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Abstract

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ON THE TEMPERATURE DEPENDENCE OF THE KINETIC CHARACTERISTICS OF EXOTHERMIC REACTIONS IN THE CONDENSED PHASE

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In studying the slow chemical transformation of explosive substances, two regularities were discovered which, apparently, are characteristic of all substances decomposing in the condensed state with a large thermal effect ([1], [2]). First, the pre-exponential factors have very large values, $Z \sim 10^{18}$—10^{28} $\sec^{-1}$, which cannot in any way be reconciled with the frequency of molecular vibrations, 10^{13}—10^{14} $\sec^{-1}$, which should be of the same order of magnitude as the pre-exponential factor for a first-order reaction. Second, the pre-exponential quantity and the activation energy (which, by their meaning, should be constants) increase with increasing temperature, and rather strongly (the activation energy by tens of kilocalories per mole, and the pre-exponential quantity by several orders of magnitude when the temperature changes by tens of degrees).

In ([1], [2]) it is indicated that one possible explanation of the increase of Z and E with increasing temperature may be the assumption that chains are present whose length increases with temperature. In the present work it is assumed that the cause of the occurrence of such chains is the thermal initiation of the reaction of an unreacted molecule adjacent to a reacted molecule.

The large amount of heat released in a strongly exothermic reaction heats the particles surrounding the reacted molecule to a high temperature. The thermal wave will reach the nearest molecule capable of reaction after a time t_1. At this moment the temperature of the surroundings of this molecule changes from T—the temperature of the medium—to the value $T + T_m$, where T_m is determined by the thermal effect of the reaction q, the distance between neighboring molecules λ, and the character of the thermal wave. Without going into the rather complicated question of the form and velocity of the thermal wave, one may say that, during small $\tau = t - t_1 > 0$, the temperature of the surroundings of the unreacted molecule will change according to the law $T + T_m - \alpha\tau$, where α is a constant.

Let us denote by E_0 and Z_0 the true values of the activation energy and the pre-exponential factor, determined for an isolated molecule. Then the probability of reaction initiation is

$$w = Z_0 \int_0^\infty \exp\left[-\frac{E_0}{R(T+T_m-\alpha\tau)}\right] d\tau \simeq$$

$$\simeq Z_0 \int_0^\infty \exp\left\{-\frac{E_0}{R(T+T_m)}\left[1-\frac{\alpha\tau}{T+T_m}\right]\right\} d\tau =$$

$$= \frac{Z_0}{\alpha}\,\frac{R(T+T_m)^2}{E_0}\,\exp\left[-\frac{E_0}{R(T+T_m)}\right].$$

Although the integration is carried out to infinity, it is sufficient to take the integrand for small τ, since these values give the main contribution to the integral. If a molecule has N nearest

neighbors, then the probability of chain continuation will be

$$x = \frac{Z_0}{\alpha} N \frac{R(T+T_m)^2}{E_0}\exp\left[-\frac{E_0}{R(T+T_m)}\right] = s\exp\left[-\frac{E_0}{R(T+T_m)}\right],$$

where s is a function that depends only weakly on the temperature of the medium.

Taking the chain into account, the reaction rate is

$$\frac{1}{n}\frac{dn}{dt} = \frac{Z_0 e^{-E_0/RT}}{1-x},$$

and the effective values of the activation energy and pre-exponential factor are equal to

$$E = E_0\left[1 + \frac{T^2}{(T+T_m)^2}\,\frac{x}{1-x}\right],$$

$$\ln Z = \ln Z_0 - \ln(1-x) + \frac{E_0 T}{R(T+T_m)^2}\,\frac{x}{1-x}.$$

It follows from these expressions that a properly chosen $x \ll 1$ can give an increase in the activation energy by tens of percent in comparison with E_0 and an increase in Z by several orders of magnitude in comparison with Z_0. However, in order to establish that the proposed scheme explains the strong dependence of E and Z on temperature, it is necessary to show, first, that reasonably chosen parameters can indeed give $x \ll 1$, and, second, that the temperature dependence of x corresponds to the experimentally determined dependence of E and Z on temperature.

The probability of chain continuation x depends on temperature chiefly through the factor $\exp[-E_0/R(T+T_m)] \sim \exp(E_0 T/RT_m^2)$. Hence

$$\frac{dx}{x} = \frac{E_0\, dT}{RT_m^2}.$$

Taking $E_0 \sim 30$–40 kcal/mole and $T_m = (1$–$2) \cdot 10^3\,^\circ$K, we find that $dx/x \sim (0.5$–$2) \cdot 10^{-2} dT$, i.e., when the temperature changes by several tens of degrees, x can change severalfold. This is sufficient to explain the experimentally observed dependence of E and Z on temperature.

To estimate the magnitude of x itself, let us assume that the thermal wave has the form of a rectangle (in the coordinates r, T), and that the coordinate of the front is related to time through the thermal diffusivity of the medium, $r^2 \sim \chi t$. In this case $T_m = 3q/4\pi\rho c\lambda^3$ (ρ is the density, and c the heat capacity of the medium) and $\alpha \sim \chi T_m/\lambda^2$. With $\chi \sim 10^{-4}$ cm^2/sec, $\lambda \sim 10^{-7}$ cm, and a normal value $Z_0 \sim 10^{13}$–10^{14} sec^{-1}, one can obtain (for the E_0 and T_m indicated above) the value $x \ll 1$.

Thus, the proposed scheme of thermal chains can in principle explain the regularities of the thermal decomposition of explosive substances. The fact that lower E and Z are obtained in solutions and vapors of such substances argues in favor of such chains.

The normal value of Z_0 could be obtained at sufficiently low temperatures; however, the low reaction rate in this case makes it difficult to determine the kinetic constants.

When the temperature is raised, a value $x = 1$ can be reached, which corresponds to ignition of the explosive substance. From this point of view, one can speak only of the flash temperature of the substance. In the usual treatment of thermal explosion, however, the conditions for ignition also include the size and shape of the sample and the conditions at its boundaries.

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CITED LITERATURE

1. K. K. Andreev, A. F. Belyaev, *Theory of Explosives*, 1960.

2. K. K. Andreev, *Thermal Decomposition and Combustion of Explosives*, 1957.

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

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