IGNITION OF CONDENSED MATTER AT A CONSTANT TEMPERATURE SURFACE

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An account is given of the technique and results of an experimental investigation of pyroxylin; a comparison with existing theory is made, and a scheme is given for calculating the kinetic constants from the ignition time lag.

Theoretical and numerical investigations have been made in a number of papers (see [1] and the references there cited) of the laws of ignition at constant temperature on a material surface (boundary conditions of the first kind). The present paper describes a method of experimental study of ignition under such conditions, and gives an experimental verification of the calculation formula put forward in [1] for ignition time lag, as well as a method of determining the effective kinetic parameters of the leading reactions.

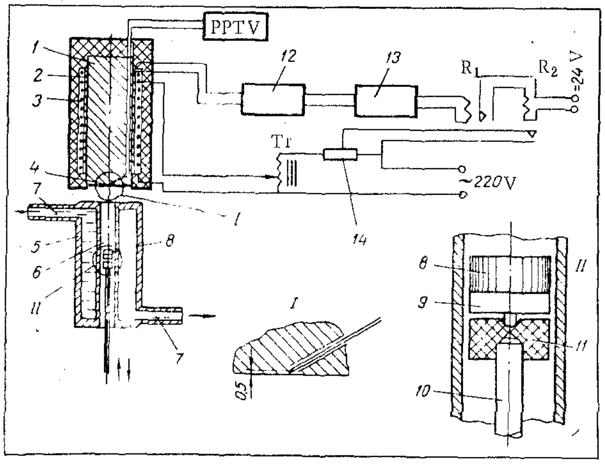

Fig. 1. The experimental arrangement for investigating the hot-body ignition of condensed systems.

Experimental technique. The surface temperature is fixed by making momentary contact between the test specimen and the surface of a massive heated block of high thermal conductivity metal. The arrangement is shown in Fig. 1.

The igniter-block 1 is an aluminum* cylinder of diameter 45 mm and length 120 mm, on the side surface of which was mounted a platinum resistance thermometer 2 and a heater winding 3. The surface of the cylinder was lagged with asbestos (except for the lower end). A platinum/platinum-rhodium thermocouple (∅ 50 micron) 4 was attached to the lower end at a distance of 0.5 mm from the surface, the surface being subsequently polished carefully with corundum powder. The free ends of the thermocouple were led away inside the cylinder by means of thin (∅ 1 mm) twin-channel porcelain tubes.

The initial temperature of the specimen was preset by means of the thermostat 5, consisting of a sealed steel vessel with an internal channel 6 (130 mm long and 12.5 mm in diameter). The heat carrier (water or carbon tetrachloride) was supplied along the connecting pipe 7 from an ultrathermostat. The specimen 8 was mounted on a textolite piece 9, fitted with a hemispherical bearing. An ebonite bushing 11 with an appropriate depression was attached to the elevator rod 10. This method ensured reliable contact with the igniter-block over the whole specimen surface.

Thermostat control of the igniter-block was accomplished using a simple on/off automatic control system, including resistance bridge 12 (MVU-49), photomultiplier 13, relay R_1 (RP-7), relay R_2 (MKU-48), and rheostat 14, which in turn was fed from an autotransformer Tr (LATR-1-9A). After the block was brought to the assigned thermal conditions, the temperature of the lower end surface was kept constant to ±0.3°.

The specimen was raised and pressed against the block by means of a 0.5 kg weight fastened to a torsion string which passed over a pulley and was connected to the elevator rod 10. Practically identical thermal contact conditions were achieved in all the tests. It should be noted that after the specimen was pressed in contact with the block, a small (0.3°–0.4° K) brief drop in surface temperature occurred. The ignition lay (time from pressing the specimen against the block to the time when a flame appeared) was recorded visually using a stopwatch with 0.1 sec divisions.

The experiments were carried out on specimens of pyroxylin No. 1, whose model properties relevant to investigation of ignition of nonvolatile condensed systems (the presence of kinetic constants, the determinant role of reactions in the condensed phase, the absence of phase transformations) are discussed in [2]. The specimens were in the form of tablets of diameter 12 and 18 mm and thickness 6 mm, pressed to a density of $\rho = 1.49–1.50$ g/cm^3. The temperature of the igniter block was varied in the range $T_0 = 485°–$

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*It proved impossible to use a block of copper, whose conductivity is twice that of aluminum, because the oxide film on its surface has low thermal conductivity and appreciable catalytic activity with regard to the reaction being studied. It is known that the oxide film on aluminum is stable, has high thermal conductivity, and has no catalytic action on the thermal decomposition of a wide range of condensed systems of practical interest.

525° K, and the specimen initial temperature in the range T_i = 255°–369° K. The specimens were kept in the thermostat for 30 min. Tests showed that the specimen heated (or cooled) reliably to T_i during this time (increase of the time in the thermostat did not produce a change in t_d).

The igniter-block surface was cleaned of scale after each test with fine emery paper. The paper was wound on the bushing over an intermediate layer of wadding, and the bushing was connected to an electric motor through a flexible shaft. The high speed of rotation prevented the paper being "scorched" onto the block.

The tests were done at temperatures such as to produce time lags of 3–20 sec. For large lags (low-temperature conditions, close to critical ignition) deformation of the model was observed (partial extrusion outwards of softened products of incomplete decomposition of pyroxylin, and the formation of a considerable amount of foam). With lags less than 20 sec, a small amount of foam also appeared before ignition at the edges of the specimen close to the hot surface, but the time for which the foam existed was short (15–20% of the time lag).

Experimental results. The following formula for calculating ignition time lag is given in [1]:

$$\tau_d = (1 + 1.6\Theta_i + 0.2\Theta_i^2)(1 + 8\Theta_i\gamma^{3/2})(1 + \beta),$$

where

$$\Theta_i = \frac{E}{RT_0^2}(T_0 - T_i); \quad \gamma = \frac{C}{Q}\frac{RT_0^2}{E}, \quad \beta = \frac{RT_0}{E},$$

$$\tau_d = \frac{QK_0Et_d}{CRT_0^2}\exp\left(-\frac{E}{RT_0}\right).$$

Neglecting terms which are small under the given experimental conditions, the formula may be written in the form

$$\frac{QK_0}{C}\exp\left(-\frac{E}{RT_0}\right)\frac{t_d}{T_0 - T_i} = 1.6 + 0.2\frac{E}{RT_0^2}(T_0 - T_i). \qquad (1)$$

It follows from (1) that the experimental points for T_0 = const and T_i = var, expressed in the coordinates $t_d/(T_0 - T_i)$ and $T_0 - T_i$, must lie on a straight line.

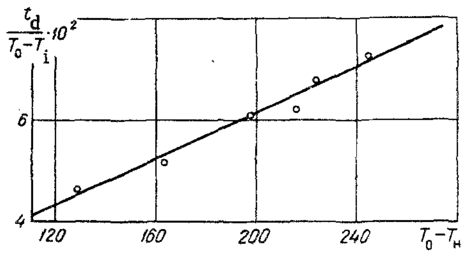

Fig. 2. Dependence of ignition time lag on initial temperature (t_d in seconds; $T_0 - T_i$ in °K; T_0 = 498° K).

Figure 2 shows the experimental results taken at T_0 = 498° K and T_i = 255°–369° K, which may be considered to fit a straight line with the equation

$$\frac{t_d}{T_0 - T_i} = a + b(T_0 - T_i), \qquad (2)$$

where $a = 1.6 \cdot 10^{-2}$ sec/deg, $b = 2.3 \cdot 10^{-4}$ sec/deg./deg.

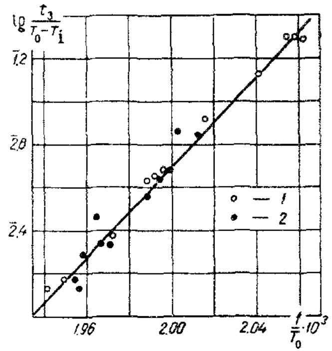

Fig. 3. Dependence of ignition time lag on ignition-block temperature (t_d in sec; T_0 in °K; T_i = 293–298° K): 1) points relating to the ∅ 12 mm specimens; 2) to 18 mm specimens.

However, the fact of obtaining a straight line in these coordinates is not itself a sufficient argument in favor of the formula given. It is also necessary to analyze quantitatively the parameters of the line obtained. It may be seen from (1) that the absolute values of these parameters depend strongly on the quantities QK_0, E, and T_0, and they cannot therefore be calculated from (1) with sufficient accuracy. It is expedient to make a quantitative comparison of theory and experiment in terms of the ratio of coefficients a and b, which is independent of QK_0, and only weakly dependent (not exponentially) on E and T_0, i.e., in terms of the quantity $a/b = 8RT_0^2/E$. Calculation of this quantity (using the activation energy value from [2]) gives

$$(a/b)_{theor} = 82°\,K, \quad (a/b)_{exp} = 70°\,K,$$

which indicates satisfactory quantitative agreement between theory and experimental results.

From (1) we may derive a method of determining the kinetic parameters QK_0 and E from the experimental data on the dependence of t_d on T_0 and T_i.

Let us write (1) in the form

$$\lg\frac{t_d}{T_0 - T_i} = \lg\left[\frac{C}{QK_0}\left(1.6 + 0.2\frac{E}{R}\frac{T_0 - T_i}{T_0^2}\right)\right] + \frac{E\lg e}{R}\frac{1}{T_0}. \qquad (3)$$

By keeping the quantity $(T_0 - T_i)/T_0^2$ constant in the tests and expressing the experimental results in coordinates lg $[t_d/(T_0 - T_i)]$ and $1/T_0$, we obtain the value of E from the slope of the straight line, and the value of QK_0 from its intercept with the ordinate axis. Usually the quantity $(T_0 - T_i)/T_0^2$ is not varied much in the conditions of the experiment. For example, in the tests carried out with $T_i = 293°-298°$ K and $T_0 = 485°-515°$ K, the value of $(T_0 - T_i)/T_0^2$ changed in all by 5%. This allowed use of the scheme described in reducing the experimental data obtained with $T_i = \text{const}$, $T_0 = \text{var}$, which was very convenient, because the tests could be carried out with the initial specimen temperature equal to room temperature. The experimental results obtained in the range of variation of T_0 mentioned are shown in Fig. 3, where each point represents the mean value of t_d from 3–4 tests. It may be seen from the figure that the tests on specimens of different diameter gave practically identical results, which is evidence that heat losses from the sides are not sufficient to influence t_d. When the data of Fig. 3 are fitted to (3), the values of the kinetic parameters obtained are $E = 200$ kJ/mole; $QK_0 = 10^{26}$ W/kg, values which are in good agreement with results obtained by other methods [2–4].

NOTATION

τ_d–dimensionless ignition time lag; Θ_i–dimensionless initial temperature; t_d–ignition time lag; T_0–source temperature; T_i–initial temperature; E–activation energy; Q–thermal effect (per unit mass); K_0–preexponent; C–specific heat; ρ–density; R–universal gas constant; a and b–constants in the equation.

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