

Observation of the upper temperature limit of ignition in low-temperature, solid-phase reactions

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A solid-phase chain reaction, in which a thermal explosion occurs as a result of cooling the sample after formation of the critical concentration of active particles, was observed.

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The rate constants of elementary processes in the solid phase, which decrease with decreasing temperature, reach a quantum limit.¹ We have observed a chain reaction whose rate is several orders of magnitude higher at low ($T \leq 60$ K) temperatures than at higher temperatures. Because of a sharp increase in the rate, the critical ignition conditions, which cannot be realized in the same test geometry for $T > 60$ K, are reached, so that a thermal explosion occurs when the sample is cooled, not when it is heated.

We investigated a vitreous, equimolar mixture of methyl cyclohexane (MCH) with chlorine, in which an unbranched chain reaction occurs as a result of photodissociation



where R is an MCH radical. The enthalpy of the total process amounts to 1.2 eV. Both reactions (1) are exothermic. The photodissociation of Cl_2 was accomplished with a nitrogen laser ($\lambda = 337$ nm). The change (ΔN) in the amount of Cl_2 in the sample was recorded as a change in the optical density ($\Delta D = \sigma \Delta N$) in its absorption band at wavelengths of 337 nm (absorption cross section $\sigma_1 = 3 \times 10^{-19}$ cm²) and 441 nm ($\sigma_2 = 5 \times 10^{-21}$ cm²). The change in the number of radicals $R(t)$ was determined from the EPR spectra.

Figure 1 shows the variation of $\Delta N(t)$ and $R(t)$ during photolysis. Below 60 K the reaction rate decreases sharply after the induction period corresponding to a buildup of the critical number of radicals [$R_c = (3-7) \times 10^{16}$ cm⁻²]. An insignificant increase ΔN during the induction ($\sigma_1 \Delta N \leq 1$) indicates that the radicals are formed only in the absorption layer, which is appreciably smaller than the sample thickness. The concentration of radicals in this layer exceeds 10^{19} cm⁻³. Subsequent propagation of the reaction front occurs through the entire bulk at a rate of about 10^2 cm/sec: almost all of the chlorine in a 0.1-cm-thick cell disappears within $\sim 10^{-3}$ sec (inset in Fig. 1). After completion of the reaction, the number of radicals left is $\sim 10^{-2} R_c$. The propagation of the reaction front is apparently accompanied by melting, as indicated by an increase in the transmission at the 633-nm wavelength (Fig. 1), where the initial decrease is due to a scattering of light in the cracks, which disappear after the reaction.

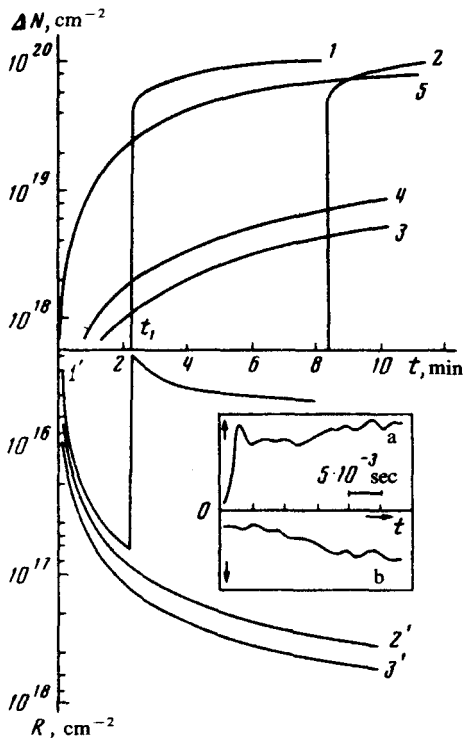


FIG. 1. Chlorine consumption and radical buildup kinetics. 1 - 5, $\Delta N(t)$ for $T = 10, 20, 60, 80,$ and 115 K; 1'-3', $R(t)$ for $10, 60,$ and 80 K, respectively. The inset shows oscillograms of the variation of sample's transmission at 10 K (a) $\lambda = 441$ nm and (b) $\lambda = 633$ nm. $t = t_1$.

In our geometry (a plane-parallel quartz cell with a 0.03-cm wall thickness and a pump-spot diameter of 0.2 cm) the rapid reaction produces an explosion that destroys the illuminated section of the cell wall. The sample can be preserved by increasing its thickness. Probing with a small-diameter light spot shows that the reaction front propagates in the form of a cone.

Initially, the reaction rate increases with increasing temperature, starting with $T \geq 60$ K; however, no explosion occurs when the number of radicals in the sample exceeds R_c . At 80 K a dark reaction after the pumping is observed with a characteristic time of 20-40 sec, during which about 10^{17} cm^{-2} chlorine molecules and 2×10^{16} cm^{-2} radicals disappear, i.e., the chain length is $\nu \approx 5$, consistent with the results obtained elsewhere.² The Cl consumption rate on the linear part of $\Delta N(t)$, which is equal to νYL (Y is the photodissociation quantum yield, which is close to unity and L is the light intensity), increases with increasing temperature; but even in the liquid phase at 140 K and at a light intensity ($L = 2 \times 10^{16}$ $\text{cm}^{-2} \cdot \text{sec}^{-1}$) $d\Delta N/dt \approx 10^{19}$ $\text{cm}^{-2} \cdot \text{sec}^{-1}$ ($\nu \approx 500$), i.e., the propagation velocity of the reaction front does not exceed 10^{-2} cm/sec.

The transition from a slow reaction to an explosion occurs after a buildup of radicals to $R > R_c$ at $T = 60-80$ K and subsequent cooling of the sample. Figure 2 shows the dependence of the thermostat temperature T_0 , at which an explosion occurs, on the illumination time at 80 K; this shows that T_0 increases with increasing illumina-

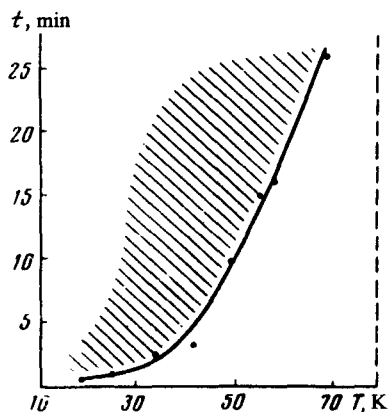


FIG. 2. Dependence of the thermostate temperature T_0 , at which the explosion occurs, on the photolysis time at 80 K. The explosion region is shaded.

tion time (i.e., with increasing R).

Both experiments (illumination at $T < 60$ K and illumination at 80 K followed by cooling) show that the light absorption during the reaction is negligible and the explosion is caused by the formation of active particles in the bulk as a result of propagation of the reaction front, and ignition is due to a buildup of these particles in the absorption layer during the induction period. The described critical effects disappear if the sample is annealed in the glass-transition region after photolysis, even though the number of radicals left after annealing is greater than R_c . No explosion occurs when the amount of Cl_2 in the sample is less than 1 : 3.

Since the heat removal increases with increasing temperature, it is impossible to obtain the upper temperature limit of ignition within the framework of Semenov theory for any temperature dependences of the rate constant and heat conductivity. The given data can be understood if we take into account the role of internal stress in the kinetics of solid-phase reactions occurring during the preparation of vitreous samples and during the reaction.¹

If we characterize the elastic stress by the excess free energy G , then we can represent the activation energy of the reaction in the form

$$E_{\text{act}} = E_0 - \alpha G, \quad 0 < \alpha \leq 1. \quad (2)$$

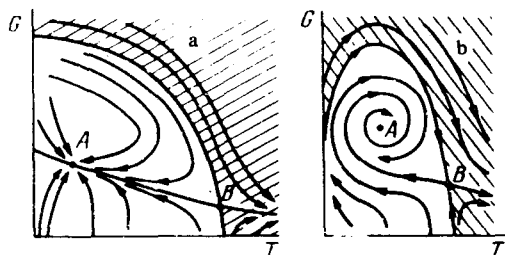


FIG. 3. Phase portrait of the system for a given concentration of radicals (\bar{R}). At points A and B $dT/dt = dG/dt = 0$; a) $R < AR_1$, b) $R < R_1$. $R_1 \sim T_0 e^{U/T_0}$, where T_0 is the wall temperature and U is the activation energy of the relaxation rate of elastic stress. The shaded area represents the ignition regions.

i.e., the elastic stress increases the reaction rate constant, and if we assume that its relaxation slows down as the temperature decreases, then we can explain the upper ignition limit. The ignition condition can be determined from the trajectories in the (G, T) plane. In plotting them, in addition to using the usual parameters of the Semenov diagram,⁴ we assumed that the relaxation rate of elastic stress increases exponentially with increasing temperature and that some of the heat of reaction is expended on their production. Two types of phase portraits of the system are possible (Figs. 3a and 3b). At $\tilde{R} < \tilde{R}_1$, the singular points A (stable node) and B (saddle) correspond to the stable and unstable points of the Semenov theory. At $\tilde{R} < \tilde{R}_1$, the node becomes a stable focus, and a low-temperature ignition region appears. According to Fig. 3b, a decrease in G (annealing) can shift the system to the intermediate-temperature region in which it is stable. With a further increase in \tilde{R} the points A and B merge, and the stable region disappears.

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¹The influence of the vibrational spectrum of the matrix on the chemical-reaction rate was pointed out in Refs. 2 and 3.

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