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Abstract

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Chain-Thermal Self-Ignition in Systems with Energy Branching

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The possibility of energy branching in the fluorination of hydrogen has been discussed rather widely in the literature. At present the reaction
$HF^* + F_2 \rightarrow 2F + HF$
(where HF^* is a vibrationally excited hydrogen fluoride molecule rich in energy) meets with no theoretical objections and, apparently, has been reliably confirmed experimentally ([1]). The question of the possibility of branching of this type in the system $H_2 + Cl_2$ remains open for the time being. Since the concentration and lifetime of energy-rich HX^* molecules are small, it is extremely difficult to detect them experimentally. The influence of vibrationally excited molecules on the course of the reaction must most often be judged from overall effects, such as ignition limits and ignition delays.

The dependence of the ignition delay on temperature, as noted in ([2]), can be used to determine, over a wide temperature range, the rate constants of chemical reactions. For this it is necessary to obtain, in analytical form, an expression relating the ignition delays to the rate constants of the elementary stages of the process and to the thermophysical characteristics of the mixture under study. Experimental verification of the relations obtained will make it possible not only to clarify the possibility of branched reactions in the chlorination of hydrogen, but also to obtain quantitative kinetic laws.

Let us write the scheme of the chain reaction of thermal chlorination or fluorination of hydrogen:

0.	$X_2 + M \rightarrow 2X + M;$	$u_0 = k_0(X_2)(M)^2 = W_0(M);$	$q_0.$
1.	$X + H_2 \rightarrow HX + H;$	$u_1 = k_1(X)(H_2)(M)^2 = W_1(X)(M);$	$q_1.$
2.	$X_2 + H \rightarrow HX^* + X;$	$u_2 = k_2(X_2)(H)(M)^2 = W_2(H)(M);$	$q_2.$
2′.	$X_2 + H \rightarrow HX + X;$	$u_2' = k_2'(X_2)(H)(M)^2 = W_2'(H)(M);$	$q_2'.$
3.	$HX^* + X_2 \rightarrow HX + 2X;$	$u_3 = k_3(X_2)(HX^*)(M)^2 = W_3(HX^*)(M);$	$q_3.$
4.	$HX^* + M \rightarrow HX + M;$	$u_4 = k_4(HX^*)(M)^2 = W_4(HX^*)(M);$	$q_4.$

Here H and X are, respectively, atoms of hydrogen and of a halogen; M is any

particle; u_i, q_i, and k_i are the rates, heat effects, and rate constants of the elementary reactions. The concentrations of the reacting components are taken in dimensionless form, referred to the total number of moles of M in 1 cm^3. Reactions of trimolecular termination of the type $X + X + M \rightarrow X_2 + M$ are not included in the present scheme because of the obvious smallness of their rates in comparison with the rates of generation of active centers.

The kinetic differential equations and the equation of conservation of energy for the case in which the ignition process proceeds under adiabatic conditions are written in the following form:

$$\frac{d(X)}{dt} = 2W_0 + (W_2 + W_2')(H) - W_1(X) + 2W_3(HX^*); \quad (1)$$

$$\frac{d(H)}{dt} = W_1(X) - (W_2 + W')(H); \quad (2)$$

$$\frac{d(HX^*)}{dt} = W_2(H) - W_3(HX^*) - W_4(HX^*) = W_2(H) - (W_3 + W_4)(HX^*); \quad (3)$$

$$c\frac{dT}{dt} = W_0q_0 + W_1(X)q_1 + W_2(H)q_2 + W_2'(H)q_2' + W_3q_3(HX^*) + W_4q_4(HX^*) \quad (4)$$

(c is the heat capacity of the mixture).

The simultaneous solution of the system of equations (1)–(4) is carried out under the assumption that the concentrations of the initial substances do not change during the ignition-delay period.

Let us divide the region of integration into two parts. In the initial segment, when the temperature remains practically constant, it may be assumed that the coefficients at the variable concentrations (H), (X), and (HX^*) in equations (1)–(4) do not change. We define the boundary of this segment so that the increase in the temperature of the mixture does not exceed the value causing a change in the rate of the decomposition reaction of X_2 by more than 10%. Then the solution of equations (1)–(4), with (X) = (H) = (HX^*) = 0 at the time $t = 0$, takes the form

$$(H + X) + b(H) + m(HX^*) = \frac{2W_0}{\beta}\left(e^{\beta t} - 1\right), \quad (5)$$

where $b = \beta/W_1$; $m = \beta(W_1 + W_2 + W_2' + \beta)/W_1W_2$; β is determined from the characteristic equation

$$\beta^3+\beta^2(W_1+W_2'+W_2+W_3+W_4)+(W_1+W_2'+W_2)(W_3+W_4)\beta-2W_1W_2W_3=0. \tag{6}$$

If it is taken into account that $W_3 \ll W_1, W_2, W_4$, then we obtain

$$\beta = \frac{2W_1W_2W_3}{(W_1+W_2+W_2')(W_3+W_4)}, \tag{7}$$

and the negative roots of equation (6) are

$$\beta_2 = -(W_1+W_2'+W_2), \tag{8}$$

$$\beta_3 = -(W_3+W_4). \tag{9}$$

In paper (2) it was indicated that the rates of the reactions W_1(X) and W_2(H) increase very rapidly with time and that in the equations containing these rates one may, without large error, neglect the rate W_0 even at the initial moment of time. Then from equations (4)–(9) the following expression is obtained for the temperature change in the initial period of the reaction:

$$c\frac{dT}{dt} = \left\{(W_3+W_4)\left[q_1+q_2+\frac{W_2'}{W_2}(q_1+q_2')\right]+q_3W_3+q_4W_3\right\}(\mathrm{HX}^*), \tag{10}$$

where

$$(\mathrm{HX}^*) = \frac{W_0}{W_3}\left(\exp\left[\frac{2W_1W_2W_3t}{(W_1+W_2'+W_2)(W_3+W_4)}\right]-1\right).$$

Integration of equation (10) leads to a transcendental equation for determining the time t_0 corresponding to a 10% change in the rate W_0 due to the change in temperature:

$$0.1r = e^{\tau_0}-1-\tau_0, \tag{11}$$

where

$$\tau_0 = \frac{2W_1W_2W_3t_0}{(W_1+W_2+W_2')(W_3+W_4)},$$

$$r = \frac{2RT_0^2 W_3^2 W_1 W_2 c}{E_0 W_0 (W_1 + W_2 + W_2')(W_3 + W_4)} \cdot \left\{ (W_3 + W_4) \left[q_1 + q_2 + \frac{W_2'}{W_2}(q_1 + q_2') \right] + W_3 q_3 + W_4 q_4 \right\}$$

In what follows, all W_i for τ and r are taken at $T = T_0$, while the temperature dependence of the reaction rates is taken into account by the factor $\exp\left[\frac{E_i}{RT_0}\frac{T-T_0}{T}\right]$. For $0.1r \gg 1$ (if one restricts oneself to an accuracy of 10%, then for $r \geq 200$) the rate of the process is determined by the branching reaction. In this case the time $\tau_0 = \ln(0.1r)$. If $r \ll 1$ (to an accuracy of 10%, $r \leq 0.05$), then the branching reaction has no effect on the process, and for τ_0 one obtains the expression $\tau_0 = \sqrt{0.2r}$.

In order to obtain an expression for the total ignition delay, we use the method of stationary concentrations, as well as an approximate representation of the Arrhenius dependence of the reaction rates W_0 and W_3 according to (3) in the form

$$W_0 = W_0|_{T=T_0} \exp\left[\frac{E_0}{RT_0^2}(T - T_0)\right]; \quad W_3 = W_3|_{T=T_0} \exp\left[\frac{E_3}{RT_0^2}(T - T_0)\right]$$

(here T_0 and T are the initial and current temperatures).

We define the ignition delay as the time at which the temperature of the system tends to infinity. Then, for $r \ll 10$, the expression for the ignition delay does not differ in any way from that obtained in work (2) for an unbranched chain reaction. The changes in temperature and in the concentration of one of the active centers in the region $\tau_0 \leq \tau$ during ignition are determined, respectively, by equations (10) and

$$\frac{d(\mathrm{HX}^*)}{dt} = \frac{2W_0 W_1 W_2}{(W_1 + W_2' + W_2)(W_3 + W_4)} + \frac{2W_1 W_2 W_3 (\mathrm{HX}^*)}{(W_1 + W_2' + W_2)(W_3 + W_4)}. \quad (12)$$

The system of equations (10) and (12) reduces to a single equation

$$\frac{d^2 y}{d\tau^2} = \frac{dy}{d\tau} e^{\alpha y/r} + e^{y/r}, \quad (13)$$

where

$$y = \frac{T - T_0}{RT_0^2} E_0 r, \quad \alpha = \frac{E_1 + E_3}{E_0 + E_1}.$$

The initial conditions are: $y_0 = 0.1r = (dy/dt)_0$ at $\tau = \tau_0$.

If the rate of the process is determined by the branching reaction, then the last term on the right-hand side of equation (13) can evidently be neglected, since it reflects the thermal generation of X atoms. Then

$$\tau - \tau_0 = \ln \frac{10}{\alpha} \frac{e^{\alpha y/r} - 1}{e^{\alpha y/r}} \tag{14}$$

and the ignition delay is

$$\tau^0 = \ln \frac{r}{\alpha}. \tag{15}$$

Substitution of the approximate solution thus obtained into equation (13) showed that neglect of the term $e^{y/r}$ introduces into the determination of τ^0 an error not exceeding 10% for $r > 200$.

The accuracy of the analytical expression for the chain-thermal ignition delay in a system with energy branching was estimated by numerical integration of the kinetic equations and the heat-balance equation. The numerical values of the heat effects and of the rate constants of the elementary reactions were:

$$W_0 = 0.25 \cdot 10^{9-11/T}\ \text{s}^{-1}; \qquad W_1 = W_2' = 0.25 \cdot 10^{9-1/T}\ \text{s}^{-1};$$

$$W_2 = 0.25 \cdot 10^{7-1/T}\ \text{s}^{-1}; \qquad W_3 = 0.25 \cdot 10^{8-3/T}\ \text{s}^{-1};$$

$$W_4 = 10^6\ \text{s}^{-1}; \qquad q_1 = q_2 = 0; \qquad q_2' = q_4 = 50\ \text{kcal/mol};$$

$$c = 5\ \text{cal/mol} \cdot \text{deg}$$

and all rates of trimolecular recombinations were chosen equal to 10^6 s^{-1} (the temperature T here is expressed in thousands of degrees).

In the integration, the change in the concentrations of the initial substances during the reaction was taken into account. The initial temperature was chosen so that $r = 200$.

Fig. 1: Dimensionless temperature $(T - T_0)/(T_\text{r} - T_0)$ vs dimensionless time τ/τ^0.

In Fig. 1, the dimensionless temperature $(T - T_0)/(T_\text{r} - T_0)$ is plotted along the ordinate (T_r is the explosion temperature), and the dimensionless time τ/τ^0 along the abscissa. As is seen from the figure, the ignition delay determined by formula (15) (solid line) differs by only 10% from the time corresponding to the

inflection point on the temperature-time curve (dashed line, numerical integration), and represents the upper possible limit for the experimentally measured ignition delay.

Thus, the expression obtained can be used to determine the ratio $W_1W_2W_3/((W_1 + W_2 + W_2')(W_3 + W_4))$. For known values of W_1 and W_2', one can calculate the ratio W_2W_3/W_4 (since $W_3 \ll W_4$).

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