

KINETICS OF HEAT RELEASE IN THE CONDENSED PHASE OF PYROXYLIN AT ELEVATED TEMPERATURES

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The pulsed calorimetric method developed by the authors has been used to investigate the kinetics of heat release in the condensed phase of pyroxylin at temperatures of 220–300° C. The heat yield and percentage dispersion have been measured as a function of temperature. On the basis of an extensive comparison of the available data, an activation energy $E = 42$ kcal/mole and preexponential $z = 10^{16.9}$ sec⁻¹ are proposed as most reliable for the initial stage of pyroxylin decomposition on the temperature interval 70–300° C.

Most studies [1] of the kinetics of thermal decomposition of nitrocellulose (NC) have been made at temperatures below 200° C. The object of the early investigations was to determine the chemical stability of NC under long-term storage conditions and, accordingly, they were conducted (insofar as the sensitivity of the existing methods permitted) at the lowest possible temperature. The upper temperature limit was established by the development of thermal explosion. In these investigations the temperature did not exceed 155–160° C.

Comparatively recently the temperature was raised to 190° C [2] (by investigating NC film 2–3 μ thick using IR spectroscopy and a quartz balance) and to 200° C [3] (thermal decomposition of NC in inert solvents).

Because of technical difficulties there have been no direct measurements of the decomposition kinetics of NC above 200° C. Only theoretical values of the heat release rate, based on ignition lags and critical temperatures measured under controlled conditions [4], have been obtained.

We have now investigated the kinetics of thermal decomposition of pyroxylin (12.0–12.4% N) above 200° C on a special pulse calorimeter [5]. The possible effect of gas-phase reactions was eliminated by conducting the experiments in a vacuum (0.05–0.5 mm Hg). Most of the experiments were performed on film $0.5 \mu \leq \delta \leq 2 \mu$ thick, which gave a sufficiently strong useful signal as compared with the noise level. Attempts to use thicker films (10 μ or more) showed that under these conditions it is not possible to maintain uniform decomposition, despite the fact that the experimental temperature was much lower than the critical temperature calculated from the equations of thermal explosion theory. Individual five-micron thermocouples, bonded [5] to a layer of pyroxylin 10–15 μ thick, register "blips" at a temperature of 220–230° C (Fig. 1), which indicate that the stationary flow of the reaction is disturbed.

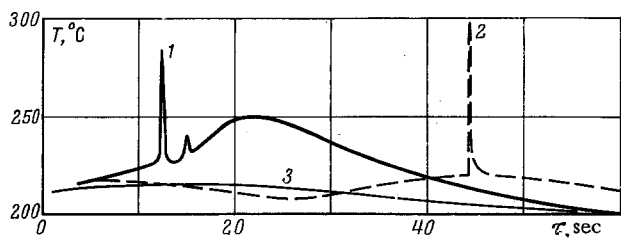


Fig. 1. Readings of individual thermocouples bonded by a standard number [5] to a layer of pyroxylin 15 μ thick: 1, 2, 3) thermocouple numbers.

The reason for the blips was discovered upon rapidly cooling the plates, on which the pyroxylin was mounted, after pulsed heating to the same (~230° C) temperature. Bubbles of "foam" up to 1 mm in diameter are clearly visible in the photograph of one such plate presented in Fig. 2. The height of the large bubbles above the surface of the plate reaches ~0.5 mm. In a photograph of an enlarged small area of the foam (Fig. 3), apart from the bubbles mentioned

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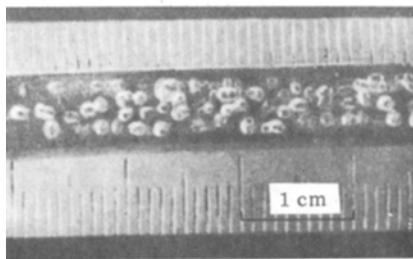


Fig. 2. Photograph of "frozen" foam in pyroxylin.



Fig. 3. Photomicrograph of part of the frozen foam.

above, it is also possible to distinguish a large number of small bubbles (diameter 30-150 μ or less). Such bubbles and cracks can also be seen in the walls of the large bubbles. Apparently, the cracks in the film are formed during hardening as a result of rapid cooling. Visual observations showed that at $\sim 220^\circ\text{C}$ the pyroxylin becomes liquid. This is confirmed by the readings of the elastic prestressed five-micron thermocouples, which lose contact with the film ($\delta = 1 - 10 \mu$) at $\sim 220^\circ\text{C}$. At the same time considerable gas release is recorded by a special tungsten vacuum gauge.

Liquefaction of NC before ignition was previously noted in [6]. The appearance of bubbles at the beginning of the vigorous decomposition associated with the autoignition of pyroxylin in a vacuum was reported in [7].

When the thickness of the film is reduced to $\sim 1 \mu$, it is not possible to freeze the foam, and the thermocouples cease to register blips at all the temperatures investigated. The above experiments with "quenching" showed that foaming may increase the effective thickness of the layer of pyroxylin by 10-30 times. Consequently, a micron film of pyroxylin may be converted into a layer of foam 10-30 μ thick. It is easy to see from the equations of thermal explosion theory that for $\delta = 30 \mu$ the critical temperature is $270-300^\circ\text{C}$ for the kinetic constants used in [5]. Accordingly, there is reason to suppose that there will be no blips at initial film thicknesses of less than 1μ .

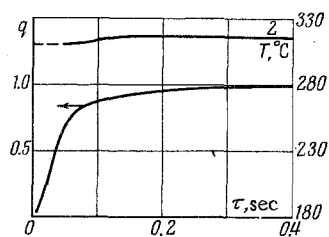


Fig. 4. Experimental curves from one of the calorimetric experiments: 1) amount of heat released in the condensed phase, 2) temperature variation according to the readings of five thermocouples.

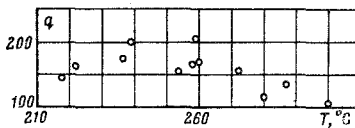


Fig. 5. Amount of heat released in the condensed phase as a function of the experimental temperature (the temperature at the instant corresponding to $Q = 0.5 Q_k$ was taken as the reference temperature.)

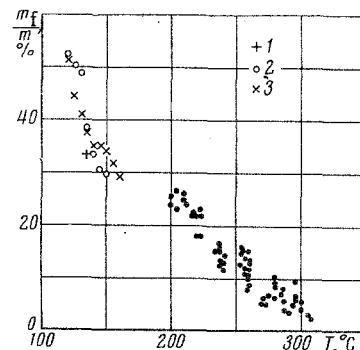


Fig. 6. Temperature dependence of the yield of precipitate during the thermal decomposition of NC: 1) 13.1% N [9], 2) 13.4% N [10], 3) 12% N [11].

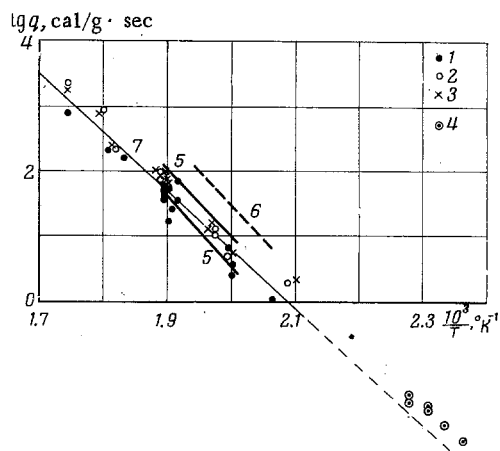


Fig. 7. Rates of heat release in the condensed phase for various temperatures. Results of measurements: 1) $Q = 5$ cal/g, 2) $Q = 25$ cal/g, 3) $Q = 50$ cal/g; points 4) $Q = 5-50$ kcal/g [12]; lines 5) [4], 6) [13], 7) calculated by least squares from points 1, 2, 3.

with a dark brown deposit, whose yield decreases almost linearly with increase in temperature, as may be judged from Fig. 6, which also presents the published data for lower temperatures [9, 11]. It was found that the sum of the deposits on the screen and the calorimetric plates is almost independent of the side of the plate on which the pyroxylin is deposited and is equal to

$$\begin{array}{ll} 36 \pm 1.5\% & \text{at } T = 300^\circ \text{C} \\ 40 \pm 1.5\% & \text{at } T = 230 - 240^\circ \text{C} \end{array}$$

From data on the pyroxylin fraction collected on the cold screens ("percentage dispersion" [7]) it is possible to make a rough estimate of the amount of heat that would be released in the condensed phase if all the pyroxylin were converted into gaseous products (as in [7]); it was found that

$$Q^* = \frac{110}{0.67} = 160 \text{ cal/g} \quad \text{at } 300^\circ \text{C}, \quad Q^* = \frac{170}{0.76} = 220 \text{ cal/g} \quad \text{at } 220-240^\circ \text{C}.$$

In the case of flameless combustion of pyroxylin after ignition in a vacuum [7] the fraction of material dispersed was 70% (i.e., 30% greater than in our experiments.) Obviously, the reason for this is to be found in the fact that in [7] the pyroxylin specimens, 0.5-1 mm thick, were heated almost uniformly to the autoignition temperature, the decomposition reaction covered the entire volume of the specimen, and the gaseous reaction products escaped less easily than in our experiments, in which, as already mentioned, layers 0.5-2 μ thick were employed.

The "freezing" experiments suggest that in pyroxylin combustion the thickness of the reaction zone is not greater than 10 μ . Therefore under combustion conditions the reaction products probably escape into the gas phase more easily than in the pyroxylin autoignition experiments described in [7], so that the fraction dispersed should be closer to the value obtained in our experiments.

This conclusion is confirmed by the results of [8], in which the yield of solid matter collected on the cold walls of the reaction vessel during the combustion of thin wafers of NC under vacuum conditions $p = 1-2$ mm Hg was only 30-50%. Accordingly, it was considered desirable to make a detailed study of the dependence of the fraction of pyroxylin dispersed on the conditions in the reaction zone.

The reaction energy of 500 cal/g measured in a vacuum at temperatures of 150-165° C [12] evidently includes a strong contribution from the secondary reactions between the primary gaseous products and the

A typical kinetic curve for the amount of heat released in the condensed phase at a pyroxylin temperature of $\sim 300^\circ \text{C}$ is presented in Fig. 4. The total amount of heat measured in this experiment $Q_k = 108$ cal/g. Its temperature dependence is presented in Fig. 5.

As the temperature rises, the reaction energy decreases to a value consistent with the results of [7] ($Q_k = 80$ cal/g for flameless combustion, when the surface temperature $\sim 300^\circ \text{C}$; calorimetric measurements of the autoignition process in a vacuum gave values $Q_k = 90-140$ cal/g).

After the experiments a yellowish deposit [7, 8] was observed in the cold parts of the apparatus. Special experiments, in which the calorimetric pack with the pyroxylin was surrounded by brass foil screens showed that at a pack temperature $\sim 300^\circ \text{C}$, $33 \pm 5\%$ and $24 \pm 4\%$ by weight of the starting pyroxylin is deposited on the screen screens at $T = 300^\circ \text{C}$. When the outside surfaces of the plates are coated with pyroxylin, the fraction deposited on the screens is still 33% at $T = 300^\circ \text{C}$ and 30% at 230-240° C.

The plates of the calorimetric pack remain covered

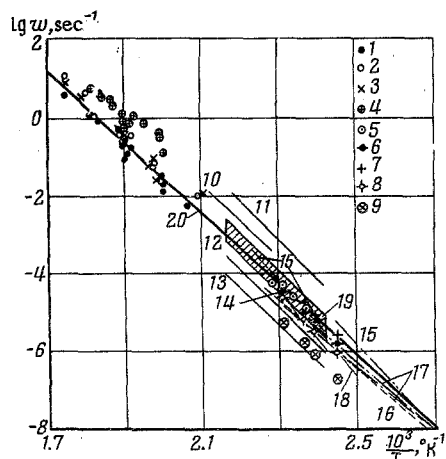


Fig. 8

indicates that the process is autocatalytic. This has already been pointed out by numerous investigators [1, 6, 9-12]. Within the limits of scatter of the experimental data the initial stage (up to $Q = 50$ cal/g, or $\sim 30\%$ at 220°C and $\sim 50\%$ at 300°C of the total amount of heat released in the condensed phase at these temperatures) can be described as a zero-order reaction with activation energy $E = 41.2 \pm 1.7$ kcal/mole and preexponential $\lg(zQ^*) = 18.84 \pm 0.70$, calculated by the method of least squares. The straight line with these parameters has been plotted in Fig. 7. Calculations for each degree of reaction taken individually lead to similar values: $E = 41.8 \pm 2.3, 42.4 \pm 2.4, 38.6 \pm 2.3$ cal/mole, $\lg(zQ^*) = 18.92 \pm 0.97, 19.44 \pm 0.99, 17.86 \pm 0.94$, $[zO^*] = \text{cal/g} \cdot \text{sec}$ for $Q = 5, 25, 50$ cal/g, respectively. Ignition by a hot gas [4] gives rates of heat release consistent with our values, as already noted in [5].

The results obtained in pyroxylin ignition experiments using a massive metal plate [13] lie considerably higher. Apparently, under these conditions, when the escape of the secondary gaseous products is impeded, the contribution of the gas-phase reactions may be considerable. The rates of heat release obtained from [11], like the total reaction energies, lie somewhat higher than the values obtained by extrapolating our straight line into the temperature region $15\text{--}165^\circ\text{C}$. It should be noted that reducing the total reaction energy for these points from 500 to 200 cal/g, i.e., by a factor of 2.5 ($\Delta \lg Q^* = -0.4$), shifts them so that they fall almost on our straight line (or just below it).

All the known results on the rate of thermal decomposition of NC, obtained by various methods under various conditions on the temperature interval from 70 to 300°C , are compared in Fig. 8 in the coordinates $T^{-1} [^\circ\text{K}^{-1}]$ and $\lg w [\text{sec}^{-1}]$. Points 1, 2, 3 denote our experimental data, 4) mass spectrometry (vacuum, maximum rate) [14], 5) initial rate (i.r.) of heat release in vacuum [12], 6) i.r. of gas formation in vacuum [1], 7) i.r. of formation of condensing gases in vacuum [1], 8) thermogravimetry in vacuum (i.r.) [1], 9) i.r. of formation of difficulty condensing gases (in vacuum) [1]; lines 10) i.r. of gas formation from solutions in inert solvents [3], 11) thermogravimetry (vacuum) [2], 12) IR spectroscopy (in vacuum, i.r.) [2], 13) thermogravimetry in vacuum (i.r.) [2], 14) i.r. of heat release and gas release in air [12], 15) [1], 16) i.r. of gas release in the presence of decomposition products [1], 18) i.r. of splitting off nitrogen, thermogravimetry in a stream of CO_2 [9], 19) shaded region, enclosing 12 experimental curves obtained in vacuum by means of IR spectroscopy and thermogravimetry [2].

It is clear from the graph that all the data are grouped within a single strip. The data that deviate most from the center of the strip are certain results relating to loss of weight [2], the yield of difficulty condensing gases [1], data on decomposition in inert solvents [3], and the results of a mass spectrometry study [14]. As for the latter, their exaggerated values are perfectly understandable, since they represent the maximum rates of release of gas with mass 30 (where the kinetic curves are clearly autocatalytic in character). The straight line describing our results (see Fig. 7) at $Q^* = 200$ cal/g passes close to the center of the strip, deviating from it somewhat in the region of 70°C . The totality of the experimental data is described by straight line 20 with parameters $z = 10^{16.9} \text{ sec}^{-1}$, $E = 42$ kcal/mole.

These values are currently the most probable for the thermal decomposition of NC on the temperature interval from 70 to 300°C .

* As in Russian original - Publisher.

starting pyroxylin and primary condensed products. Unfortunately, the authors of [12] do not state the pressure at which the measurements were made.

By differentiating kinetic curves of the type shown in Fig. 4 we obtained values of the rate of heat release for various temperatures and degrees of reaction. As a measure of the degree of reaction we used the amount of heat released up to a given time. Clearly, since the process of dispersion is parallel to, or, more accurately, a consequence of the chemical reaction, the initial section of the experimental heat release curve should give the greatest reliability in determining the kinetic law. The same section is the most important in connection with the development of the ignition process and steady-state combustion.

The results of such an analysis for three degrees of reaction ($Q = 5, 25, 50$ cal/g) are presented in Fig. 7. It follows from the graph that the experimental points corresponding to $Q = 5$ cal/g lie below those corresponding to $Q = 25$ and 50 cal/g, which

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