = 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$	$W = 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$	$W \neq 0$
	$T'_0 =$ 300°K, $T'_r =$ 1950°K	$T'_0 =$ 300°K, $T'_r =$ 1280°K											
By (5) and (6)	146	140	144	148	173	202	8.58	5.10	5.45	5.79	8.05	10.2	20.3
By (8), (9) and (10)	146	135	139	142	164	181	8.58	5.11	5.47	5.82	8.08	10.2	20.3
By (8), (9) and (11)	146	137	143	148	186	224	8.58	5.11	5.47	5.82	8.08	10.2	20.4

From relation (8), if n_r is expressed through the equilibrium constant, it follows that, when the pressure P_Σ is lowered, n_r will increase, and this will lead to an increase in u_0. For combustible mixtures with low heat release, when P_Σ is lowered, T'_r will practically not change, and therefore in a dependence of the type $u_0 \sim P_\Sigma^k$, the value of the exponent k, calculated from relation (8), will be approximately $k = -0.25$. For lean hydrocarbon mixtures in de···

depending on the initial composition, may be $k < -0.25$. In combustible mixtures with medium and high heat release, the drop in T'_r as P_Σ decreases may partly or completely compensate the effect due to the increase in n_r, and therefore $k > -0.25$ or $k = 0$ (u_0 does not depend on P_Σ). A decrease of u_0 with falling pressure is also possible ($k > 0$).

Let us consider the role of the coefficients φ and ψ. In mixtures with high T'_r, as P_Σ decreases, q will increase, and this, for $x > 1$, will lead to an increase in φ (9) and, consequently, to a decrease in k. As P_Σ decreases, the second term in the denominator of (11) will decrease, since $W \sim \rho^3$, while $K \sim \rho^2$. This will lead to a decrease in k. The fall of P_Σ will therefore lead to a stronger increase in u_0 (compared with the increase at $k = -0.25$) in mixtures with low T'_r (see Table 1). As P_Σ is lowered, $t = n_r/2$ increases. As a result, the influence of linear chain termination will decrease (if $Kv < 0$ or $i < 0$), which will lead to an increase in ψ (a decrease in k). This influence of the decrease in P_Σ will be more sharply expressed in mixtures with low T_r' because of the more rapid increase of n_r. A decrease in P_Σ will likewise lead to a reduction in the influence of linear chain branching (if $i > 0$) and, consequently, to a decrease in ψ (an increase in k).

The dependence of u_0 on D_P and λ is expressed mainly by the radical in (8) and by the coefficient φ (9). From (9) it is seen that the influence of x on u_0 may be different depending on the ratio $2q/x$. As x decreases, the rate of quadratic chain termination will exert a more significant influence on u_0, since ψ decreases. Linear chain termination will act in the same direction (if $i < 0$). A decrease in x will lead to an increase in the role of linear chain branching (11). All this is connected with the fact that, when x decreases, the number of active centers delivered to the reaction zone by diffusion is relatively reduced, and therefore the role of initiation, branching, and chain termination increases.

Institute of Chemical Physics
Academy of Sciences of the USSR

Received
4 VII 1958

REFERENCES

1. L. A. Lovachev, DAN, 120, No. 6, 1287 (1958).

2. D. B. Spalding, Phil. Trans. Roy. Soc. London, A, 249, No. 957, 1 (1956).

Note: Figure translations are in progress. See original paper for figures.